6th International IUPAC Conference On Green Chemistry

IUPAC SEMPER VIRIDIS

Sustainability through Green Chemistry

4th-8th September 2016 Venezia, Italy

Chairman: prof. Pietro Tundo

	Sunday September 04
14.00	Registration *Exhibition room*
17.30 - 19.00	Welcoming Reception

	Monday* September 05			
9.00	Opening Ceremony *Toniolo Theatre*			
11.30	Coffee Break			
12.00	PL1 - Prof. Isabel Arends *Toniolo Theatre*			
12.45	Lunch			
14.15	K1 F. Sevilla *Toniolo Theatre*	K2 A. G. Correa *Auditorium*	K3 X. Wu *Conference room*	K4 G. Ferrari *Small Conference room*
14.45	M1 R. Tuba	B1 S. Vecchiato	OP1 A. Hay	R1 B. De Carvalho Bello
15.05	M2 Y. Tsujii	B2 B. Ramalingam	OP2 F. Fumian	R2 L. Scrano
15.25	M3 M. Galimberti	B3 C.P. Ferraz	OP3 P. Anastas	R3 F. Trovò
15.45	M4 H. Arafune	B4 K.P. Ho	OP4 Y. Chen	R4 C. Samorì
16.05	M5 A. Grassi	B5 A. Kulazhskaya	OP5 B. Abegaz	R5 A. Guida
16.25	Coffee Break			
16.45 - 17.30	Poster Session *Exhibition room*			

* Monday afternoon: open round table: Industries *Small room Toniolo Theatre*

	Tuesday* September 06			
9.00	PL2 - Prof. Chao-Jun Li *Toniolo Theatre*			
9.45	K5 P. Metrangolo *Auditorium*	K6 L.-N. He *Small Conference room*	K7 O. Demchuk *Conference room*	K8 I. Evstigneeva *Toniolo Theatre*
10.15	M6 A. Moores	B6 M.A. Jhons	IP1 N. Ishito	B. Han A.S. Elsayed Sayed A. Akhmetshina I. Carrera M. Ismail
10.35	M7 D. Wibowo	B7 W. Oberhauser	IP2 M.J. Muldoon	
10.55	Coffee Break			
11.25	M8 D. Suttipat	B8 O. Haske-Cornelius	IP3 A. Gervasini	P. Tundo B. Abegaz-Molla E. Ravera W.C. Wanyonyi J.C. Rodriguez--Reyes A. Hubina S.R. Wan Alwi N. Moreau N. Orlandi
11.45	M9 A.K. Rathi	B9 M. Tudorache	IP4 A. Goswami	
12.05	M10 M.E. Çorman	B10 S.T. Ahmed	IP5 Y.M.A. Yamada	
12.25	M11 E. Sabbioni	B11 S. Trita	IP6 M. Yadegari	
12.45	Lunch			
14.15	PL3 Prof. Takashi Tatsumi *Toniolo Theatre*			
15.00	K9 S. Tantayanon *Auditorium*	K10 D. Bianchi *Small Conference room*	K11 W. Zhang *Conference room*	K20 N. Tarasova *Toniolo Theatre*
15.30	M12 T. Sato	B12 F.-T. Luo	IP7 T. Liu	Z. Lerman M. De Martino X. Wu C. Brett R. Ballini
15.50	M13 T. Morinaga	B13 L. Yan	IP8 O. Piccolo	
16.10	M14 P. Barthelemy	B14 G. Selvaraju	IP9 D. Tschaen	
16.30	Coffee Break			
16.50 - 17.30	Poster Session *Exhibition room*			
19.00 - 22.00	Gala dinner			

* Tuesday afternoon: open round table – Natural products/plants extractions *Small room Toniolo Theatre*

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WELCOME MESSAGE FROM THE CHAIR OF THE CONFERENCE

After Dresden, Moscow, Ottawa, Foz do Iguaçu and Durban, the IUPAC Green Chemistry Conferences will move to Italy...to Venice. We believe that the perception that Society has of the role of chemistry is being elevated by these IUPAC Conferences, and that chemists deserve to be perceived as people who create a dialogue with politicians, economists, entrepreneurs, and opinion formers. Green Chemists map the way to a sustainable future, and foster the development of industrially significant, and economic, breakthrough technologies.

It is my pleasure, together with the Organizing Committee, to welcome you to Venezia for the 6th IUPAC Conference on Green Chemistry. This edition will gather more than 350 scientists from more than 70 countries all over the world.

Pietro Tundo
Chairman, Organizing committee
University of Venice, Ca' Foscari, Italy

WELCOME MESSAGE FROM THE IUPAC PRESIDENT

On behalf of the International Union of Pure and Applied Chemistry – IUPAC- I sincerely welcome participants and guests of the 6th International IUPAC Conference on Green Chemistry. Five topics to be discussed at the Conference: Green Materials, Green Bioprocesses, Green Energy, Green industrial processes and Molecular innovation, Green Policy, Sustainability and Safety, - cover the areas of great importance, enabling the humanity with the tools to achieve the Sustainable Development Goals. I hope, that the broad exchange of opinion and experience in the fields of elaboration of specific technologies and production structures, which will be performed in the framework of the Conference, will help chemists worldwide to implement principles and approaches of green chemistry into practice. And the beauty of Venice will make the 6th International IUPAC Conference on Green Chemistry unforgettable.

Natalia P. Tarasova
IUPAC President
Corresponding member of the Russian
Academy of Sciences
Director of the Institute of Chemistry and
Problems of Sustainable Development
D.I. Mendeleev University of Chemical
Technology of Russia

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CONFERENCE TOPICS

Green Materials

Chairs: Attilio Citterio, Elvio Mantovani

- Innovative materials for sustainable construction and cultural heritage
- Nanomaterials
- Polymers and polymer composites

Green Bioprocesses

Chairs: Mauro Marchetti, Janet Scott

- Biocatalysis and biotransformation
- Biofuels
- Bio-based renewable, chemical feedstocks
- Bio-based materials

Green Energy

Chairs: Buxing Han

- Energy storage to facilitate uptake of renewable energy sources
- Chemistry for improved energy harvesting
- Nuclear power
- Pollution Prevention

Green industrial processes and Molecular innovation

Chairs: Wolfgang Hoelderich, Philip Jessop, Kenneth Seddon

- Green catalysis
- Green solvents
- Pharma
- Microwave, ultrasound and flow chemistry technology
- Separations and analysis

Green Policy, Sustainability and Safety

Chairs: Paul Anastas, Liliana Mammino

- Green metrics and Greenness evaluation
- Green Chemistry Education
- How to influence policy to drive acceptance of Greener Technologies?
- Climate Change Mitigation

TRANSPORT

Public Transport

Tram, Bus, Water-bus lines allow to travel around Venice, Mestre and the Marco Polo airport very easily.

However, please bear in mind that most of Venezia island is not served by taxi or car but only by waterbus and water-taxi (the latest are very expensive).

Taxi and car are allowed only as far as Piazzale Roma a specific part of Venezia near the train station.

In the rest of the island cars/taxi are not allowed!

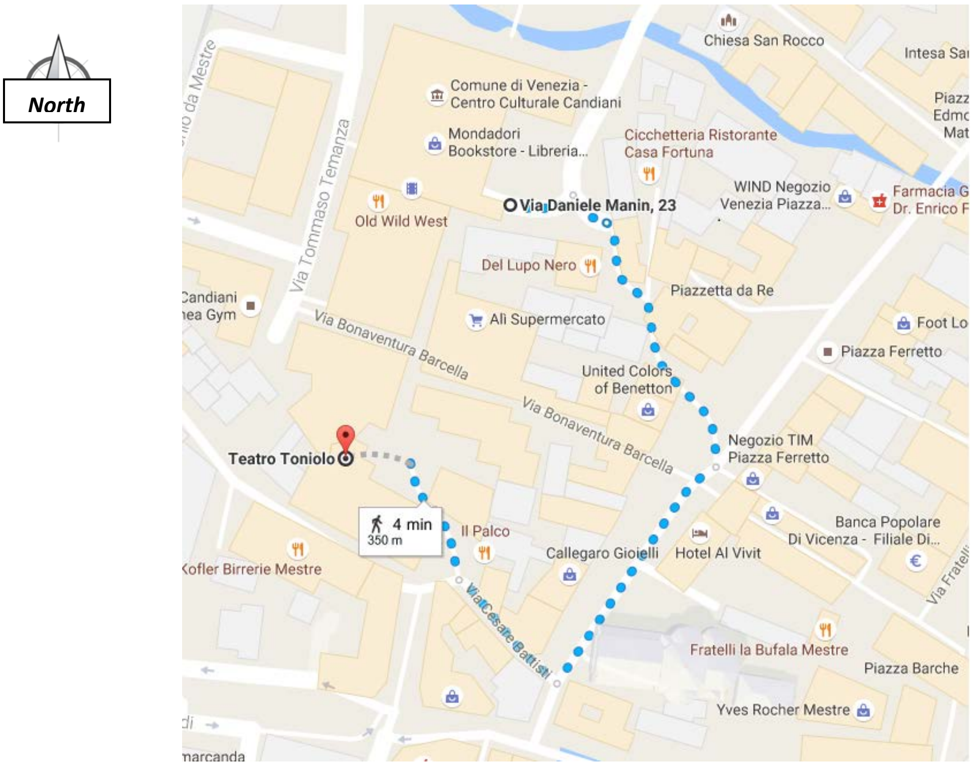
On the other hand Venezia Mestre is served by taxi, tramway and car can be freely used.

CONFERENCE VENUES

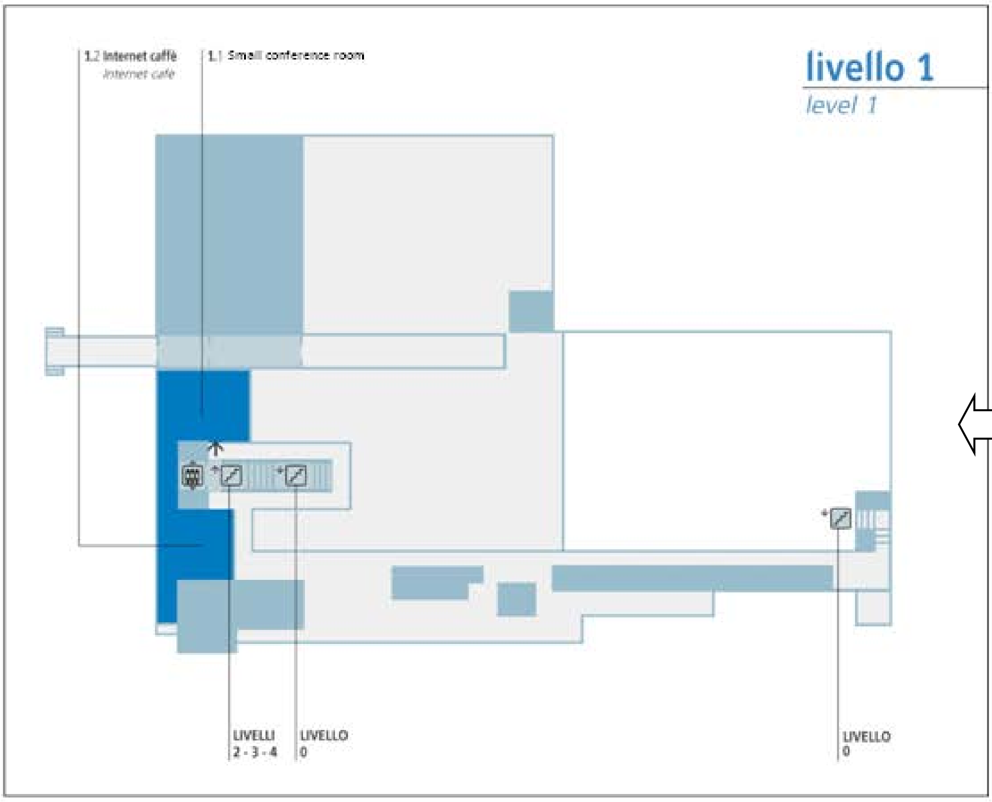
The 6th International IUPAC Conference on Green Chemistry will take place in two venues about 5 minutes walk from each other:

1. Centro Culturale Candiani which is Cultural Centre of the City of Venice. Address: Piazzale Candiani, 7 – 30174 Venezia Mestre

2. Teatro Toniolo, Andress: P.tta Cesare Battisti, 1 - 30172 Mestre-Venezia



CENTRO CULTURALE CANDIANI MAP



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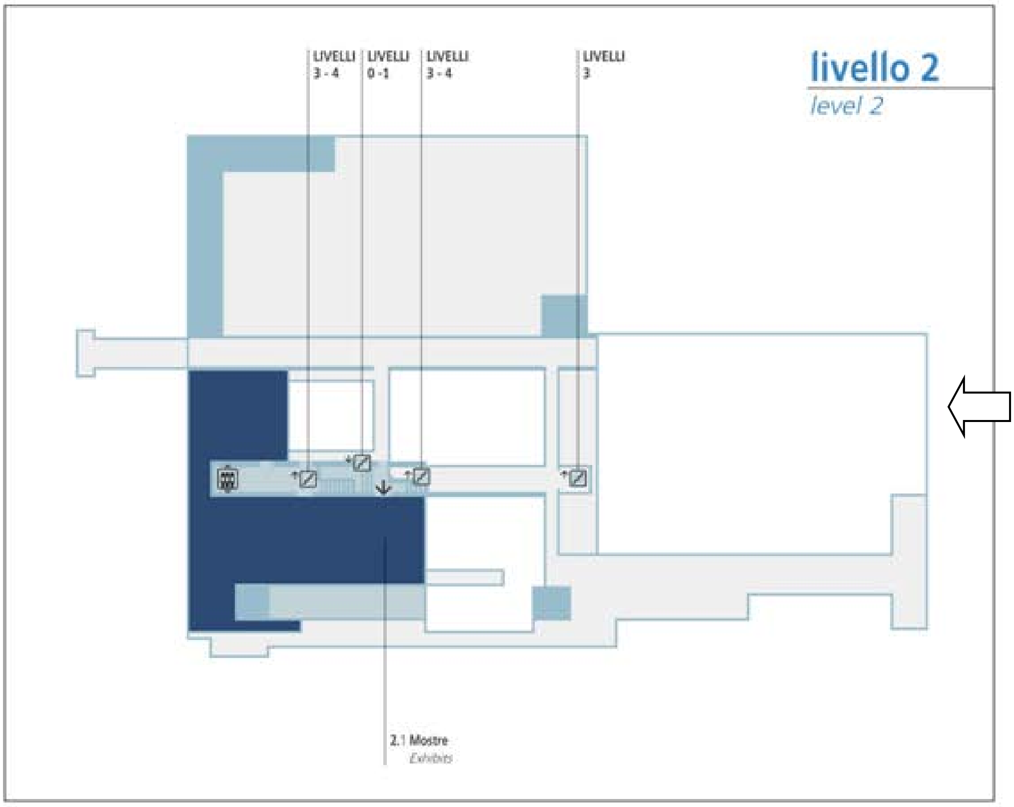
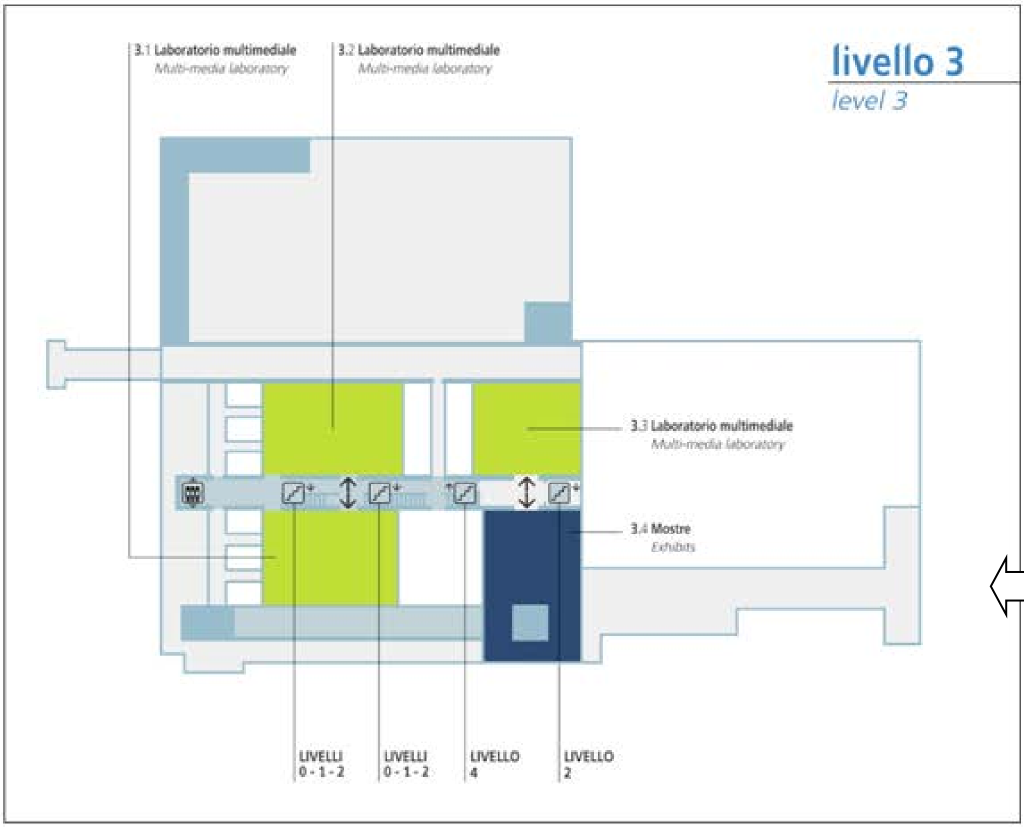
North

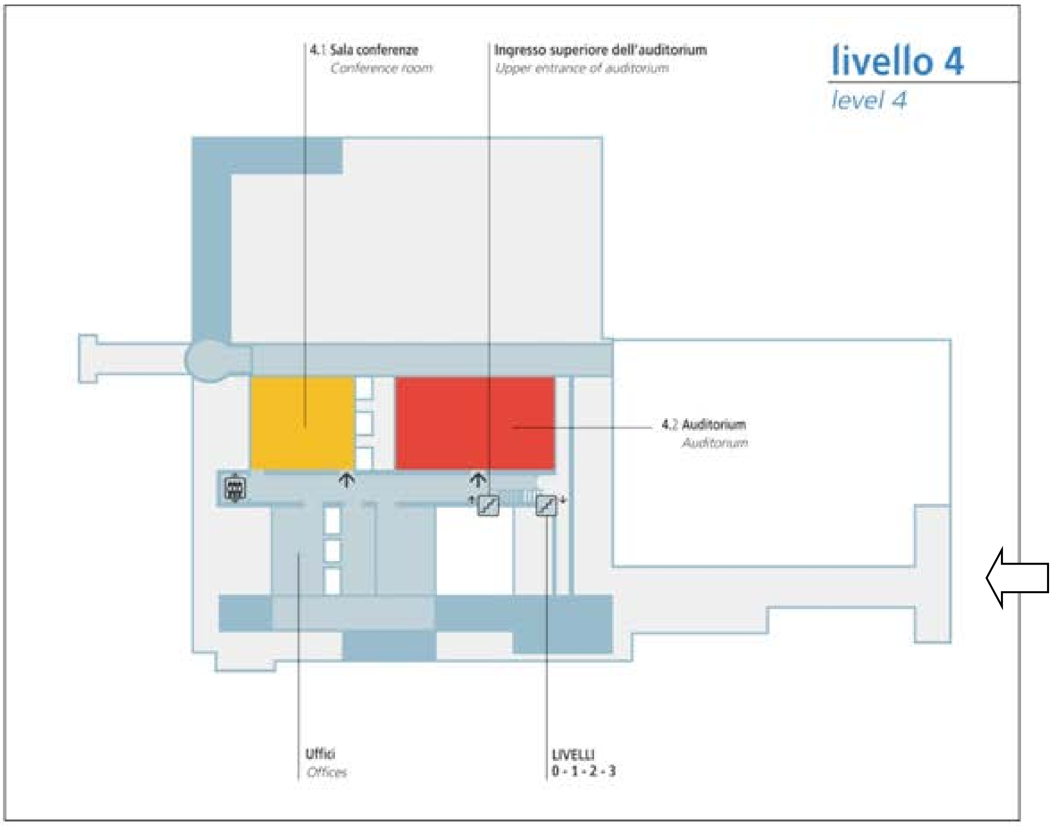


Main entrance Level 0



Main entrance Level 0

North



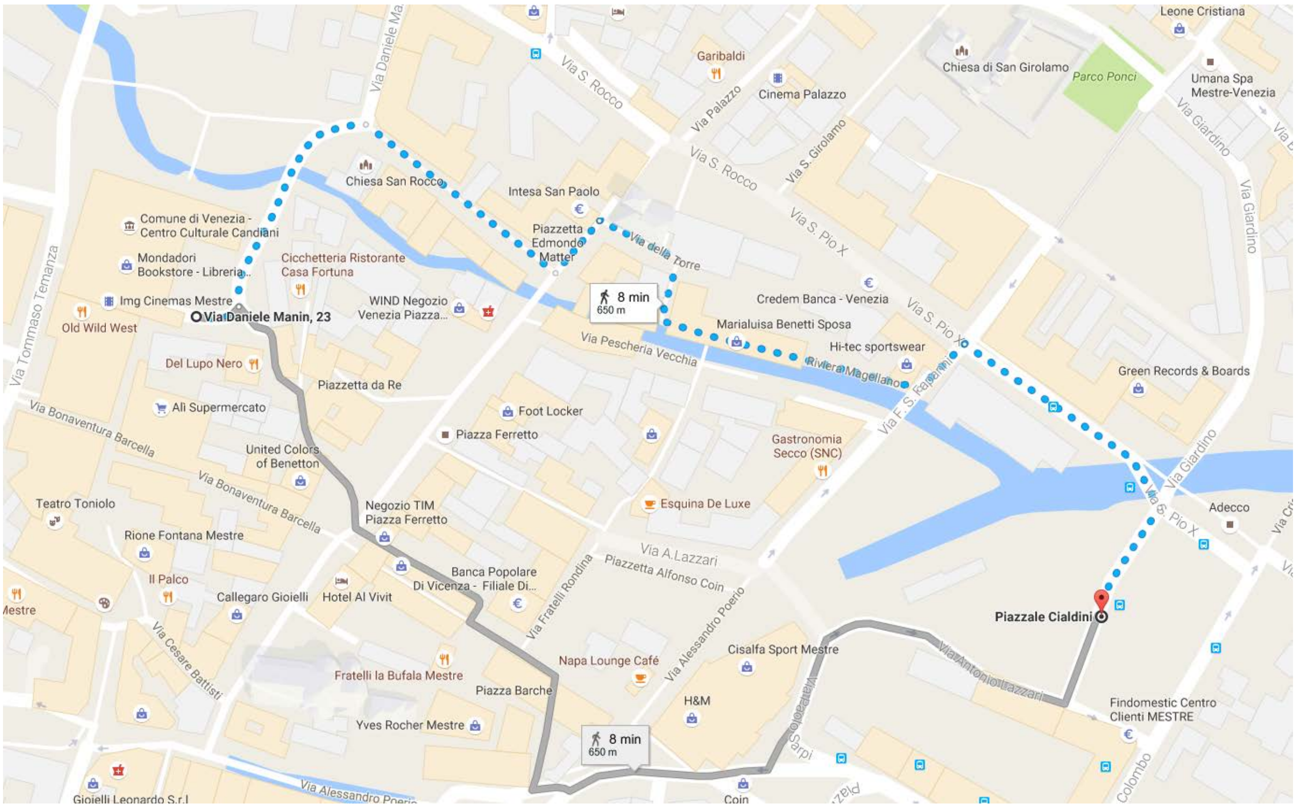
Main entrance Level 0

GOING TO VENEZIA

Going to Venezia from Centro Culturale Candiani is quite easy. You have to reach Piazzale Cialdini (tram stop Mestre Centro A1 Cialdini) e take **tram number 1** direction Venezia). last stop will be Venezia (see tram Map).
Departures from Mestre to Venezia every five minutes; From 6:20 am until 0:02 am (Monday to Saturday); Sunday From 6:20 am until 0:32 am.
Departures from Venezia to Mestre every five minutes; From 6:48 am until 1:30 am (Monday to Saturday); Sunday From 6:20 am until 0:32 am.

You can use also the **bus number 4L** leaving from Piazzale Cialdini (stop Mestre Centro B1).
Departures from Mestre to Venezia every ten minutes; From 6:16 am until 0:20 am (Monday to Sunday).
Departures from Venezia to Mestre every ten minutes; From 6:14 am until 11:56 pm (Monday to Sunday).

Map from Centro Culturale to Piazzale Cialdini



ABSTRACTS ORAL PRESENTATIONS

PLENARY LECTURES

PL1 – Monday, the 5th of September

Enzymes as Green Catalysts for conversion of Biobased Molecules

I.W.C.E. Arends*, C.G. Boeriu, L.G. Otten, F. Hollmann.

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Keywords: biotransformations, oxidations, reductions, oleic acid.

Abstract

Nature uses enzymes to catalyze a wealth of biotransformations. However in practice these transformations are carried out *in-vivo* under conditions which are far from suitable for large scale production of chemicals. It is our challenge to engineer or design enzymes in such a way that they can be employed *in-vitro* as catalysts [1]. In the lecture it will be discussed how different classes of enzymes can be employed as highly promising catalysts for a variety of reactions that are pivotal for the conversion of biobased molecules.

Some notable examples from our lab which will be presented are the reduction of volatile fatty acids using *Pyrococcus furiosus* strains [2], the oxidation of alcohols using a variety of enzymes and cofactor regeneration methods [3], enzymatic reductions using water as electron donor [4], the hydration of oleic acid leading to i.e. polymeric building blocks [5, 6]. Also the need for integrated processes with upstream treatment of biomass will be highlighted.

References

[1] F. Hollmann, I.W.C.E. Arends, K. Buehler, A. Schallmey and B. Bühler, *Green Chem*. **2011**, 13, 226-265.
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PL2 – Tuesday, the 6th of September

Exploration of New Chemical Reactivities for Synthetic Efficiency

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Keywords: Reactions in water, C-H functionalization, OH-actiavtion

Abstract

Rapid and efficient molecular making plays an important role in the development of any new product in the pharmaceutical, fine chemicals, materials, and biotech industries. However, conventional tools for chemical synthesis commonly starts with fossil feedstocks and often requires lengthy routes as well as overall low efficiency in time, manpower, and material utilizations. Thus, exploration of new reactivities towards high efficiency is crucial for future sustainability in chemical syntheses. Toward this long-term objective, we have been exploring various unconventional chemical reactivities that can potentially simplify synthesis, reduce overall waste generation and maximize resource utilization. These include: (1) developing Grignard-type reactions in aqueous media to simplify protection-deprotections; (2) developing nucleophilic addition reactions by using C-H bonds as surrogates for organometallic reagents, to simplify halogenation-dehalogenation and avoid the utilization of a stoichiometric amount of metal for such reactions (possibly in water); (3) developing direct C-H and C-H coupling (Cross-Dehydrogenative-Coupling) to explore the possibility of chemical transformations beyond functionalization and defunctionalization in syntheses; and (4) developing direct transformation biomass alcohols, amino acids, and lignin-based phenols. This talk will present some of the more recent progress on these topics from our laboratory.

References

[1] Li, C.-J. *Acc. Chem. Res.* **2002**, *35*, 533.
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PL3 – Tuesday, the 6th of September

Advance Zeolite Catalysts for Sustainable Production of Basic Chemicals

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Keywords: Zeolite, MTO, Biomass conversion, CO_2, Solar H_2

Abstract

Our comfortable modern life is supported by numerous chemical, in particular petrochemical, products. We need to develop the methods for manufacturing chemical products from more substantial fossil resources and for the long term, preferably from renewable resources.

Because of the shale gas revolution, the use of methane as chemical feedstock as well as fuels to the lower olefins. At this time methanol is considered as getting more available chemical feedstock. Methanol to olefins (MTO) reaction is a promising route to the lower olefins. For the MTO reaction, currently, industrial processes use ZSM-5 (**MFI**) and SAPO-34 (**CHA**) zeolites. We have found CIT-1 (**CON**) zeolite is promising for selectively converting methanol to propylene and butenes without serious loss of activity. It is to be noted that in China lower olefins started to be produced from coal through coal gasfication followed by the MeOH synthesis and subsequent MTO reaction.

While fossil fuels will be the dominant factor in the future energy and chemicals scenario for a couple of decades to come, we need to develop methods of alternative chemicals production. Bioethanol has been widely used as additive and alternative to gasoline. Ethanol can be easily converted to ethene and in Brazil etc. BiproPE and PET30 (30% from biomass and 70% from petroleum) are commercialized. Even PET100 can be manufactured by synthesizing *p*-xylene via various routes using zeolite catalysts starting from biomass resources. These are called drop-in replacements.

Compared to petroleum and natural gas, biomass has low H/C and high O/C ratios and low calorific value. Thus biomass could be useful for the production of chemical products that are not manufactured on a massive scale in the current petrochemical industry instead of drop-in replacements. It has long been recognized that 5-hydroxymethylfurfural (HMF) is a bio-based “platform” material for producing useful chemicals and polymers. Increasing research interest has been paid to the synthesis of HMF from sugars, particularly from glucose. We have found an effective transformation of glucose to HMF over Beta (*__BEA__) zeolite by finely tuning acid properties. Meanwhile, a great deal of effort has been devoted to the production of sorbitol, as bio-based feedstock, from cellulose. For example, sorbitol can be converted to isosorbide (1,4:3,6-dianhydrosorbitol) through double intramolecular dehydration. Isosorbide can be used to produce polymers such as polyester and polycarbonate. We have developed highly active zeolite catalysts for the dehydration of sorbitol to isosorbide in water.

For a future sustainable chemicals scenario, it may be desirable to develop efficient methods for utilizing CO_2 by using renewable energy, which could be the ultimate goal. Photocatalytic decomposition of water by visible light, which accounts for a great majority of sunlight, is an enormous challenge and it is absolutely necessary to activate the research in this field. In Japan a 10-year national project named ARPChem (Artficial Photosynthesis of Chemicals) that targets the recycling CO_2 by using solar H_2 started in 2012. At this moment this project focuses on the production of light olefins as chemical feedstock. We are developing the process consisting of methanol synthesis from CO_2 and H_2, followed by the MTO reaction catalyzed by zeolites.

PL4 – Wednesday, the 7th of September

Sustainable Chemistry – Addressing future societal challenges

Martin Kayser
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Abstract

Chemistry is essential in modern life as more than 95% of all manufactured goods are directly touched by chemicals. The global chemical industry has developed countless products improving people’s lives, enabling life-saving medical solutions, cleaner water, a healthy and more abundant food supply, cleaner and more efficient sources of energy and advanced building and construction materials to design the cities of the future. Therefore, chemicals address a variety of today’s societal challenges and contribute to sustainable development. However, some chemicals possess intrinsic hazardous characteristics and hence require applicable management practices to control their risk. Science- and risk-based regulation in combination with voluntary industry initiatives like Responsible Care® and the Global Product Strategy (GPS) are best suited to achieve sound management of chemicals, which forms the prerequisite for Sustainable Chemistry. Sustainable Chemistry is not limited to substitution of hazardous chemicals, but describes a more holistic approach taking the entire product life cycle, recycling aspects and the three sustainability pillars (economy, ecology, society) into consideration.

PL5 – Thursday, the 8th of September

Chemistry in water usingmicelles: Applications in the pharmaceutical industry

J. Kaschel[1], J. Klee[1], T. Lindner[1], J. K. Pratt[2], A. M. Reingruber (née Linsenmeier)[1,3]and W. M. Braje[1*]

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Keywords: metal-catalyzed reactions, micelles, water

Abstract

In a typical chemical reaction in the pharmaceutical industry, solvent use accounts for 60-90% of waste created. [1] Additionally, organic solvents play a dominant role in the overall toxicity profile of most processes and are therefore the chemicals of greatest concern. Strategies to minimize the economic and environmental footprint of organic solvents are of utmost interest.

One alternative to organic solvents follows the lead of Nature: water. To circumvent the solubility issues, newly developed surfactants by the group of Prof. Lipshutz offer an opportunity to enable organic reactions to proceed efficiently in water at room temperature. These environmentally benign surfactants spontaneously self-aggregate in water and the resulting micellar arrays serve as nanoreactors.[2]

We will disclose applications of micellar catalysis for the most important reaction types performed in the pharmaceutical industry (e.g. transition-metal-catalyzed reactions such as Buchwald-Hartwig aminations, Suzuki and Negishi couplings). Often times such reactions in water display advantages compared to conventional reaction conditions in organic solvents. [3] This green and cost effective methodology enables reactions to be performed under environmentally benign conditions by avoiding hazardous, toxic and expensive organic solvents and shows potential to bridge the different needs of medicinal and process chemistry.

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PL6 – Thursday, the 8th of September

Synergy in Bioenergy, Food and Materials from Biomass

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Keywords: Synergy, Biomass, Food, energy and materials, Sustainability

Abstract

The use of biomass as a source of energy and raw materials shows an overall growing trend with ups and downs related to oil prices that are in turn heavily affected by political and strategic factors. Nevertheless, there are many signs of increasing use of renewable resources but at different rates, depending on the country and world region. A frequent objection to the growing use of biomass as a source of energy and raw materials is that this will compete with food production, contributing to increase food prices and thus decreasing the possibility to have adequate supply for a growing population across the world.

The Brazilian experience from the past four decades shows that synergy [1] may be created in the multipurpose use of agricultural land showing how the energy push took place in parallel with a large increase in food supply and a relatively small increase in the used land, thanks to technological inputs in every front: soil conservation and improvement, agricultural practice, logistics and industrial processing.

A side product is the large increase in the production of biomass residues that leads to efforts for their utilization, contributing to CO_2 sequestration from the atmosphere while increasing fuel and raw materials supplies.

Some specific cases will be presented [2], discussing opportunities offered by biomass, together with two special features of materials from biomass that were understood only recently: the "mystery of natural rubber" and the ever surprising richness of the properties of cellulose.

The presentation will conclude with the examination of research needs [3] and perspectives for increased food, energy and materials production from biomass, leading to a sustainable global economy.

References

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KEYNOTE LECTURES

K1 – GREEN MATERIALS

Green Analytical Chemistry: Chemical Sensors Based on Green-Synthesized Nanostructured Reagents

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**Email: fortunato.sevilla@ust.edu.ph*

Keywords: Green nalytical chemistry; Chemical sensors; Green synthesized sensing reagents; Nanostructured reagents

Abstract

Chemical sensors present a green methodology in analytical chemistry. These analytical devices peerform measurements through the transduction of a physicochemical property, such as color and electrical conductivity, of the sensing phase into an electrical signal. The sensing phase consists of a solid-phase or immobilized reagent which interacts with the analyte and consequently exhibits a change in its property. Nanostructured materials, such as gold nanoparticles, carbon nanotubes and graphene, have been employed in the sensing phase, enabling the measurement of low concentrations of analyte.

Measurements with chemical sensors are consistent with the paradigm of green chemistry, involving small amounts of samples, minimal or no pretreatment and practically zero reagent consumption. Likewise, green synthesis, particularly of nanomaterials, have been applied in the preparation of the sensing phase of some chemical sensors. Examples of these sensors will be presented.

K2 – GREEN BIOPROCESSES

Organocatalytic Multicomponent Reactions in the Discovery of Enzyme Inhibitors

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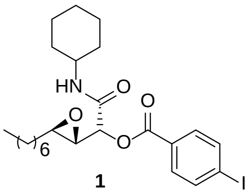
Keywords: organocatalysis, multicomponent reactions, asymmetric synthesis, microwave

Abstract

A number of organocatalysts and processes, such as one-pot, tandem, cascade or multicomponent reactions, have been reported. The many advantages of organocatalysis - robust, non-toxic, affordable, inert atmosphere, easy reaction manipulation, etc. - allow the preparation of bioactive compounds using simple and metal-free procedures, thus avoiding false positives in the biological evaluation [1]. In this presentation, we will discuss our latest results on the synthesis of natural-product-like hybrids employing organocatalytic multicomponent reactions, such as Passerini (**1**) and Ugi (**2**) [2], and their evaluation as potent inhibitors of cholinesterases and cysteine proteases.



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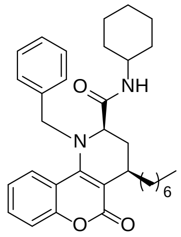

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K3 – OPCW SESSION

Promoting peaceful chemistry and ensuring chemical safety, security and sustainability -

The OPCW's role and its initiative on Green Chemistry

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Article XI of the Chemical Weapons Convention (CWC) provides a set of objectives which are designed to foster international cooperation between States Parties for the sustainable economic and technological development in the area of chemistry. The cooperation involves different stakeholders including S&T, National Authorities (NA) and aims at removing burdens related to and hence facilitating the right of States Parties to conduct scientific research, develop, store, produce and transfer chemicals for peaceful purposes. Thus, the Convention offers tangible benefits to the States Parties in addition to the disarmament goals. In the framework of the implementation of article XI the support actions of the OPCW-TS are focusing on the peaceful applications of chemistry. Green chemistry meets the OPCW objective to foster safety and security at chemical plants by providing the alternative to replace potentially hazardous toxic chemicals,.

The OPCW initiative on green chemistry is being implemented within the framework of the decision on the "Components of an Agreed Framework for the Full Implementation of Article XI" (C-16/DEC.10, dated 1 December 2011), taken by the Conference of the States Parties at its Sixteenth Session, which calls upon the Secretariat of the OPCW to "cooperate with and advise National Authorities with a view to finding non-toxic chemical substitutes to reduce the risks associated with toxic chemicals as well as to promoting activities from a health, safety, anti-terrorism, and general security point of view".

K4 – RESTORATION OF CULTURAL HERITAGE

New Sustainable Technology to Recover Returned Concrete

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Keywords: Construction, Concrete, Aggregates, Sustainability, Circular economy

Abstract

Concrete is the second most used material in the world, after water. More than 10,000 million cubic meters are globally produced every year, with the consumption of more than 19,000 million Tonnes of natural aggregates (coarse aggregates and sand). For different reasons, about 200 million cubic meters of concrete (2 per cent of the global production) are not placed at the jobsite and are returned to the ready-mixed production plant where, in most cases, are disposed to landfill as waste material. Recently, a new technology to treat returned concrete has been developed: one cubic meter of returned concrete is treated with non-dangerous additives and transformed, in few minutes, into 2.3 Tonnes of aggregates, without any waste production. The new aggregates can be used to produce new concrete materials, with excellent mechanical performance and environmental compatibility. The new method has many advantages because it allows to save virgin aggregates and to reduce the natural resource depletion. Furthermore, returned concrete is 100% recovered and no waste is produced, completely eliminating landfill disposal. For these reasons, the new technology has a positive effect on the environmental impact of returned concrete, with hundred-fold reductions of the main parameters characterizing the environment footprinting. Furthermore, the new technology allows a reduction of the costs both for waste disposal and for aggregates supplying, representing an excellent example circular economy.

Figure 1. Example of newly formed aggregate from returned concrete

K5 – GREEN MATERIALS

Innovative Solutions for a Greener Fluorine Chemistry

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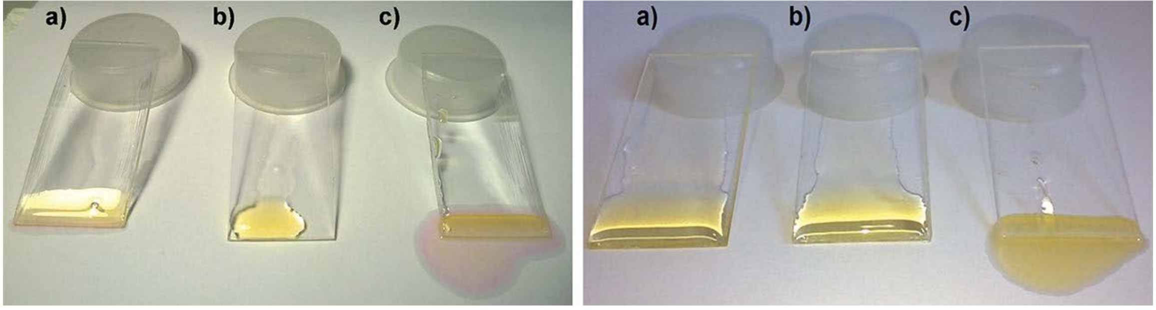
Keywords: Hydrophobin, Natural Surfactants, Fluorine, Coating, Nanomaterials

Abstract

Under the major background of current economic shifting, a lot of new applications of fluorine chemical products is springing up and becoming the new growth points of fluorine chemical products. In particular, the new energy, new materials, energy saving and environmental protection, electronic information, high-end medicines, pesticides, textile and other fields are needing more and more fluorine-containing fine chemicals. On the other hand, the use of fluorinated chemicals have raised numerous environmental and health concerns due to, e.g., their persistency in the biosphere. This has prompted many new research directions in the search for more sustainable fluorinated solutions.

In this lecture, it will be presented how Hydrophobins, natural biosurfactants containing no fluorine, are very effective surfactants for fluorinated oils [1], polymers [2] (see Figure), and gases [3,4]. Furthermore, new, more sustainable branched fluorinated molecules will be presented as effective ^{19}F MRI contrast agents, as well as ligands for innovative fluorinated nanomedicines.



A protein nanosized primer layer enables the otherwise inefficient binding of a perfluoropolyether onto a polystyrene surface, reducing its oleophilic character.

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K6 – GREEN BIOPROCESSES

Carbon Dioxide Chemistry: Carbon Capture and in Situ Conversion

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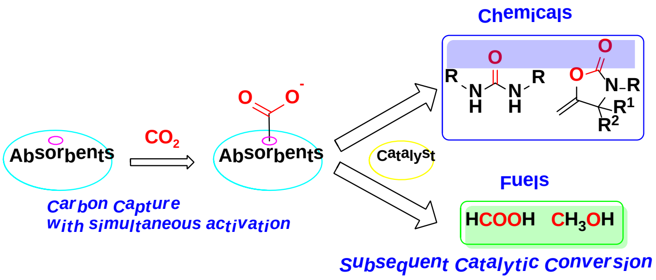
Keywords: Carbon dioxide, Catalysis, Sustainable chemistry, Synthetic methods

Abstract

As an abundant, nontoxic, non-flammable, easily available, and renewable carbon resource, CO_2 is very attractive as an environmentally friendly feedstock for making commodity chemicals, fuels, and materials[1]. Unfortunately, few reactions involving CO_2 are thermodynamically feasible originating from low reactivity of CO_2. In addition, On the other hand, the reactions involving CO_2 are commonly carried out at high pressure, which may not be economically suitable and also pose safety concerns. Therefore, developing efficient catalysis for CO_2 conversion especially under mild conditions is extraordinary desirable and remains a great challenge. In 2011, we proposed the “carbon capture and utilization” strategy as an alternative approach to circumvent the energy problem in carbon capture and storage process [2]. The essence of this strategy could be simultaneous activation of CO_2 upon its capture and thus in situ catalytic transformation into value-added chemicals and fuel-related under mild reaction conditions, avoiding additional desorption step [3].



As a consequence, we have developed efficient absorbent to reach equimolar absorption. The capture CO_2 could simultaneously result in its activation, thus subsequent conversion into chemicals and energy related products more easily rather than going through desorption process.

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K7 – GREEN INDUSTRIAL PROCESSES AND MOLECULAR INNOVATION

New Green Catalysts for Cross-coupling Reactions

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Keywords: Cross-coupling reactions, *C,P*-ligands, Catalyst design, Water-soluble phosphines, Fluorous-phase-soluble phosphines

Abstract.

The majority of the catalytic reactions could be considered as “green” or “partially green”, since they always satisfy some principles of Green Chemistry. Nevertheless, especially in the cases of homogeneous transition metal mediated cross-coupling reactions, only rarely all twelve the principles are obeyed. Most cross-coupling reactions are still carried out in organic solvent at relatively high temperature, and they are promoted by significant amount of conventional catalysts, suitable for a single use only [1]. Such traditional approach also complicates a procedure of products isolation, and may force a chromatographic purification step. The multiphase homogeneous catalysis, mediated by highly active, even at low temperature, transition metal complexes of special phosphines [2] (soluble only in one of the phases), could be considered as an alternative to that.

Herein we are intended to demonstrate synthesis and application of new highly electron rich, sterically hindered, chelating monophosphine ligands of *C,P*-type of complexation, designed to be used in difficult cross-coupling reactions under the mild and sustainable conditions. Several ligands, soluble in water or soluble in fluorous solvents, could be obtained in syntheses, based on the common modular synthetic pathway, in high yields.

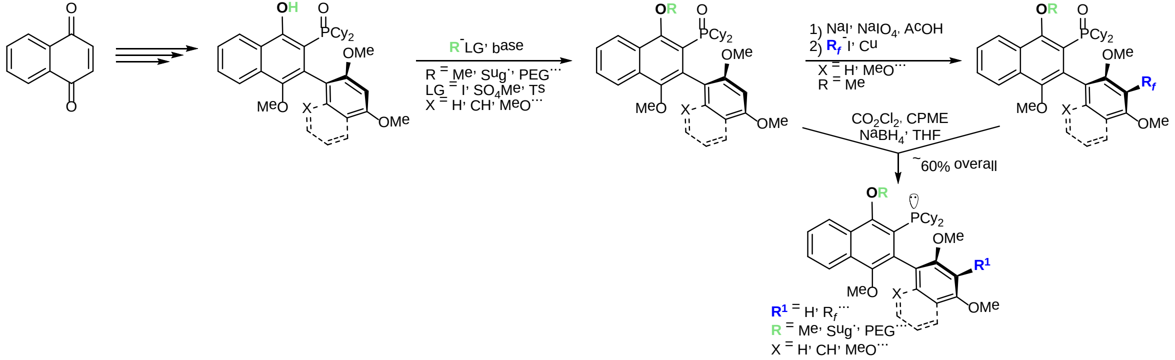

Figure1. The synthesis of new ligands.

The results of our studies on catalyst design and synthesis, green catalysis, and finally, on catalyst recovering and reusing, as well as some other issues, will be discussed in details.

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K8 – UNESCO/PHOSAGRO/IUPAC SYMPOSIUM

Reducing heavy metals in our food chain with greener mineral fertilizers

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Abstract

The danger of heavy metals pollution. Influence of selected heavy metals on humans, animals, plants. Pathways of heavy metals in the food chain of animals and humans.

Systematic policies to reduce pollution with heavy metals as a tool to improve the efficiency of land use and the use of groundwater resources.

Labelling, regulation of content and other ways of environment protection from the harmful effects introduced into the soil of nutrients.

K9 – GREEN MATERIALS

Chrysophyllum cainito (Star apple) leaf extract stabilized colloidal metal nanoparticles and their applications

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Keywords: *metal nanoparticles, green synthesis, Chrysophyllum cainito, polyphenols, catalysis.*

Abstract: A simple green chemical method for the one step synthesis of metal nanoparticles (MNPs) has been described by reducing the metal salts with the leaf extract of *Chrysophyllum cainito* in aqueous medium at room temperature. The phytochemicals present in the leaf extract were highly efficient to reduce the metal ions into metal atom (0) and stabilize the as synthesized MNPs without any additional capping agents. The synthesized MNPs are stable at room temperature. The stabilized MNPs have been characterized in detail by spectroscopic, electron microscopic, light scattering and X-ray diffraction measurements. Interestingly, the synthesized MNPs have been shown as efficient catalyst for reduction reactions and C-C coupling reactions. In addition, the MNPs have significant in vitro antibacterial activity against both gram positive and gram negative bacteria. A novel organic-inorganic trihybrid material has also been synthesized by in-situ generation of palladium nanoparticles (PdNPs) in a hybrid gel matrix based on renewable chemicals [1]. The xerogel of this trihybrid material has been used as a recyclable heterogeneous catalyst for C-C coupling and reduction reactions in aqueous medium.

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K10 – GREEN BIOPROCESSES

From biomass to advanced biofuels

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Keywords: Waste biomass, Biofuels, Biological processes, Thermochemical processes

Abstract

Liquid carbon-neutral biofuels are largely considered a possible way to face the new energy needs without dramatically increasing the carbon dioxide concentration in the Earth atmosphere. For European oil companies, diesel fuels are most important since, in Europe, the diesel to gasoline ratio is steadily increasing.

Few technologies are currently applied to produce diesel fuels based on renewables, most of them based on first generation feedstock, in competion with the food, feed and land use.

This contribution will be focused on the emerging technologies for the production of "advanced" biofuel starting from waste biomass including those under development by eni SpA.

Considerable industrial achievements have been recently reported, for instance, in the hydrotreating of vegetable oils and animal fats (HVO). Ecofining HVO technology [1], jointly developed by eni/UOP, has been already applied by eni in the green refinery of Venice (Italy).

In order to find alternative feedstocks, there is also significant interest for routes to transform cellulosic sugar (i.e., produced via a proper hydrolysis of lignocellulosic biomass) into microbial lipids [2]. This fermentation would provide a possible way to overcome the productivity limitations of classic oleaginous crops.

Even larger oil productivity can be achieved, by cultivation of photo synthetic microalgae, growing on carbon dioxide from industrial activities, power plants and natural gas wells, able to accumulate a significant amount of oils (triglycerides) as energy storage material inside the cell.

Alternatively, diesel biofuels can be obtained by thermochemical transformation, such as pyrolysis, gasification and hydrothermal liquefaction of waste biomass followed by the upgrading of the resulting liquid or gaseous intermediates [3].

Eventually, it is most likely that the success of one or the other of these technologies will depend on several factors, including the availability and the quality of the feedstock, the complexity of the process, the integration with the existing refinery processes, and the quality of the final biofuel.

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K11 – GREEN INDUSTRIAL PROCESSES AND MOLECULAR INNOVATION

Pot-Economic Cascade Reactions with Recyclable Organocatalysts

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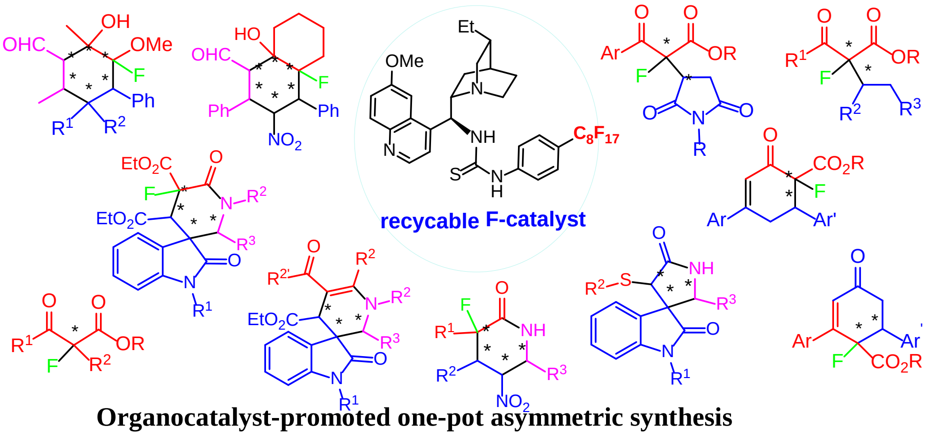
Keywords: Organocatalysis, Pot Economy, Asymmetric synthesis, Fluorous, Cascade reaction

Abstract

Organocatalysis has advantages of toxic heavy metal-free, mild reaction conditions, novel mood of activation, and good structural amenability. However, organocatalysis usually requires high catalyst loading (up to 20 mol%). Fluorous technology provides an efficient way to address the catalyst separation and recovery issue. This presentation highlights our recent effort on the development of recyclable organocatalyst-promoted cascade reactions involving fluorination, Michael addition, Robinson annulation, Mannich reaction, and other transformations for asymmetric synthesis of biologically interested compounds with multiple stereocenters.



Organocatalyst-promoted one-pot asymmetric synthesis

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K12 – GREEN MATERIALS

The Sustainable Development Challenge: Pirelli Tyre's View

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Keywords: Tyres, Rubber, Sustainability, Life Cycle, Open Innovation

Abstract

Tyres are complex engineered products, integrating hundreds of raw materials and diverse technological inputs.
Tyres account for 20-30% of the Carbon Footprint of the EU medium car: a cornerstone of Sustainable Transportation is the development of more and more sustainable tyres, achievable through the integration of electronics and through new design, processes and materials (polymers, nanofillers and chemicals).

Pirelli adopts a management approach integrating the Economic, Social and Environmental dimensions of Sustainability, involving all company functions from Research and Development to Purchasing, Human Resources and Finance.
Pirelli's sustainability plan [1] integrates and supports the group's industrial plan with a vision to 2020, and was developed in accordance with the "Value Driver" model inspired by the UN PRI (Principles for Responsible Investment) and UN Global Compact to encourage dialogue between investors and firms on sustainability issues (ESG, Environmental, Social, Economics).
Pirelli's Environmental Strategy is based on a Life Cycle approach identifying the impact of each stage in terms of energy and water KPIs and setting Objectives accordingly.

Tyre development is driven by vehicles manufacturers, legislation and market forces: Pirelli integrates the former inputs into an Open Innovation Model, involving collaborations with leading OE manufacturers, selected Suppliers and Research Institutes.
Environmental Sustainability is a key objective of technical developments, aiming at minimizing tyre Rolling Resistance while keeping the other tyre performances. New Materials are a fundamental part of Pirelli's Innovation Strategy: Pirelli is developing, through Joint Development Agreements with suppliers, polymers featuring exclusive solutions to resolve trade-offs between Rolling Resistance, Wet and Winter performances, and through University Collaborations new Biofillers and Nanofillers to support lighter structures and further contribute to reduce the environmental impact of tyres minimizing the impact of raw materials (developing renewable materials and low footprint mineral-origin fillers). Pirelli set the target to reduce the RR of its car tyres by 40% in 2020 vs 2009.
Green Performance Products, which combine performance and respect for the environment, represented 48% of total Pirelli tyre 2015 turnover.

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K13 – GREEN POLICY, SUSTAINABILITY AND SAFETY

L'Oréal's Commitment to Green and Sustainable Chemistry

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The integration of green chemistry principles [1] in the development of any new process or new ingredient is a pivotal element of sustainable development.

The objective of this presentation is to provide a rapid description of the commitment of L'Oréal [2], worldwide leader in cosmetic products.

Within the scope of its Sharing beauty With All sustainability agenda, L'Oréal will innovate so that by 2020, 100% of its products will have an environmental or a social benefit. The reduction of the environmental footprint of formulae, combined with the increasing use of renewable raw materials that are sustainably sourced or derived from Green Chemistry will be major drivers for reaching this objective.

The approach of L'Oreal group [3] in the use of renewable raw materials [4], the development of eco-friendly processes [5] and the development of new ingredients with favorable environmental profile are presented in more details.

As an illustration of green process implementation, several examples of development were selected. Among them, C- glycosides of interest in our different applications such as skin care active ingredients [6] will be described.

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K14 – GREEN INDUSTRIAL PROCESSES AND MOLECULAR INNOVATION

A Green Procedure for Solketal Production from Acetone and Glycerol using CO_2 as Switchable Catalyst

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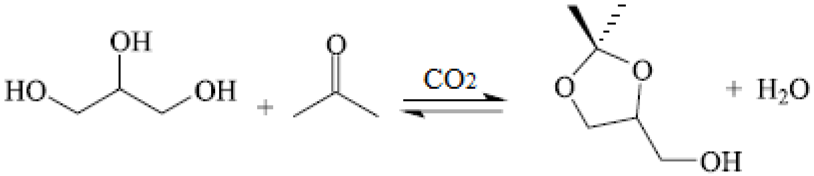
Keywords: Glycerol, Carbon dioxide, Bioaddtives, Design of Experiments

Abstract

Biodiesel is one of the main biofuels used worldwide. The increase of its use has reduced the price of glycerol, which is produced in approximately 10 wt% as byproduct of biodiesel production [1]. Glycerol is used in a large variety of applications such as personal care products, pharmaceuticals, polymers, food, etc. Nevertheless, these applications cannot drain the large amounts of glycerol being produced. Solketal is produced from the acid-catalyzed reaction of glycerol and acetone [2] and can be used as a renewable fuel additive [3]. We wish to report the production of solketal from the reaction of acetone with glycerol in the presence of CO_2, which acts as switchable acid system (Scheme 1).



Scheme1. Reactionofglycerolwithacetoneunder CO_2 as acidcatalyst.

In this work, a design of experiments (DoE) was used to study the ketalization of glycerol with acetone using carbon dioxide as switchable homogeneous catalyst. Experimental tests were carried out according to a fractional factorial design, with 2 levels and 4 parameters (2^{4-3}). A Parr® reactor of 100 mL volume and mechanical stirring was used to run the reactions. The parameters studied were temperature, initial pressure of CO_2, glycerol/acetone molar ratio and reaction time. The results of glycerol conversion were analyzed by GC-MS. In all cases, solketal was the only product observed. The highest conversion observed was 71%, at 110°C, 45Bar, 1:2 molar ratio and 2 h.

The procedure is being tested in reactions of crude glycerol of biodiesel production, where the excess of basic catalyst and other salts impairs the use of heterogeneous acid catalyst [4].

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K15 – GREEN ENERGY

Rational Design of Nanostructured Photocatalysts for Efficient Solar Fuels

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Keywords: Photocatalysis, Water splitting, CO_2 photoreduction, Solar fuels, Hydrogen

Abstract

The efficient conversion of solar energy into fuels through the photocatalytic water splitting into hydrogen and photoreduction of CO_2 into high value-added chemicals is very important for the development of a sustainable energy future [1]. To achieve this goal, photocatalysts must be rationally designed and controllably synthesized for improved performances. Nanostructured phtocatalysts have attracted much attention due to their unquie physical and chemical propertires compared with corresponding bulk materials. Recent research progress in my group has been reported on the rational design and controlled synthesis of nanostructured photocatalysts for highly efficient visible light-driven H_2 evolution and photocatalytic conversion of CO_2 and CO into fuels by enhancing the light absorbance and separation of electron-hole pairs of photocatalysts. (1) By developing high conductive support for photocatalysts, the quantum efficiency of photocatalytic H_2 production achieved 33% at 420 nm; (2) By creating more defects in photocatalysts, the photocatalytic reduction of CO_2 with water by ultrathin ZnAl-LDH nanosheets exhibited stable activities of $\approx 7.6\ \mu mol\ g^{-1}\ h^{-1}$; (3) By constructing heterogeneous interface structure, NiO/Ni nanocatalysts exhibited an unexpectedly high selectivity for C2+ hydrocarbons in the CO hydrogenation reaction under visible-light irradiation.

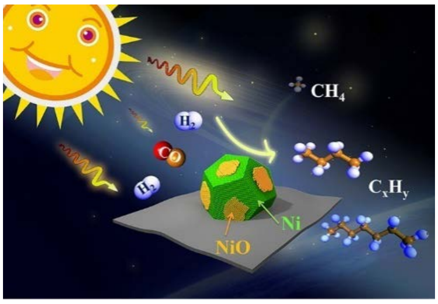

Figure 1. Illustration of NiO/Ni nanocatalysts selectively photocatalized the CO hydrogenation reaction for C2+ hydrocarbons under visible-light irradiation.

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K16 – GREEN ENERGY

Design and Synthesis of Organic Dyes and Their Application in New Generation Photovoltaics

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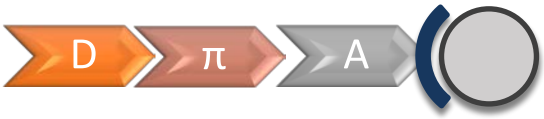
Keywords: Dyes, renewable energy, solar cells.

Abstract

Dye-Sensitized Solar Cells (DSSC) represent a very promising technology to convert solar energy in electric current, due to their low cost of production and their colorful and decorative features.[1]
The core component of a DSSC is the sensitizer. In this contest metal-free organic dyes[2] have been successfully used, offering the advantages to enhance light harvesting by tuning the absorption over a broad spectral range and pursuing high extinction coefficents. Furthermore, expensive and hazardous metals are avoided.
Our interest in the field involved the design, with the aid of DFT computational analysis, and the synthesis of new organic dyes in order to study their structure–property relationships and exploit a possible application in DSSC.[3]



- **D** Donor group
- **π** Conjugated spacer
- **A** Acceptor/ and anchoring group

Organic dyes possessing donor and acceptor moieties bridged by a π-conjugated unit (called D-π-A structure) have been mainly investigated. Some of these dyes showed interesting features such as extremely intense light absorption in the visible spectrum, good stability and very good power conversion efficiencies,[3c] proving to be suitable for application in transparent thin-layer DSSCs.

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K17 – GREEN POLICY, SUSTAINABILITY AND SAFETY / EDUCATION

Building biorefineries for the bioeconomy: an interdisciplinary postgraduate green chemistry course

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Keywords: bio refineries, green chemistry in HEI, postgraduate courses.

Abstract

Nowadays there is a demand for the introduction of new concepts and practices related to sustainability in RD&I and education in Chemistry, especially in the undergraduate and postgraduate courses, when green chemistry and biorefinery are considered in the context of the bioeconomy. In this work an interdisciplinary short-course at the post-graduate level developed at UFSCar in 2015 titled "Building biorefineries for the bioeconomy" - connecting several areas as chemistry, economy, biology, social sciences, management and law - will be presented [1]. The course involved lectures, interactive exercises and real case studies. Analyzing the availability, composition and production methods of different Brazilian agro-industrial resources and their by-products was vital for exploring their valorization, industrial challenges for their use and associated environment, social and economic impacts. For instance, searching the volumes available of some biomass residues helped identifying whether they can be used for a high-volume low-value application such as solvents or plastics or for a high-value low-volume application such as cosmetics or nutraceuticals. The students´ projects showed their integrated building capacity and knowledge exchange. The proposal contributed to develop a new understanding of the role of chemistry in the context of the bioeconomy, comprehending (and expanding) the original content knowledge presented in the syllabus course. More than this, the socio-construction of knowledge were understood as constituent elements of science and technology processes radically compromised with critical thinking and actions towards socio-eco-justice and sustainability, especially important in Brazil [2,3].

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Fapesp, Newton Fund and CNPq

K18 – GREEN INDUSTRIAL PROCESSES AND MOLECULAR INNOVATION

Definition of green synthetic tools based on safer, recoverable and biomass derived reaction media

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Keywords: Catalysis, Biobased chemicals, Flow chemistry, Waste minimization

Abstract

Our research program is mainly committed to the definition of efficient and sustainable synthetic tools by combining the development of several crucial areas of investigation: i) use of safer reaction media (such water, azeotropes or bio-based reaction media) or solvent-free conditions (SolFC), ii) preparation and use of heterogeneous recoverable and reusable catalytic systems based on supports tailor-made for their use in greener reaction media or under SolFC; iii) definition of flow reactors able to allow the recovery of products with minimal waste production [1].

Our efforts have been recently directed towards the development of chemically and environmentally-efficient synthetic protocols for metal-catalyzed transformations for C-C bond formation[2] and some representative examples from our laboratories will be presented in this communication.

References

1. For some recent examples see: L. Vaccaro et al. *Org. Lett.***2016**, *18*, 2680–2683; *Adv. Synth. Catal.***2016**, DOI: 10.1002/adsc.201600287; *Green Chem.***2015**, *17*, 365-372; *Chem. Commun.***2015**, *51*, 15990-15993; *Green Chem.***2015**, *17*, 365-372;

2. For some frecent examples see: L. Ackermann, L. Vaccaro et al. Green Chem., 2016, DOI: 10.1039/C6GC00385K; Green Chem., 2016, DOI: 10.1039/C6GC00385K.

K19 – GREEN INDUSTRIAL PROCESSES AND MOLECULAR INNOVATION

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K20 – UNESCO/PHOSAGRO/IUPAC SIMPOSYUM

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WINNER OF THE 2016 IUPAC-CHEMRAWN VII PRIZE FOR GREEN CHEMISTRY

Green Reaction Media Protocols: From Solvent-Free to Catalysis State-of-the-Art

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Keywords: Nanomaterials, Biopolymer composites, Magnetically recyclable, Heterogeneous nanocatalysts, Multicomponent reactions.

Abstract

In the last decade, upon classification and introduction of twelve principles for green chemistry by Anastas and Eghbali in a critical review in 2012 [1], diverse reports have been shown in literature. Nowadays, green reaction media includes various subjects such as solvent-free, water, ionic liquids, green catalysts and catalytic reactions including magnetically recyclable and reusable heterogeneous nanocatalysts, one-pot multicomponent reactions [2] that deserve least reaction steps and side-reactions or by-products, high yields, saving energy, high atom economy and bond forming efficiency in the synthesis of organic compounds, and bionanomaterials like natural and synthetic biopolymers composites. Recently, magnetically recyclable and reusable heterogeneous nanocatalysts have attracted much attention in alternative environmentally-benign organic methodologies. Due to importance of the field, a comprehensive review article was published in the fast-growing field of magnetically recyclable nanocatalysts in 2014 [3]. Our research group is mainly focused on design and development of green and sustainable reaction media, especially on biopolymers composites as green catalysis and green solvents in organic synthesis [4].

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ORAL CONTRIBUTIONS

MONDAY, THE 5TH OF SEPTEMBER

M1

Synthesis of Recyclable Polymers via Equilibrium Ring Opening Metathesis Polymerization

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Robert H. Grubbs[1,3]

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Keywords: Metathesis, ROMP, equilibrium polymerization, ruthenium, macrocyclic polymers

Abstract

The unique feature of the equilibrium polymerization reactions opens a way for the synthesis of durable, environmentally friendly elastomers where polymers including synthetic tire additives, wrapping and bio-materials can be not only synthetized but also readily recycled by the same transition metal catalyst system.

The linear *trans*-polypentenamer has unique relevance among the synthetic rubbers since it has similar physical properties to the natural rubber. Polypentenamer was synthetized by equilibrium ring-opening metathesis polymerization (ROMP) using well-defined ruthenium catalyst systems. The activation enthalpy and entropy were determined as $\Delta H = -5.6$ kcal · mol^{-1} and $\Delta S = -18.5$ cal · mol$^{-1}\cdot$ K^{-1}. One of the most exciting new possibilities is the capability of preparing cyclic polypentenamers. Since many of the properties of polymers are controlled by end group and the defects they introduce, cyclic polymers that contain no end groups should show new and valuable physical properties. New approaches to the synthesis of cyclic polypentenamers have been recently developed. Highly pure cyclopolypentenamer (MW: 36 kDa; PDI: 1.3) have been synthetized in equilibrium ring opening metathesis polymerization by silica supported Hoveyda-Grubbs second-generation catalyst systems. The Mark-Houwink "a" parameters show significant difference between the linear (0.59 ± 0.4) and cyclic (0.92 ± 0.05) polypentenamers indicating the formation of high number of double bond containing, rigid cyclic polyolefins. The silica supported catalysts systems could be recycled three times without significant reduction of polymerization yield.

Highly polar well-defined poly(vinylalcohol) co-polymers (MW: 16.6 kDa; PDI: 1.5) have been synthetized by equilibrium ROMP of 3-cyclopentene-1-ol. The thermodynamic parameters were determined as $\Delta H = -6.4$ kcal · mol^{-1} and $\Delta S = -21.4$ cal · mol$^{-1}\cdot$ K^{-1}. Because of the similar ring strain energies of cyclopentene and 3-cyclopentene-1-ol, their equilibrium copolymerization results in a polymer having randomly distributed dyads. The concentration of hydroxyl groups along the polymer chain determines its polarity and thus the barrier properties of the polymer. Additionally, tuning of the polarity of PVA copolymers used in drug delivery applications can control targeted drug release.

The synthesis of recyclable tyre additives, polypentenamers and polyhydroxy polypentenamers with tunable polarity are reported.

M2
Concentrated Polymer Brushes as Soft and Resilient Tribo-Materials for Green Tribology

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Keywords: Polymer Brush, Graft Polymerization, Tribology, Streibeck Curve

Abstract

In high-density, concentratedpolymer brushes (CPBs) prepared by surface-initiated living radical polymerization, graft chains in a good solvent are highly stretched, nearly to their full length, giving properties quite different and unpredictable from those of semi-dilute polymer brushes (SDPBs) previously studied.[1] We revealed by atomic force microscopy that the CPBs of e.g., poly(methyl methacrylate) and poly(styrene) showed dramatically low frictional coefficients in good solvents compared with those of the corresponding SDPBs. This was reasonably ascribed to confronted CPBs hardly mixing with each other due to their huge osmotic and elastic interactions. The lubrication mechanism of CPBs was discussed according to the sliding-speed dependency of frictional coefficient, and two different mechanisms, boundary and hydrodynamic lubrications, were suggested.[2]

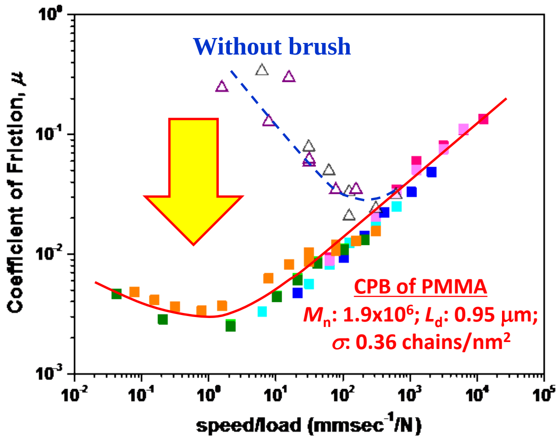

Fig.1 Streibeck curv for the thick CPB of PMMA in a good solvent.

Recently, we succeeded in synthesizing CPBs with extraordinarily large thickness using surface-initiated living radical polymerization under high pressures and in ionic liquids. With performing living radical polymerization under these conditions, the rate constant of propagation increased and the rate constant of termination decreased, making it possible to rapidly grow polymer chains with less termination. Thus obtained thick CPBs were studied in good solvents by macro-tribological measurements and demonstrated to show an excellent lubricating property as shown in Fig. 1 [3]. In other words, the thickening of CPB could eliminate the abrasion from any mixing hard particles and fully realize its potentials. This has opened up a new concenpt as soft and resilient tribological materials for green tribology.

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M3

Isocyanate-free Polyurethane via cationic ring opening polymerization of six-membered cyclic carbamates

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Keywords: cyclic carbamates, isocianate free polyurethanes, ring openining cationic polymerization

Abstract

Polyurethanes (PUs) are extremely versatile polymers: they can be thermoplastic, elastomeric, thermoset and foams, they cover a wide span of applications and their annual production is more than 18 kilotons, about 5 mass % of total worldwide polymer production. Linear PUs are usually prepared from the reaction of diols with diisocianates in the presence of catalysts, through addition step-growth polymerization.

Nowadays, more sustainable PU preparation is a hot research topic. An intriguing sustainable approach to PU, only scarcely investigated, is based on the Cationic Ring Opening Polymerization (CROP) of cyclic carbamates.

Six-membered cyclic carbamates have a great potential as monomers for the preparation of PUs via ROP. However, the use of these monomers is limited by very laborious or low yielding synthetic procedure for their preparation. Recently, dialkyl carbonate (DAC) chemistry has been exploited to develop several new approaches to six-memberd cyclic carbamates.[1]

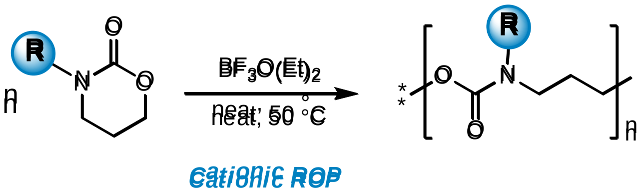

Figure 1. Cationic ROP of 1,3-oxazin-2-one leading to aliphatic polyurethanes

In this work, is reported the first example of facile, green and versatile preparation of poly(trimethylene urethanes) via cationic ROP of 1,3-oxazin-2-ones. Polymerizations were performed in the absence of solvents, at different temperatures, investigating different initiators. Various cyclic carbamates were used as monomers, bearing substituents on the nitrogen atom, such as hydrogen, alkyl, benzyl groups and phenylhydrazine.[2]

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M4

A Robust Lubrication System Based on Ionic Liquid Polymer Brushes

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Keywords:polymer brushes, ionic liquids, lubrication, low friction, surface chemistry

Abstract

Concentrated polymer brushes formed by living radical polymerization possess uniform polymer chain length and high surface density, which can be utilized for controlling surface properties including surface wettability, adhesion and tribological properties. While polymer brush lubrication is expected as an elegant method for energy conservation, volatility of swelling agents and an abrasion of polymer brushes make it difficult to maintain low frictional interface, limiting their application for industrial use.

In this study, we applied ionic liquids for both a backbone of polymer brushes and swelling agent since their negligible volatility is suitable for maintaining brush lubrication system [1]. Fabricated ionic liquid polymer brushes (ILPB) were combined with a smooth 10 mm□glass ball (SGB; maximum height difference = 2.4 nm) as a facing material to avoid the abrasive wear of brushes from a substrate.

Friction forces were measured at a friction pair of SGB-Si or SBG-ILPB by sliding the sample stage at 1.0 × 10^{-2} m/s under 4.9N (Figure 1). In case of SGB-Si, 0.67 N of friction force was obtained which corresponds to a coefficient of friction (COF) of 0.13. In contrast, SGB-ILPB showed a friction force of 0.015 N (COF = 0.003), a 45-fold reduction compared with SGB-Si. In addition, combining ILPB and SGB resulted in superlow frictional interface (COF$\leqq 10^{-3}$) which is maintained after 4000 friction cycles under 9.8 N, in contrast to the result of a conventional glass ball (maximum height difference = 220 nm) showing rapid increase of a friction within 10 friction cycles under much lower load (0.98 N). We will also discuss about recent data obtained for this system.
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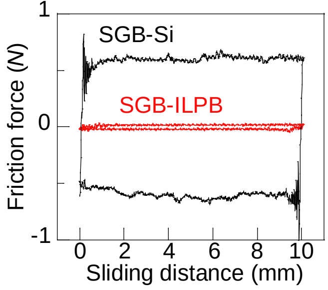

Figure 1. Friction loops of SGB-Si (black) and SGB-ILPB (red) measured at a constant sliding speed of 1.0 × 10^{-2} m/s under 4.9 N.

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M5

Thermoremendable Styrenic Polymers by Controlled Radical Copolymerization of Styrene with bioderived 2-vinylfuran

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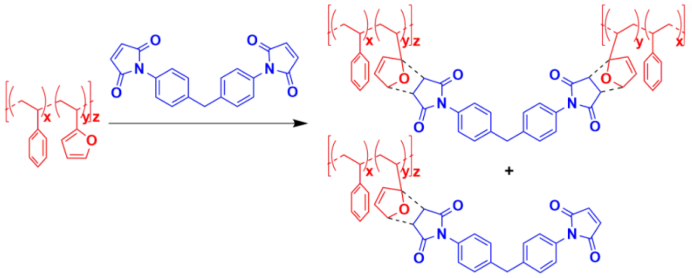
Keywords: Biosourced olefins, functional olefin copolymer, furan-maleimide Diels Alder reaction.

Abstract

2-vinylfuran (2VF) is a bioderived olefin synthesized by Peterson methylenation of furfural, a cheap platform molecule resulting from acid catalyzed hydrolysis and dehydration of pentosanes from lignocellulosic biomass. Ideal ATR copolymerization of styrene with 2VF yielded random copolymers (S-*co*-2VFs) in a wide range of composition and high monomer conversion.[1] The S-*co*-2VFs are stable for years in solution and solid state at room temperature; radical oxidation of the furan moieties starts in air at temperature higher than 120°C whereas thermal degradation occurs at 380°C. Diels Alder (DA) cycloaddition reaction of S-*co*-2VFs with bismaleimide (BMI) produces thermorevesible crosslinks: the thermodynamic and kinetic parameters of this reaction were investigated by NMR and FT-IR spectroscopy to assess the optimal condition for high crosslink degree and self healing conditions. The mechanical properties of the S-*co*-2VFs, before and after reaction with BMI, were compared using INSTRON analysis and nanoidentation of polymeric thin films by Atomic Force Microscopy.[2] Moreover simple thermal treatment of mechanically fractured films of S-*co*-2VFs reacted with BMI allowed full repairing in 80 min (Figure 1).



Scheme. Diels Alder reaction of S-co-2VFs with BMI.

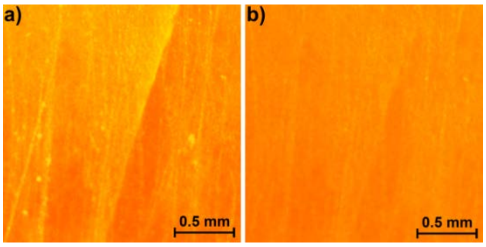


Figure 1. Fractured (a) and healed (b) polymer film of S-co-2VF crosslinked with BMI after thermal annealing at 150°C.

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B1

Renewable enzymatic recycling of high value pigments and glucose from viscose fibres

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Keywords: cellulose, pigments, glucose, hydrolysis, cellulases

Abstract

In this last decadethe estimated total world-wide fibre consumption is 102 million metric tons [1]. Out of these, man-made cellulosic (MMC) fibres account for more than 10 million metric tons with an average annual growth of more than 2%. Cellulose is the most abundant available natural material, and it represents a major renewable resource for sustainable production of bulk commodities such as fibres [2]. The spinning technologies developed over the last hundred years, such as the classical viscose, lyocell or most recently the Ioncell-F process [3], have all in common that the textile fiber properties (tenacity, titer, elongation at break, etc.) can be adjusted in a wide range. The incorporation of functional pigments, such as colour, fluorescent or flame retardant polymers allow the production of multifunctional, cellulosic fibres for various applications, such as personal protection equipment (PPE). From an economical as well as from an environmental point of view, certain functional pigments, such as phosphor-based flame retardants or day-light pigments represent high valuable products. Their recovery from low-grade or waste material would be highly appreciable, but due to their inherent chemical liability, acidic hydrolysis of the cellulosic matrix is not technically feasible.

In this work we present a new strategy for the recovery of chemically labile viscose fibres constituents. The key step (Fig.1) is based on the enzymatic hydrolysis of the cellulose fibre matrix below 60°C thereby "releasing" the water insoluble pigments without chemically attacking or degrading them.

To the best of our knowledge this is the first time that cellulases are described for the recovery valuable rayon additives like organic flame retardants which could be re-use instead of being discharged.

A completely eco-sustainable and simple process is presented for the hydrolysis of multifunctional viscose fibres in order to recover incorporated, high value pigments and obtain glucose of high purity. The preliminary results are promising while further studies are necessary to increase the glucose recovery and to make the process available in production scale.

Figure 1: Rayon complete degradation

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B2

Towards Synthesis of Low Molecular Weight Lignin-like Oligomers by Laccase Catalysed Oxidation of Lignin Model Compounds

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Keywords: Laccase, Lignin models, Oxidative polymerization, UV stabilizers

Abstract

Lignin, the second most abundant natural polymer has attracted much attention as one of the potential feedstocks for the sustainable production of fuels [1], chemicals [2] and materials [3]. This aromatic natural polymer mainly consists of phenylpropane units that are linked through various types of C-O and C-C bonds. The inconsistant structure of native lignins which varies with its source, their high molecular weight, and incompatibility with polymers hinder their use as renewable materials for various applications. Synthesis of lignin-like materials with similar characteristics of lignin by greener methods would help to exploit the natural polymers for more applications with better understanding on the materials.

In the present study, synthetic dimeric lignin model compounds were used as precursors to obtain lignin-like oligomers by a simple laccase catalysed oxidative polymerization [4] in aqueous medium using oxygen as an oxidant. We were delighted to find that the oxidative polymerization leads to the formation of oligomeric species with controlled molecular weight distribution (M_w in the range 1500-2500 daltons) and polydispersity (1.1-1.2). The intermediate (i.e. tetramer) of the oligomerization process has been isolated successfully and characterized by NMR and mass spectroscopy. We found that the redox potential of enzymes, pH and enzyme concentration have dramatic influence on the initial progress of the reaction as well as the formation of oligomers. The oligomeric material obtained from lignin model compounds showed good UV absorption properties and photostability. The oligomeric material was dispersed into polymers by solvent casting methods and their UV blocking characteristics were studied. The scope and limitation of this green methodology in obtaining the low molecular weight oligomers will be presented at the conference.

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B3

Biomass valorization through 5-HMF oxidation catalyzed by Au, Pd and AuPd nanoparticles

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Keywords: 5-HMF conversion, AuPd catalysts, base-free, titanosilicate, oxidation reaction.

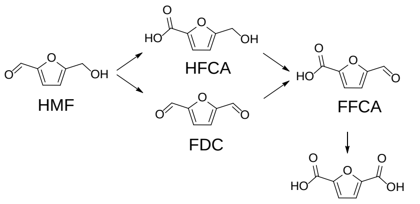
Abstract

The growing concern regarding the gradual depletion of fossil oil reservoirs and the awareness of climate change has stimulated recent research activities for the utilization of renewable biomass resources for the sustainable production of fuels and chemicals [1]. 5-hydroxymethylfurfural is a promising platform compound from cellulose or cellulose-derived carbohydrates. Its derivatives can be used as six-carbon monomers that could replace other petrochemical-based monomers [1]. The aerobic oxidation of HMF requires several tandem oxidation steps. Another issue is the requirement of an excess amount of a base additive. Strategies to prevent the use of base consist in adopting a basic and/or nanosized support and/or by adding a second metal (bimetallic). We have prepared a titanosilicate support in which Au, Pd and bimetallic AuPd nanoparticles were encapsulated. The metal-support interaction was effective to provide catalytic activity in absence of base (Table 1). The results highlight the synergistic effect of the Au_1Pd_1 bimetallic catalyst over HMF conversion. Observing the selectivities along reaction time, HFCA and FFCA are accumulating for Au and Pd catalysts. For the bimetallic catalyst, HFCA selectivity was lower and constant, while FDC is consumed forming FFCA in high selectivity. This is an indicative of the reaction pathway through FDC for the Au_1Pd_1 [2]. The effect of bimetallic composition was also evalauted in studies with Au_1Pd_4 and Au_4Pd_1.

Table 1. Aqueous base-free oxidation of 5-HMF

Cat	t (h)	Conv. (%)	Selectivity (%)			
			HFCA	FDC	FFCA	FDCA
Au	2	5	37	26	35	2
	24	16	51	6	39	4
Pd	2	2	46	33	19	2
	24	12	40	16	37	8
Au_1Pd_1	2	6	20	46	33	1
	24	39	15	19	55	11

Reaction Conditions: 5 mg cat, substrate:catalyst = 18, T = 90 °C, 1 bar.



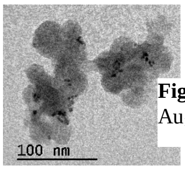


Fig. 1. TEM image of Au_1Pd_1/titanosilicate catalyst.

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B4

Removal of Cr(VI)by Silica-coated Alginate Immobilized Fungal Biomass

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Keywords: Hexavalent chromium, adsorption, *Mucor rouxii*, immobilization, alginate

Abstract

This study investigated the immobilization of *Mucor rouxii* and its application in the removal of Cr(VI) from wastewater. Silica coating was applied to the calcium alginate microspheres encapsulating fungal cells of *M. rouxii* using amino-functionalized silica sol. The resulting silica-coated alginate immobilized *M. rouxii* (SAIM) demonstrated excellent biomass-liquid separation, improved chemical resistance, mechanical strength and Cr(VI) removal ability, compared to alginate immobilized *M. rouxii* without silica coating. The SAIM was utilized to remove toxic Cr(VI) in both batch and continuous adsorption modes (Fig. 1). The surface morphology and elemental composition of pristine and Cr-loaded SAIM were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR),energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). Results indicated that both biosorption and bioreduction were involved in the Cr(VI) removal process [1].Moreover, the effects of initial concentration, biomass content, solution pH and adsorbent dosage on the Cr(VI) adsorption behavior were examined by batch adsorption study. The highest Cr(VI) biosorption capacity of SAIM was achieved at pH 2.0.Elovich kinetics and Sips isotherm were the best in describing the kinetic and isotherm data with the lowest root-mean-square error (RMSE) value. In the desorption study, sixteen desorbing agents were tested for their Cr desorption ability and 2 M HNO_3 was found to desorb 90% of the adsorbed-Cr fromthe Cr-loaded SAIM. The continuous removal of Cr(VI) was studied in a fixed-bed column packed with the SAIM.

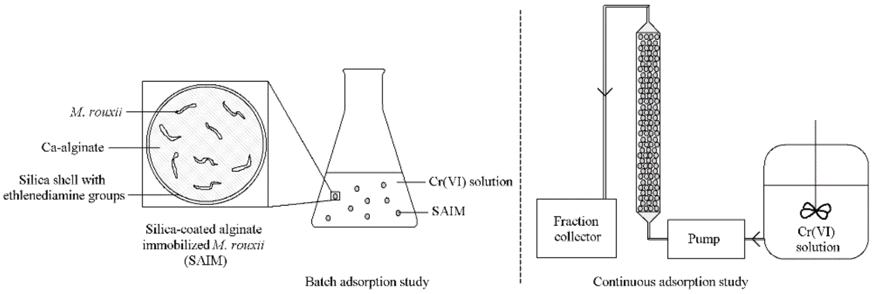

Figure 1. Batch and continuous fixed-bed column adsorption studies on the removal of Cr(VI)

Acknowledgments

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B5

Production of bio-based plasticizers and intermediates for organic synthesis by aerobic epoxidation of fatty acid methyl esters

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Keywords: bio-based plasticizers, aerobic epoxidation, fatty acid methyl esters, epoxide-containing mixtures

Abstract

Modified vegetable oils or fatty acid esters have already been established as environmentally friendly alternatives for commonly-used chemicals. Epoxidized oils and their derivatives are employed as polymer plasticizers and lubricants and it is promising to use them for producing monomers of epoxide resins and polyurethane [1]. In this work the obtaining of epoxide-containing mixtures by oxidation of fatty acid methyl esters (FAME) by air at the presence of molybdenum catalyst was suggested. The introduction of this method allows to make the process of epoxidation of oils and FAME harmless, eco-friendly and cheaper compared with well-known ones [2].

Epoxidation process was proceeded in bubble column. It has been found out that the changing of the parameters, such as temperature and air supply speed do not influence on the character of the process and the ratio of products got. The selectivity of epoxide rings formation depends on the raw material content only. The highest selectivity was observed when the monounsaturated fatty acid esters are oxidizing.

The scheme of aerobic oxidation of FAME as well as the mathematical model describes adequately the process was composed. The ways of by-products formation have been proposed based on the different analysis (GLC, SEC, FTIR and NMR-spectroscopy). It should be noted that there were found no oligomerization products.

The epoxide-containing mixtures obtaining by this method demonstrate the fairly good plasticizing ability for polyvinylchloride.

This work was funded by RFFI and Ministry of Education and Science (Project № 4.2512.2014/K).

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OP1

Principled approaches to Chemistry

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Keywords: chlorine, sarin, misuse,ethics

Abstract

For many years chemical weapons (CW) were considered to be an aberration in the history of chemistry. Talk about them was also viewed as suspect in the field as they drew unfavourable attention to chemistry, a blemish, so-to-speak, on chemistry's image. Unfortunately, the current conflict in Syria and the repeated use of chlorine to harm people, plus the attack on a Damascus suburb in 2013 with the nerve agent sarin in which some 1000 were killed has demonstrated that chemical weapons are not just something historical, but are a very real current threat.

Chemists, amongst others, are necessary for the production of chemical weapons and so efforts are being made to reach out to the chemistry community to alert it to the problem, but also to persuade it of the need to support the 1997 Chemical Weapons Convention (CWC). The CWC forbids any production, stockpiling and use of CW and as well as destruction of stockpiles and 192 states are now party to the convention.

Part of the initiative to inform chemists about the CWC was an agreement in 2015 by some 35 scientists from 24 countries on an ethical code called The Hague Ethical Guidelines, a set of some 9 overarching principles which should inform the practice of chemistry [1]. The guidelines, which have been endorsed by IUPAC, are available in 5 other languages besides English [2].

This presentation will discuss The Hague Ethical Guidelines and show how they relate to the 12 principles of Green Chemistry as well as to the United Nations 17 Sustainable Development Goals agreed in September 2015. Educational approaches to chemists to enable discussion of both appropriate and inappropriate use of chemicals, the so called 'dual use' dilemma, will also be discussed with a view to enquiring how green chemistry can support the aims of the CWC with reduction in the use of certain chemicals, or tighter controls on their availability and even their replacement.

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OP2

The Role of the National Authority of State Parties in the Promotion of a Safer World

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OP3

The Future of Green Chemistry to Bring About Transformative Change

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The redesigning of the material basis of our society and our economy is required to be able to sustain our civilization. The current unsustainable trajectory that society is on needs to be replaced. There needs to be a fundamental transformation in the way that we think about the materials that we design and use including the materials used to generate, store, and transport our energy. Those who benefit financially from our current products, processes, and systems will likely resist change if possible. What needs to be done such that the science and innovation that green chemistry has and continues to produce can be used to bring about the transformational changes in the timeframe required? That question will be explored in this talk.

OP4

Wanhua's approach towards green chemistry

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Keywords: Wanhua, Sustainable,green,chemistry,china

Abstract

Wanhua, as a global manufacturer of MDI, polyurethanes, petrochemicals, functional and specialty chemicals is fully dedicated to sustainable development. Along with our economic targets, Wanhua is actively engaged in strengthening the core pillars of sustainable development through enhancements in human resource, social and community development, technology innovation and green chemistry. Our HSE Management System has three strict zero(0) goals of (0) emission, (0) injury and (0) accident and in pursuit of these challenging goals we have additional ten(10) non-violating rules which included the mandated three(3)-"No"s rule, to ensure our processes are: 1) leak free 2) odour free and 3) noise free. Wanhua's dedication in environmental protection(EP) and sustainable development(SD) has gained huge recognition from the surrounding communities, employees, national organisations as well as the government. As a result of our direct engagement, our manufacturing centres look like green gardens.

This presentation will give an overall view of the challenges and positive outlook of Wanhua as a globalised company prioritising, sustainable development and green chemistry.

OP5

Green chemistry for ensuring chemical safety and security in the developing world

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R1

Hemp fibers combined with cementitious mortar: alkali sensitivity and mechanical behaviour

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Keywords: Natural fibers, Hemp, Durability, Alkali, Mechanical properties

Abstract

Recently, many researches are developing innovative composites with natural fibers as a sustainable alternative to synthetic and petroleum-based materials. The effort to produce renewable materials is actually an important target in many engineering fields as automotive, civil and aeronautic.

This research investigates hemp fibers to stabilish if this natural material would replace the most common used synthetic fibers for structural engineering interventions, in particular, Textile Reinforced Mortar -TRM - also known as Fiber Reinforced Cementitious Matrix - FRCM.

Considering alkali sensitivity of non-wood fibers, this experimental work aims to set hemp fiber mechanical properties combined with the most used construction materials: i.e. mortar material.

Here the results of experiments on hemp wires with several alkali environments are presented. The hemp fibers strength is measured at natural condition. Afterwards, the fibers strength are measured after progressive time periods of immersion into different boundary conditions: three solutions that reproduce mortars chemical compositions, to test material durability. Hence a method that allows setting hemp fiber mechanical behavior based on its durability properties and helps to understand better non-wood fibers alkaline sensitivity.

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R2

Stone Autochthonous Microorganims: An Efficient Help On Historical Stone-Buildings Bio-Restoration

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Keywords: historical stone-buildings, bio-deterioration, bio-cleaning, bio-restoration

Abstract

Different microorganisms in addition to lichens and algae, can cause problems to the conservation of cultural heritage because of their bio-deteriorative potential. This holds true for all types of historic artifacts, and even for art made of modern materials in public buildings, museums etc. The variety of bio-deterioration phenomena observed on materials of cultural heritage is determined, also, by several factors, such as the chemical composition and nature of the material itself, climate and exposure of the object, biological colonizers. The synergistic actions of all these factors can cause not only aesthetic deterioration of the cultural heritage but also structural damages.

Currently, studies are focused towards the use of living organisms as antagonist of destructive colonizers (algae or fungal colonies) or as producers of biocalcite to restore the surface of stones.

In previously published works we showed the cleaning bioactivity of secondary metabolites produced by bacteria and vegetables (Caligine et al., 2013; Sasso et al., 2013) on two bridges located in two different places close to Potenza (South Italy). Successively, we identified and cultured several bacterial colonies, collected from the same bridges, belonging mostly to the genus Bacillus, which is known as an organism having a specific ability to induce the precipitation of minerals, especially calcite. Having in mind that the natural formation of biocalcite can reduce, and successively limit the bio-contamination and infestation of destructive organisms, we decided to test the effectiveness of some identified bacterial species. The experiments, carried out *in vitro* by using calcium acetate as source of Ca showed the formation of well-defined biocalcite crystals resulting by FT-IR spectrophotometry, Xray diffraction analysis, and SEM coupled with EDS analysis. Among all autoctonous bacteria tested, *Bacillus thuringiensis* worked as the best producer of biocalcite.

These results encouraged strongly our research: our aim is actually the implementation of new bio-restoration methods of cultural heritage reducing maintenance intervals and costs: "adopt a monument and take care of it with love"

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R3

The role of chemistry in contrast to the "graffiti" in art cities

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Keywords: cultural heritage, graphic vandalism, graffiti, art cities

Abstract

The *Sorpintendenza ABAP per il comune di Venezia e laguna* is one of the subjects responsible for the Unesco site Venice and its lagoon. The management plan [1] provides for the conduct of actions to address the critical issues and to promote the development of good practices.

In this context, the Soprintendenza has joined a research project funded by the Ministry of University and Research [2] named "Product and process innovation for maintenance, conservation and sustainable restoration and programmed cultural heritage".

The project is aimed at developing products for the restoration and preservation of historical building surfaces and components that can ensure a healthier and more environmentally friendly than those on the market with the same efficiency.

The study also concernes the development of measures to contrast the graph vandalism, widespread phenomenon even in a city of art, with very negative effects on cultural heritage, requiring the development of models for new conservation strategies.

Part of the study are integrated strategies of action as meetings with students to kick off a process of awareness, measures to reduce bureaucracy and enlargement also in individuals without technical qualifications to carry out the cleaning of graffiti in certain cases, not omitting legal requirements relating to the interventions of cultural and landscape heritage, very numerous in the city of Venice.

For this aim a collaboration was initiated with Venice municipality, homebuilders association (ANCE) and citizens association (Masegni e nizioeti), and it was signed an agreement.

The project includes also the development of guidelines, which give directions on techniques to use in relation to the type of material (wood, metal, stone, brick) and the type of graffiti.

Besides testing *in situ* are included in the study, in order to verify the behavior of the products for cleaning already on the market and also in order to test new chemical products, which ensure effectiveness, easiness of application, holding safety requirements and eco compatibility, allowing an enlarged use without special safety precautions.

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R4

The Green Attitude in Art Conservation: Polyhydroxybutyrate-based Gels for the Cleaning of Oil Paintings

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Keywords: Gel, Green Chemistry, Oil Paintings, Polyhydroxyalkanoates, γ-Valerolactone

Abstract

The application of eco- and user-friendly approaches to conservation of Cultural Heritage is beneficial not only for the artworks themselves, but also for human health and the environment [1]. Specifically, traditional methods for cleaning paintings imply the removal of the upper protective varnish layers (10-50 μm of terpenes, oils or synthetic polymers), using volatile organic solvents or aqueous-based systems. In both cases the migration of the solution to surrounding areas can cause 1) swelling of the underlying painted layers; 2) leaching of pigments, dyes and binders, and 3) an unwanted mixing of protective and pictorial layers. In recent years various alternatives were proposed to overcome the main drawbacks of the traditional approaches, mainly based on gel systems that can provide a better localization of the solvent release, thus reducing its permeation into underlying paint layers [2]. In this paper the production of novel organogels composed of bio-based components, poly-3-hydroxybutyrate PHB, γ-valerolactone (GVL) and triethyl citrate (TEC), is presented together with their application as cleaning agents for painted surfaces. Different gelling conditions have been tested and characterized in terms of mechanical properties, thermal behavior, crystallinity and molecular weight. The most promising formulation was tested on mockups prepared by applying an artificially aged layer of dammar on a 40 years old naturally aged oil paint. PHB-gel was highly effective in removing the protective dammar resin coating after 5 min application, without affecting the pictorial layer. No gel-traces were left on the mockup surface after the application, whereas GVL residues were < 0.1 wt%. Finally, the efficacy of the gel was validated on a portion of a real ancient oil canvas painting, "Sant'Antonio" by Benedetto Gennari (XVII sec, Ravenna, Italy) (Figure 1). The cleaning performances of PHB-gel were as good as those obtained by traditional protocols based on DMSO, but with two great advantages: one in terms of sustainability, by using a completely renewable bio-based material, and one in terms of protection of the artwork, by using a less aggressive solvent, less concerning in terms of retention into the paint layers.

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R5

PRODUCT AND PROCESS INNOVATION FOR MAINTENANCE, PRESERVATION AND SUSTAINABLE PROGRAMMED RESTORATION OF CULTURAL HERITAGE

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Keywords: Cultural Heritage, Sustainable Architecture and Materials

Abstract

The degradation of the cultural heritage begins immediately after its implementation and the speed of degradation depends on both natural and anthropogenic factors. The process of deterioration is progressive and irreversible, and the timing and mode of impact is different depending on the characteristics of materials and "compatibility" between them as well as on constructive techniques, physical-chemical agents and biological processes that are involved.

At today, limits imposed by European Community about the air pollution have been issued by States aiming at the safeguard of human health and ecosystem, but without any concern about the possible damages to the archaeological site. The protection and restoration of cultural heritages can be reached thought experimental studies, in the laboratory and outdoor, on the alterations/modifications affecting the materials and the technological systems used for the construction of the artistic patrimony. Then, it will be consequential and strategic to develop innovative biological methodologies that employ micro-organisms and henzimes, which can reproduce the same biological processes occurring in the environment, enabling the "bio-restoration" of artistic materials. The use of these innovative tools (biocides) together with new soft chemicals will favour the maintenance of the dynamic ecosystem equilibrium allowing the implementation of non-invasive treatment methods. For the purpose, a great variety of diagnostic techniques will be used to determine the influence of each factor in the process of degradation.

Moreover, strategies for a low cost maintenance of cultural heritage based on archeo-technologies including wireless sensors, *in situ* and *ex situ* measurements, a data storage and processing system, coupled with a predictive model for the economic evaluation of interventions, will be performed and a specific software of "governance" will be implemented and demostrated in different cases of study.

The project will carry out an economic evaluation of optimized new techniques.

The final goal of the project is:

1) implement actions and interventions for the management of the resources available for cultural policies through the development of a technological platform for scheduling preventive maintenance actions;

2) develop new products for restoration of monuments, not harmful for human health, of low environmental impact, highly selective and of low cost.

3) suggest all local authorities to adopt and maintain active plans for long term maintenance of cultural heritage.

TUESDAY, THE 6TH OF SEPTEMBER

M6

Mechanochemical, Solvent-free Synthesis of Metal and Metal Sulfide Nanoparticles

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Keywords: Nanosynthesis, Mechanochemistry, Gold, Bismuth Sulfide, Silver

Abstract

Metal and metal-based nanoparticles (NPs) have shown vast potential and rapid advancement in various applications including electronics, optics, catalysis, or public health products. While their properties are very exciting and inspire many research groups, the impact of their synthesis on the environment and health is often neglected in the search for purer and better defined products. In an effort to reduce synthetic footprint in nanoscience, we developed a novel method for the scalable production of metal NPs under solvent-free, mechanochemical conditions.[1] The synthesis of Au NPs proceeds fast (1.5 hours) and provides access to gram amounts of monodisperse and ultra-small NPs in the size range of 1 - 4 nm, without external reducing agents or bulk solvents. We used as a stabilizer long chain amines and observed a dependency of the NP size on the amine carbon-chain length. Navel methods, using biomass-based reducers allow access to other metal NPs, including Ag, Pd, Ru, Re and Rh.[2] We also developed a mechanochemical synthesis of functional bismuth sulfide NPs. These nanomaterials have recently been intensely researched as contrast agents for X-ray computed tomography imaging.[3] This novel method allows access to multigram-scale quantities of monodispersed NPs, which solubility in either water or organic solvents properties may be finely tuned, notably using liquid assisted grinding (LAG).[4]

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M7

Green Chemical Engineering of Controlled-Release Silica Nanocapsules

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Keywords: Biomimetic; Silica; Nanocapsule; Nanocarrier; Controlled release

Abstract

Silica nanocapsules having oil-core silica-shell structure synergistically combines silica-shell properties and nanocapsular configurations. Traditionally, silica nanocapsules are synthesized based on templating method involving the use of toxic chemicals at high pH and/or temperature [1]. Here, we present a novel emulsion and biomimetic dual-templating strategy to synthesize oil-core silica-shell nanocapsules at environmentally friendly conditions, thereby designing a bifunctional SurSi peptide having modularized amino acid sequences. One module facilitates formation of a stable nanoemulsion core (surface-active module), and the other module direct silica-shell assembly at the oil–water interface (biomimetic silicification-active module) simultaneously [2]. Silica shell thickness can be easily tuned at room temperature through control of pH, reaction time and silica precursor concentration [2,3]. We demonstrated facile encapsulation of fipronil and its sustained release *in vitro* [2,3] and *in vivo* against termites [3]. The core provides high-capacity and facile loading of active agent via solubilization in the oil core prior to silica shell formation, and the silica shell serves as a protective envelope and diffusional barrier enabling sustained release. The release of fipronil from silica nanocapsules is tunable through control of silica-shell thickness, hence controlling the killing rate of termites [3]. This technology presented here represent a new strategy for the synthesis of oil-core silica-shell nanocapsules using components and processes that are environmentally friedly.

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M8

Novel Design of FAU@ ZIF-8 Composite in Core/Shell Structures via a Layer-by-Layer Method

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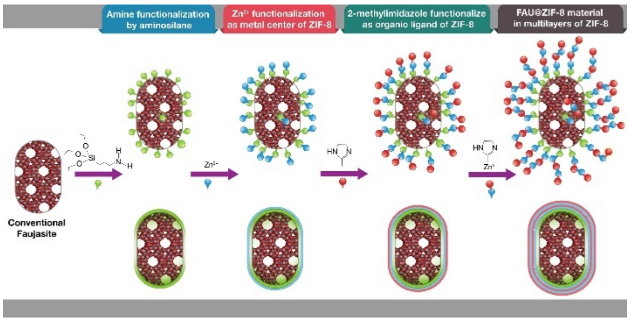
Keywords: Zeolite, Metal Organic Framework, Zeolite@MOF composite, Core/Shell structure

Abstract

The novel composite of faujasite and zeolitic imidazolate framework (FAU@ZIF-8) in core/shell structures has been successfully prepared via a layer-by-layer method. The ZIF-8 nanospheres were attached on the external surfaces of the amine-grafted FAU crystals. The synthesized FAU@ZIF-8 composite was characterized by means of XRD, FT-IR, TGA, SEM, TEM, N_2 adsorption technique, NH_3-TPD and CA equipment. Compared to the direct growth of MOF materials on the zeolite surfaces[1-4], the ZIF-8 particle size and the thickness of shell obtained by this method can be easily controlled by adjusting the number of deposited MOF layers. For example, a size of ZIF-8 nanospheres is approximately 37 nm when a number of deposited MOF layers are 15 layers. The novel designed FAU@ZIF-8 composite can also enhance the hydrophobicity of zeolite surface due to the MOF surface-layer characteristicswhereas its acidity does not significantly change. This first example demonstrates the simple and controllable synthesis method of zeolite@MOF composite and it is expected to be useful for the aqueous-phase reactions which are green chemistry.

Scheme 1. Schematic illustration of the synthetic process for FAU@ZIF-8 composite obtained by a layer-by-layer method.



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M9

Synthesis and Catalytic Applications of Sustainable Nanocatalysts

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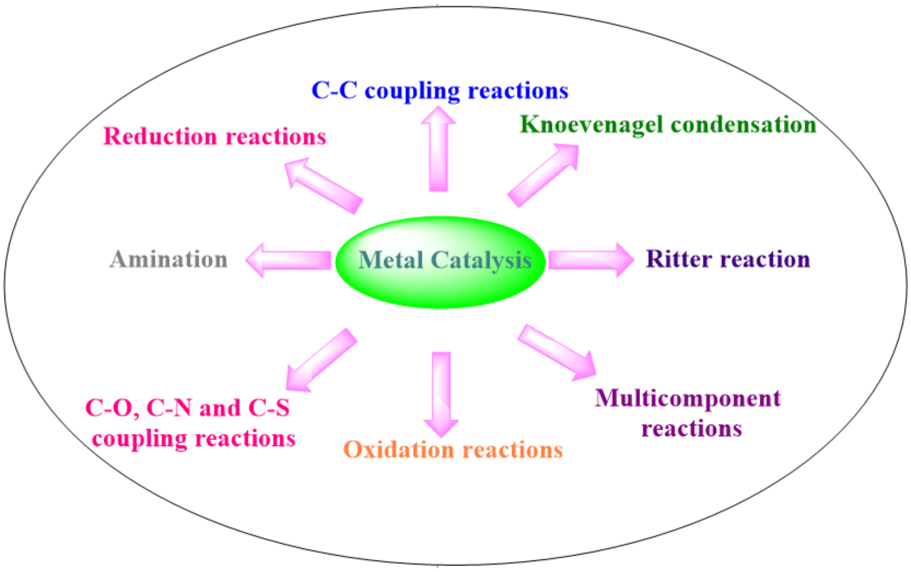
Keywords: Nanoparticles, Metal Catalysis, Green Chemistry

Abstract

Sustainable and functionalized nanomaterials comprising solid-supported nanocatalysts, such as iron oxide-supported Pd, Cu, Au, sulfonic acid and other metal catalysts are prepared by simple co-precipitation method. The chemical nature, morphology, size, and leaching of metal nanoparticles during organic transformations will be described using TEM/EDX, HAADF-STEM chemical mapping, XPS, AAS/ICP-MS, and in-field ^{57}Fe Mössbauer spectroscopy. Various types of catalytic applications for several name reactions such as Suzuki, Heck-Mizoroki cross-coupling reactions, Ritter reaction, oxidation and reduction reactions etc. will be highlighted. The sustainable attribute of these nanocatalysts is that they could be easily isolated from the reaction mixture using an external magnet or via centrifugation and reused several times without any loss of activity [1].



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M10

Rapid Analysis of Polycyclic Aromatic Hydrocarbons in Aqueous Solutions by Two-Dimensional HPLC System Using Monolithic Column*

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Keyword: monolithic affinity column, polycylic aromatic hydrocarbon, 2D-HPLC

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds having mutagenic, toxic and carcinogenic effects to human health that formed by incomplete combustion of organic items. Several analytical methods for the separation of PAHs have been reported[1]. Unfortunately, most of them are tedious, time consuming and require labor and considerable amount of high purity of organic compounds. Two dimensional chromatographic separation (2D-HPLC) is considered as an alternative techniques to these shortcoming. The most impressive feature of this study is forming high performance liquid affinity column (HPLAC) with the combination of monolithic affinity columns[2]and HPLC. In the first step, the selective extraction and pre-concentration of desired substance was separated by monolithic affinity columns and then determination of trace amounts of PAHs was carried out by second PAH column. All automation process including of extraction, pre-concentration and determination process performed by "on-line". Herein, monolithic columns were firstly prepared by the in-situ bulk polymerization of N-methacryloyl-L-phenylalanine (MAPA) as a pseudospecific ligand and 2-hydroxyethyl methacrylate (HEMA) conducted in a stainless steel columns. After characterization of the monolithic columns by FTIR, SEM and elemental analysis, they were used for pre-concentration of Benzo[a]pyrene (BaP) through regular one dimensional HPLC system (1D-HPLC). Secondly, most common PAH types found in the hazardous waste sites were investigated with taking into consideration of toxicity and hazardous[2] effects through two dimensional HPLC system (2D-HPLC) for their on-line pre-concentration and determination. As a conclusion, the lower concentration of PAH solutions pre-concentrated by monolith affinity columns were successfully monitored by 2D-HPLC.

*This study was supported by The Scientific and Technological Research Council of Turkey with a grant number as TUBITAK-KBAG-214Z236.

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M11

The role of ICPMS in nanosafety research on engineered nanoparticles

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Keywords: nanotoxicology, nanoparticles analysis; single particle ICPMS; Single Cell ICPMS

Abstract

The nanotech tsunami of engineered nanomaterials (NM) raises the issue of the impact of nanoparticles(NPs) on environmental and human health, being more and more widespread in industrial and biomedical applications, as well as in everyday life. Since emerging evidence that even at the cellular level NPs behave differently from the corresponding bulk materials, the protection of public health, consumers and workers in this sector is now a topic of enormous interest that is taken into serious consideration by the competent authorities in charge in environmental and health safety. However, one decade of nanotoxicology research, a recognized sub-discipline of toxicology, has documented that the interactions between NPs with biological systems and the environment as well as the mechanisms of NPs toxicity are remarkably complicated, requiring dedicated analytical methodology and tools. In this context, there are a large number of challenges for the analytical chemist involved in the different steps of the research that, among other things, impose the physicochemical characterization of NPs (i.e.determination of chemical composition, particle size and size distribution, mass/particle number concentration) in complex matrices such as water, soil or food. Consequently, the strong multidisciplinary character of nanotoxicology research requires an integrated use of analytical techniques, i.e. spectrochemical, specialized microscopy, bioanalytical, and molecular biology techniques.

Herein we discuss the role of ICPMS in nanotoxicology research of metal-based NPs, the largest volume of engineered nanomaterials. In particular, emphasis is given to the applicability of single particle ICPMS (spICP-MS), an evolution of ICPMS that allows the elimination of many matrix effects and that relies on the extremely sensitive elemental detection capability of ICPMS. Although spICP-MS concerns single element detection todata it is considered a “conventional” analytical technique for the detection of metal-based NPs, providing the direct quantification of particle size, particle size distribution, particle concentration of NPs inside solutions in which they are suspended. So spICPMS is the first analytical technique capable of determining all three nano-specific metrics from a single sample. Moreover, spICPMS has provided an analytical means to distinguish in solution between nanoparticulate and dissolved ions as released from the metal constituent of NPs.

Typical applications of spICPMS in nanotoxicology research refer to zerovalent metallic (AgNPs, AuNPs, UNPs) and metal oxide (Al_2O_3, FeOOH, SiO_2, ThO_2, TiO_2, ZrO_2) NPs.

In addition, we report here a case of cisplatin-resistant A2780-CP70 ovarian cancer cell lines as example to look at nanoparticle uptake by individual cells as based on the use of ICP-MS operating in single particle mode (Single Cell-ICPMS (SC ICP-MS) analysis).

M12

A Novel Highly Resilient Double Network Ionic Gel for Low Friction Material

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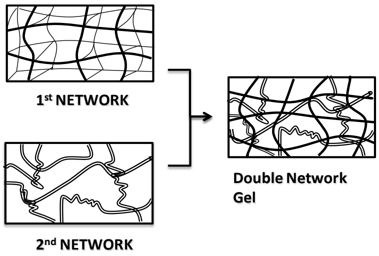
Keywords: Ionic liquids, Polymer, Gel, Low friction, High durability.

Abstract

Hydrogels made by a double network (DN) technique have excellent mechanical properties such as a high strength and a super toughness. Figure 1 showed the concept of DN-gel. The first network has hard and brittle feature by high cross-linking density and the second network has soft and high elastic feature by low cross-linking and high molecular weight. The DN-gel structure was that the second soft reticulation entangled to the first rigid framework prepared by two step sequential free radical polymerization process. This double network composite has high strength and high elasticity features despite it containing the solvent of 90% or more.

Fig. 1. Schematic illustration of the formation of Double network gel (DN-gel)



In some cases, because the DN-gel also exhibits low friction resistance, it attracts attention as a next generation's energy conservation material [1]. However, one big issue of the hydrogel using in the industrial fields is the instability of physical properties due to the evaporation of water. We attempt to prepare the newly DN-ionic gel (DN-ionic gel) containing non-volatile ionic liquid as a swelling agent. The first network has constructed by using the ionic liquid type polymer that has high affinity for the ionic liquid used as a swelling agent. It was prepared from ionic liquid type monomer, *N*, *N*-diethyl-*N*-methyl-*N*-(2-ethylmethacrylate) ammonium bis(trifluoromethanesulfonyl)imide (DEMM-TFSI). In order to make the second network, we used a poly(methylmethacrylate) network with relatively high molecular weight. Our tough gel not only showed the highest compression strength among previously reported gel materials including ionic liquids, but also indicated an extremely low coefficient of dynamic friction during 1000 times of the friction examination in vacuum and high temperature condition. These results would show high potential as a low friction material of the DN-ion gel.

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M13

Synthesis of Monodisperse Silica Particles Grafted with Concentrated Ionic Liquid-Type Polymer Brushes by Surface-Initiated Atom Transfer Radical Polymerization for Use as a Solid State Polymer Electrolyte

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Keywords: Ionic liquid, Polymer brush, Living radical polymerization, Polymer electrolyte

Abstract

The growing attention has been paid to some solid electrolyte films made from ionic liquids and poly(ionic liquids) materials. Generally, an ionic liquid (IL) is defined as a salt having a melting point lower than 100°C. They have a very low volatility, are flame retardant, and possess relatively high ionic conductivities.

Recently, we have developed a totally newconcept for fabricating a non-volatile, non-flammable solid electrolyte that is free from liquid leakage that has highly-conductivecontinuous ion-channel network [1]. It uses a surface initiated living radical polymerization (SILRP) grafting method applied to a new polymerizable ionic liquid. This process allows us to construct a crystal-like hybrid polymer/silica particles (PSiPs) having “concentrated” polymerbrushes (CPBs) of ionic-liquid type polymers attached to the surface of a monodisperse silica surface. In this paper, we report data for the poly(IL) made by ATRP of the polymerizable ionic liquid, *N*,*N*-diethyl-*N*-(2-methacryloylethyl)-*N*-methylammonium bis-(trifluoromethylsulfonyl)imide (DEMM-TFSI).

DEMM-TFSI was polymerized via copper-mediated atom transfer radical polymerization (ATRP).The polymerization proceeded in a living manner producing well-defined poly(DEMM-TFSI) of target molecular weight up to about 400 K. The accurate molecular weight as determined by a GPC analysis combined with a light scattering measurement, and the molecular weight values obtained exhibited good agreement with the theoretical values calculated from the initial molar ratio of DEMM-TFSI and the monomer conversion. Surface-initiated ATRP on the surface of monodisperse silica particles (SiPs) with various diameters was successfully performed, producing SiPs grafted with well-defined poly(DEMM-TFSI) with a graft density as high as 0.15 chains/nm^2. Since the composite film made from the silica-particle-decorated polymer brush and ionic liquid shows a relatively high ionic conductivity, we have evaluated the relationship between the grafted brush chain length and the ionic conductivity.

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M14

Innovation in the chemical industry: the key for a sustainable future

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”.

Keywords: Sustainability, Resource Efficiency, Alternative feedstocks, Value chains

Abstract

More than 10 years ago Cefic was one of the founders of SusChem, the European Technology Platform for Sustainable Chemistry [1], and it remains strongly committed to keeping the network alive and to delivering on the key priorities defined with all SusChem stakeholders. Early 2015, SusChem published its updated Strategic Innovation and Research Agenda (the SusChem SIRA) structured according to the new framework program of the European Commission Horizon 2020 [2]. In this presentation, the key priorities of SusChem will be reviewed and will be examplified with concrete actions undertaken by the European Chemical Industry to contribute to a more sustainable society. The chemical industry is a key player in the overall sustainability agenda because chemistry holds the key to solving many societal challenges and because it enables innovation in many value chains. The impact of the chemical industry is manifold: alternative feedstocks, better processes to improve energy and resource efficiency, industrial symbiosis with other sectors to maximize the value of resources across sectors, new materials developed by the chemical industry to reduce energy consumption in downstream applications, new materials to improve the generation and storage of renewable energies … SusChem has also been instrumental in the creation of Public Private Partnerships such as SPIRE (Sustainable Process Industry through Resource and Energy Efficiency) [3], the objectives and achievements of which will be reviewed in the presentation. The sustainability agenda of the European Chemical Industry also targets longer term objectives. By way of example, the new flagship initiative on CO2 conversion will be briefly reviewed and commented.

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B6

Interfused Cellulose-Chitosan Hydrogels for Tissue Engineering Applications

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Keywords: Cellulose, Chitosan, Tissue Engineering

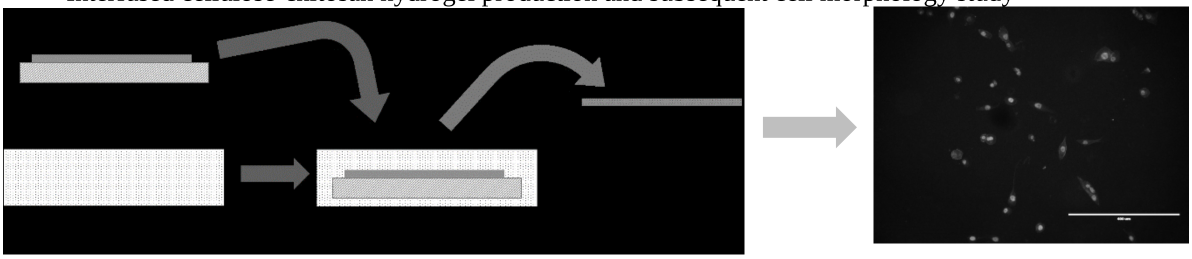
Abstract

In the UK today there is a 55 % chance of a person dying from disease of their organs or tissue, excluding cancers [1]. In order to minimise this, tissue engineering aims to develop cell-based therapies that can restore, repair or improve tissue functionality. Current methodology requires a source of cells, a material to support the cell growth, and the use of protein-based ligands to promote cell attachment and differentiation *in vitro*. However, these proteins are expensive to source and are difficult to store for extended periods of time. It is ideal to develop materials that support cell attachment and growth without the addition of proteins or ligands whilst being biocompatible, enabling *in vivo* use.

Here we describe the development of a novel methodology for generating interfused hydrogels containing both cellulose and chitosan without chemical cross-linkers. We demonstrate that the inclusion of chitosan in the hydrogel improves cell attachment by 3000 % compared to native cellulose. No proteinaceous ligands are required. Morphology studies reveal that a mean cell aspect ratio of 1.6 can be achieved within 24 hours for bone fibroblast cells indicating polarisation – a typical stage in their proliferation [2]. We also investigate the effect of changes in the chitosan molecular weight and loading in the hydrogel.

Current work is aimed at developing further understanding of how changes in the chitosan loading and molecular weight affect the subsequent cell morphology based on the surface chemical and mechanical properties of the films. We are also investigating cheap and facile methodologies for patterning the chitosan onto the cellulose with the aim of directing cell attachment and alignment.

Interfused cellulose-chitosan hydrogel production and subsequent cell morphology study



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B7

Ethylene-Stabilized Platinum Nanoparticles for Glycerol to Lactic Acid Conversion

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Keywords: Glycerol, Lactic acid, Platinum nanoparticles, Ethylene

Abstract

Lactic acid (LA) is an important platform molecule which can be converted into acrylic, 2,3-pentadione, 1,2 and 1,3 propandiol [1]. The demand of LA is steadily increasing due to its application as monomer for the production of the biodegradable poly(lactic acid). Most of the reported heterogeneous synthesis procedures employed in LA synthesis use supported metal nanoparticles in combination with air or oxygen as hydrogen acceptor. This latter synthesis approach leads to the fomation of undesired side products (Figure 1), which stem from the oxidation of glyceraldehyde (*i.e.* key intermediate in LA synthesis from glycerol) [2]. Recently, we showed that the formation of the oxidation products can be circumvented upon replacing air or oxygen by ethylene pressure (Figure 1) [3]. Our catalytic system consists of Pt-nanoparticles (NPs), generated by the metal vapor synthesis technique, supported onto Ketjenblack (CK) (*i.e.* a high surface carbon support, 1400 m^2/g) (Pt@C^K). The contemporary presence of ethylene pressure during the catalytic glycerol to LA conversion avoided the aggregation of the Pt-NPs. As a consequence, high catalytic activity (780 h^{-1}) and LA chemoselctivity up to 95% were obtained, which is the highest value found for a heterogeneous LA synthesis. Moreover, the heterogeneous catalyst showed in three consecutive runs a comparable catalytic performance.

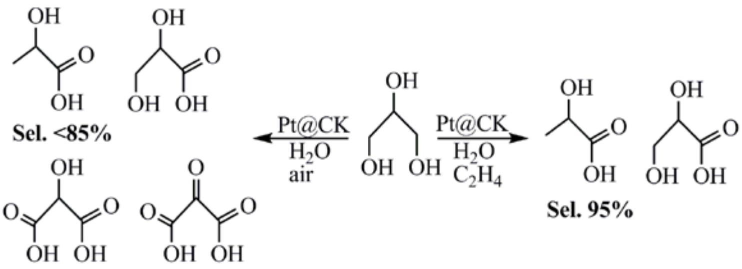

Figure 1. Pt@CK-catalyzed glycerol to LA conversion in the presence of air or ethylene.

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B8

Enzymes, Specialists in Cellulose Fibrilation – Prediction of Action on Fiber

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Scientific topic: Green Bioprocesses, Green Materials

Keywords: Cellulase, Cellulose, Fibrilation, Pulp and Paper

Abstract

Refining aims at the fibrillation of cellulose pulps to increase fiber to fiber bonding. Cellulases can help to make this production step more efficient by reducing refining intensty about 30 % [1]. Therefore, enzyme action on different pulps is of interest and simple methods to predict effects of enzymes on cellulose fibers are necessary. In an ongoing project scientists and industrial partners try to develop easy test methods to quantify essential activities in cellulase formulations. Next to classical activity measurements, enzyme analysis in this project involves purity determination, quantification of the protein content, behavior on different pulps and measurement of several fiber related parameters after cellulase treatment. Simple and fast assay procedures are an important tool for cellulose processors to evaluate cost-benefit of a potential new enzyme on site. Purity tests can elucidate how many different individual enzymes a formulation contains. This information is of high importance considering the fact that cellulases are a mixture of several individual enzymes with different modes of action. In contrast to other cellulase based applications no total saccharification of the substrate is desired. Rather a specific cleavage action within the fiber is required.

So far, significant differences in lab scale activity tests of enzymes related to pH, temperature and reaction time were demonstrated. Interestingly, the potential of the various enzyme preparations depends on the individual substrate to be treated. Thereby, fiber length is an important factor in accessibility for cellulases. This makes an internal investigation of potential new formulations even more important. Scanning electron microscopy can help to visualize effects of enzymes on fibrillation. The effect of the enzyme treatment on different fiber properties such as grinding degree, work absorption and air permeability was elucidated. A further adoption of enzyme assays is needed to increase predictability. Usage of different substrates like soluble cellulose derivate may help to overcome these limitations. Investigating enzyme side activities will allow specific mixing of individual enzymes to adjust their action to individual requirements. All this contributes to an improved enzyme usage in the participating companies, helping them to withstand international competition in the globalized field of cellulose processing.

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B9

Biocatalysis for the valorization of renewable α-pinene - process sustainability through the biocatalyst "architecture"

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Keywords: biocatalysis, alpha-pinene, turpentine, value-added products

Abstract

Renewable α-pinene is the main component of the monoterpene fraction in some essential oils (e.g. mastic oil) and turpentine, which is a paper and pulp industry residue available in bulk quantities at a low price. Approximately 350,000 tons of turpentine is produced annually worldwide. Commonly, its applicability is limited to fuel of the recovery boilers, although it could be effectively utilized in other processes on site. On the other side, α-pinene is considered a platform molecule with a great potential for the production of pharmaceuticals, agrochemicals and fine chemicals.

In this context, we developed several biocatalytic model-systems for the conversion of α-pinene into value-added derivatives (e.g. α-pinene oxide, campholenal, camphene, carveol, verbenol, verbenone, etc). One of the models involved the lipase- based cross-linked aggregates design of the biocatalyst for the epoxidation of α-pinene. The activity of the biocatalys has been evaluated in a green organic solvent (ethyl acetate) with H_2O_2 as oxidant. Screening of the lipase sources indicated *Aspargillus niger* lipase as the most efficient biocatalyst for this reaction. Then, the cross-linking design (cross-linked enzyme aggregates (CLEA) and cross-linked enzyme aggregates onto magnetic particles (CLEMPA)) were compared to enzymes aggregated following a covalent design (e.g. covalent immobilized enzyme (CIE) on magnetic particles (MP) supports). Both CLEA and CLEMPA designs afforded better epoxidation yields of α-pinene (around 30 % for both biocatalysts) compared to CIE (14 %). Also, the investigated biocatalysts allowed the production of α-pinene oxide (40 %) and derivatives such as camphene (15 %) and campholenal (20 %).

Second model investigated the biotransformation α-pinene using a bifunctional catalysts designed as carbohydrate biopolymers entrapping lipase enzyme. Lipase assisted the epoxidation of α-pinene using H_2O_2 as oxidation reagent and ethyl acetate as both acetate-supplier and solvent affording α-pinene oxide as the main product. Further, the biopolymer promoted the izomerization of α-pinene oxide to campholenic aldehyde and *trans*-carenol. The presence of biopolymers enhanced the catalytic activity of the biocomposites as compared to the free enzyme (*ie* 13.39×10^3, $19.76\times10^3$and 26.46×10^3 for the free lipase, lipase-carrageenan and lipase-alginate, respectively).The biocatalysts stability and reusability was confirmed in six consecutively reaction runs.

Thus, we offers different alternatives for α-pinene valorization into value-added products related to the biocatalyst design involved in the biochemical process.

Acknowledgements

This work was financially supported by UEFISCDI, Romania (PCCA 105/2014) and the COST Action CM1303.

B10

Synthetic Application of Phenylalanine Ammonia Lyase in Cascade Reactions

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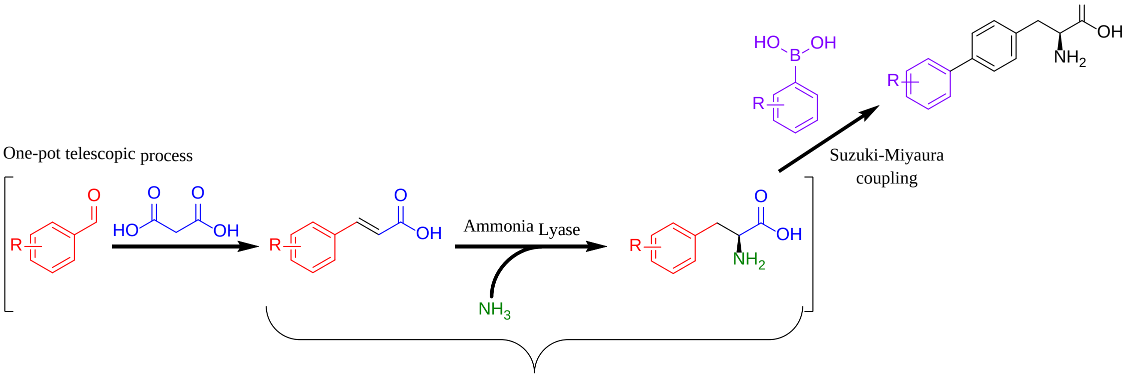
Keywords: Biocatalysis, Chemo-enzymatic synthesis, Phenylalanine ammonia lyase, Non-natural amino acids.

Abstract

Biocatalysisishas allowed access to key chiral compounds with relevance in the pharmaceutical and agrochemical industries. Despite the success of enzymatic reaction in organic synthesis, many are still somewhat limited to narrow substrate scope and industrial application. One of the most attractive biocatalytic routes to optically pure L-arylalanines is the asymmetric hydroamination of arylacrylic acids catalysed by phenylalanine ammonia lyases (PALs)[1]. This class of biotransformation proceeds from readily available starting materials to valuable chiral building blocks with 100% atom efficiency and no need for expensive cofactor supplementation. Synthesis of non-natural amino acids has been demonstrated with PALs[2], however, access to unusual phenylalanine derivatives including biaryl and di-halogenated analogues are yet to be reported. Herein we demonstrate the synthesis of API substructures by combining PAL from *Anabaena variabilis* (*Av*PAL) and an engineeried d-amino acid dehydrogenase (DAADH) with a versatile Suzuki-Miyaura coupling in aqueous conditions, to obtain novel optically pure non-natural L-and D- amino acids[3]. In addition we apply our method in the synthesis of non-commercial halophenylalanines starting from benzaldehyde in a one-pot telescopic process[4]. Intensification of the process results in an industrially viable green alternative to chemical based procedures with a space time-yield of 237 $gL^{-1}d^{-1}$ which is an improvement on the current method of fine chemical synthesis.



Conv.: 92% ee: 99% (S)
E factor: 5.3 STY: 237.6 g L^{-1} d^{-1}

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B11

Valorisation of renewables by isomerising metathesis

Enhancing biodiesel

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Keywords: renewables, isomerising metathesis, biodiesel

Abstract

Isomerising olefin metathesis has recently emerged as a valuable tool for the valorisation of renewables [1]. In the presence of a bimetallic catalyst system, fatty acid derivatives are converted into industrially useful olefin blends with a tunable chain length distribution (Figure 1) [2]. This orthogonal tandem process is mediated by the combination of a dimeric Pd (I) isomerisation catalyst and state-of-the-art Ru-based metathesis catalysts. Moreover, if ethylene is added as cross-metathesis partner, the resulting olefin blends show a uniform product distribution with a boiling point curve comparable to diesel fuel. This process represents a promising pathway towards replacing petrochemical fuel with biodiesel.

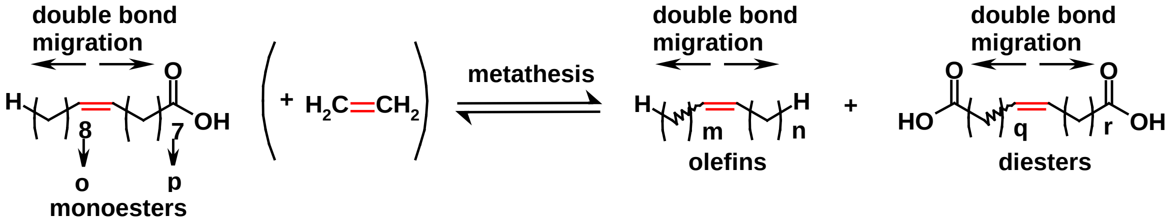

Figure 1 Isomerising metathesis of fatty acid derivatives

A similar synthetic approach was successfully applied in the synthesis of valuable styrenes from naturally occurring allylarenes[3] and in the synthesis of tsetse fly attractants from cashew nut shell liquid (CNSL), a waste by-product of the cashew nut industry [4].
These applications demonstrate the potential that isomerising metathesis has on the incorporation of renewable resources in the chemical value chain.

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B12

High Throughput to Make Biochar in Molten Salt for Climate Change Mitigation

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Keywords: Biocoal, Biochar, Activated carbon, Molten salt

Abstract

Carbonization of biomass in a heated environment devoid of oxygen is a proven technique of locking up renewable carbon in a fixed form that will not rot or decay, leading to unwanted emissions. Traditional pyrolysis using hot flue gas to effect the heat transfer is not in line with economics. We used hot liquid instead to effect the fast heat transfer to comply with economics and to be adaptable for commercialization in the future [1]. Normally, the volumetric heat capacity of liquid is about 2000 times larger than that of gases so that the speed of heat transfer by liquid is at least several hundred times faster than that of gases. Depending on the conditions of production of the charcoal – temperature, resident time, and possible pretreatment of the biomass with common environmentally friendly reagents – the resulting porous biocarbon is suitable for use as *biocoal*, a coal replacement, in thermal power-plants with carbon capture and storage capability; *biochar*, for burial as a soil amendment that can improve water retention and/or provide filtration of chemical toxins and pollutants; *activated carbon*, a material with high specific area that can be used for filtration of liquids and gases, or as a substrate for support in catalysis or for electrochemical reactions. The technology is completely scalable from test-tube experiments, to tabletop machines, to pilot-plant demonstration equipment. So far, the biochar with molar ratio of hydrogen to carbon less than 0.6 can be produced in two minutes, and the BET-N_2 value of activated carbon can reach to 2088 m^2/g. With suitable precautions, it also produces no noxious emissions, soot, or fly ash. The primary liquid by-products of the process, e.g. acetic acid, acetone, methanol can be employed as a feedstock for industries. The primary gaseous by-product, syngas, can be burnt to generate electricity utilized by the plant or the surrounding community. At a commercial scale of processing several hundreds of tonnes of biomass per line per day, rather than transporting the biomass to the facility, the compact equipment is transportable on trucks to the harvest site. Estimates for the worldwide amount of biomass that can be harvested by this strategy, without impacting food production, shows, if the rest of the global economy is carbon neutral, that this technology can restore CO_2 levels in the atmosphere to 350 ppm within this century.

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B13

Efficient Degradation of Cellulose in its Homogeneously Aqueous Solution over 3D MOF/graphene Catalyst

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Keywords:graphene, MOF, cellulose, catalyst, formic acid.

Abstract

Catalytic degradation of cellulose to chemicals is an attracting topic today for the conversion of biomass, and the development of novel catalysts is a key point. Since Metal-Organic Frameworks (MOFs) possess uniform, continuous and permeable channels, they are valuable candidate as catalysts. Here, a new 3D MOF/graphene catalyst has been prepared by in situ growth of the zeolitic imidazolate frameworks (ZIF-8) nanoparticles inside the pore of an as-formed 3D reduced graphene oxide (rGO) hydrogel. The ZIF-8/rGO nanocomposite owns both micropores and mesopores with large specific surface area and plenty of acids sites, which is an idea catalyst for biomass degradation. Here, cellulose was dissolved in alkaline aqueous solution at first, and then it was degraded efficiently over the new catalyst under hydrothermal condition. The conversion reaches 100% while the main products are formic acid with a maximum yield of 93.66%. In addition, the catalyst can be reused with high activity.

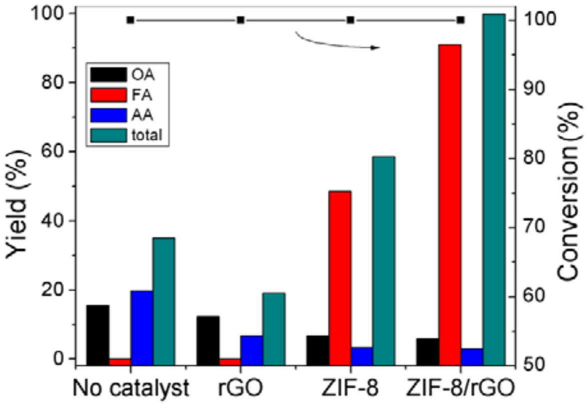

Figure 1. Conversion of cellulose in its aqueous solution over different catalysts. Reaction condition: 8.0 ml cellulose solution, catalyst 0.15g, temperature: 573K, reaction time:1h.

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B14

Economical Zero-Footprint Treatment of Chlorinated Aliphatic Hydrocarbons-Contaminated Water using a Novel Eco-Friendly Bio-Sorbent

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Keywords: Bio-sorbent, Zero-footprint, Chloroethenes, Removal, Water treatment

Abstract

In this study, a novel inexpensive green bio-sorbent was produced from an agro-industrial residue abundantly available in Malaysia (*Artocarpus Integer* fruit processing waste) through a total environmentally benign production route. The sorbent preparation conditions were optimized and the optimal bio-sorbent was characterized by several techniques (N_2 adsorption-desorption, FTIR, XPS, FESEM, TEM, XRD, EDX, TGA and DSC). This newly produced bio-sorbent was evaluated for the removal of cancer causing chlorinated aliphatic hydrocarbons (tetra-, tri- and dichloroethene) from contaminated water. The effects of bio-sorbent dosage, pH, temperature, initial concentration of chloroethenes and contact time on removal of chloroethenes were examined by GC-MS. Our findings indicated that the as-produced bio-sorbent is highly micro-mesoporous (BET surface area ~853 $m^2\ g^{-1}$, t-plot micropore surface area ~506 $m^2\ g^{-1}$, t-plot mesopore surface area ~346 $m^2\ g^{-1}$ and average pore width 2.9 nm) with amorphous structure and predominantly basic surface functional groups, which are all advantageous properties for adsorption applications [1-3]. EDX spectra revealed the presence of chloride peak and elemental mapping analysis showed a high distribution of chlorine in the bio-sorbent after sorption experiments, proving that the bio-sorbent is capable of effectively extracting chloroethenes from contaminated water. The maximum removal of tetra-, tri- and dichloroethene was obtained at pH 8 as 87 %, 85% and 82% respectively for bio-sorbent dose of 5 g L^{-1} and 50 mg L^{-1} initial chloroethene concentration at 40 °C. The study on capability of the newly produced bio-sorbent to remove other contaminants from polluted water is still on-going. Nevertheless, the cost-effectiveness, facileness and greenness of the sorbent production process and water treatment approach, allow the practical application of the bio-sorbent to treat polluted water, especially in low- and middle-income countries where the present conventional water treatment systems used are costly and have large footprints.

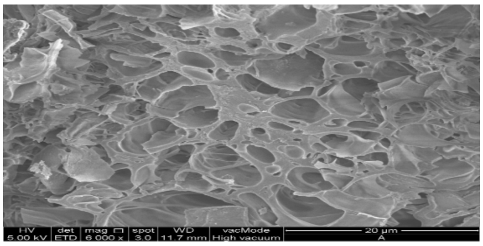

Figure 1: Surface morphology of optimal bio-sorbent obtained by Scanning Electron Microscopy (SEM) showing high porosity.

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IP1

Synthesis of Ru-immobilized periodic mesoporous organosilica and application for selective oxidation of alkanes

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Keywords: Periodic mesoporous organosilica, ruthenium, oxidation

Abstract

Periodic mesoporous organosilica (PMO) is a unique material that has a crystal-like wall structure with coordination sites for metal complexes [1]. A Ru complex is successfully immobilized onto 2,2’-bipyridine-incorporated PMO (BPy-PMO) surface to form a single site catalyst, which has been confirmed by various physicochemical analyses, diffuse reflectance UV-vis spectroscopy, Fourier transform infrared spectroscopy, X-ray absorption fine structure, energy dispersive X-ray spectrometry and nitrogen adsorption [2]. Ru-immobilized PMO was applied for the catalytic oxidation of alkanes using NaClO as an oxidant. This solid catalyst oxidizes the tertiary C−H bonds of adamantane to the corresponding alcohols at 57 times faster than the secondary C−H bonds, thereby exhibiting remarkably high regioselectivity. Moreover, the catalyst converts cis-decalin to cis-9-decalol in 63% yield with complete retention of the substrate stereochemistry. In addition to intrinsic catalysis of the Ru complexes, good durability of the catalyst was achieved because the direct immobilization of Ru complexes within the mesoporous framework gives a rigid structure.

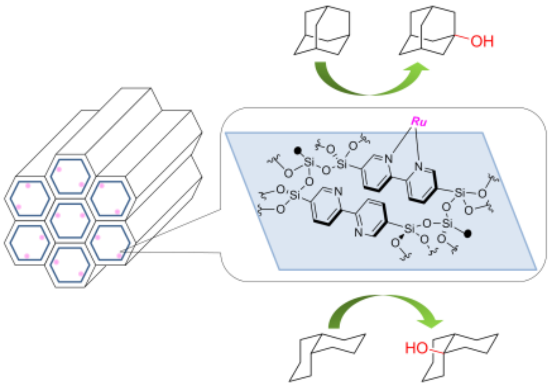

Figure. Selective oxidation of alkanes over Ru-immobilized BPy-PMO.

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IP2

Selective oxidative transformations using molecular Pd(II) catalysts: addressing the challenges of sustainability and practicality

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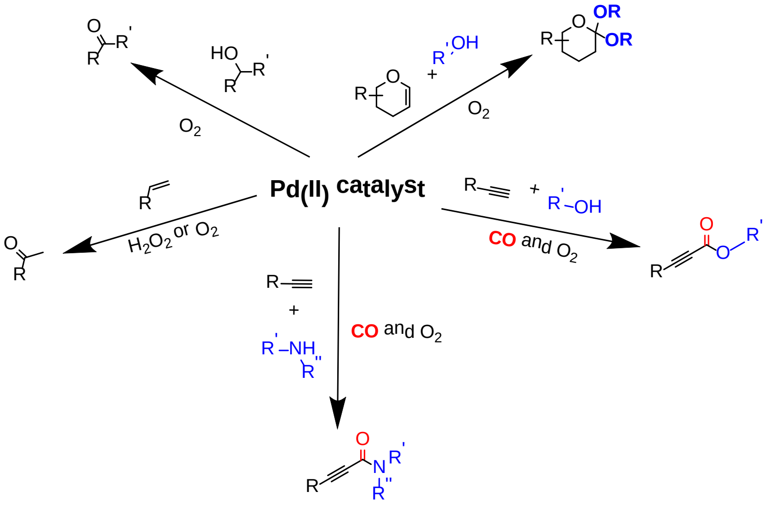
Keywords: Palladium, carbonyls, homogeneous catalysis, carbonylation

Abstract

Palladium(II) complexes are potentially powerful tools for a range of oxidative transformations. Pd(II) catalysts have a long history in oxidation catalysis, but there are significant challenges in order to make many reactions viable on a larger scale. There is a need to develop more effcient catalysts (improved selectivity and lower catalyst loadings), employ greener solvents and also address the safety issues around using green oxidants such as O_2 or H_2O_2.

We have been studying a number of Pd(II) catalysed reactions and we will discuss some of our recent work (including unpblished work)[1] which aims to develop more sustainable and practcal methods.

We have examined oxidative transformations of alkenes (*i.e.* Wacker type chemistry), alcohol oxidation and oxidative carbonylation reactions. We will discuss the new catalytic methods that we have developed for these reactions, as well as our work towards future generations of catalysts. We will also discuss the important issues surounding the safety and sustainablity of these important catalytic reactions, with solvent choice being a key factor here.



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IP3
Direct Catalytic Synthesis of Hydrogen Peroxide: Influence of the Acidity of Niobia-Silica Materials as Supports of Dispersed Palladium Phase

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Keywords: Hydrogen peroxide, Heterogeneous catalysts, Palladium, Niobia-Silica Materials

Abstract

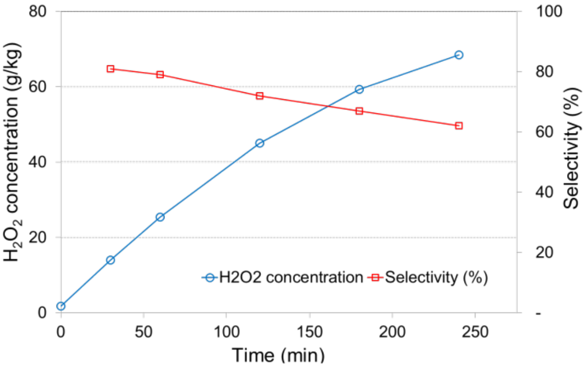
Hydrogen peroxide (H_2O_2) is an important commodity chemical and its demand is growing significantly in the chemical syntheses due to its green character. H_2O_2 is a versatile and environmentally friendly oxidizing agent alternative to chlorine, chlorine containing bleaches, and other common oxidant species since the by-product of its decomposition/reduction is only water. The liquid phase catalytic direct synthesis of H_2O_2 offers an attractive green technology in particular for small-scale/on-site production of H_2O_2. The main drawback limiting the H_2O_2 direct synthesis process is associated with the poor reaction selectivity due to decomposition and hydrogenation of H_2O_2 as well as non-selective oxidation of H_2 to water. The most extensively studied catalysts are supported palladium or palladium-based multimetallic catalysts. Besides the active phase, the support also plays a key role in determining the catalytic performances for H_2O_2 production [1]. It is known that acidic supports enhance the electron deficiency on the metal particles so favoring the reactant adsorption.

In this work, we present our study focused on a large series of acidic niobia-silica (NbS, 6-15 wt.% Nb) materials used as supports of dispersed Pd particles (1.0 to 2.3 wt.% Pd). for the direct synthesis of H_2O_2 conducted in water and methanol.

NbS supports and the relevant supported Pd-catalysts were fully characterized by different techniques: XRD, N_2-adsorption-desorption, TEM, SEM-EDX, UV-vis-DRS, TGA, and acidity measurements [2]. Reaction has been studied in autoclave with continuous gas phase introduction under different conditions. Typical conditions of the catalytic tests were: 1.5 g of catalyst in 150 g of methanol at 5°C, 50 bar of pressure, in the presence of halide ions (HBr , ca. 40 ppm).

During the catalytic reaction of H_2O_2 synthesis, limited Pd sintering occurred that caused some deactivation (Figure). Reaction rate decreased with time on stream as well as selectivity to H_2O_2. TEM images on the fresh and used Pd-catalysts showed Pd-particles of 4.5 nm and 13 nm of size, respectively.

The high exothermal reaction could be responsible of Pd sintering. The NbS acidity might play a key role in anchoring the metal phase and limiting the Pd metal sintering during reaction.



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IP4

Nanodiamond-supported Metal-based Nanocatalysts for Sustainable Organic Transformations

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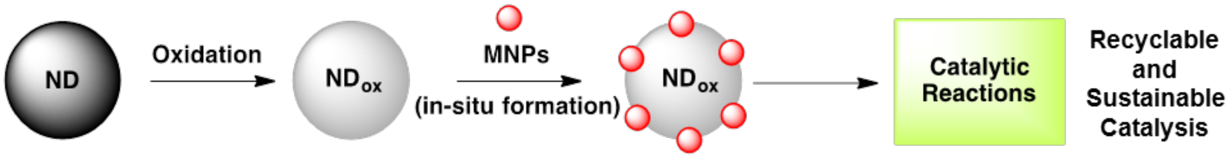
Keywords: Catalysis, Nanodiamond, Metal Nanoparticles, Green Chemistry

Abstract

The design and development of sustainable processes, especially for the selective and efficient transformations using advanced heterogeneous nanocatalysts, is an integral part of catalysis research and in this context, metal or metal-based nanocatalysts have been the front-runners [1]. Along with the intrinsic reactivity of the nanocatalysts, the successful utilization of the appropriate solid supported materials renders the overall process highly recyclable [2]. In addition, such supported nanocatalytic systems have often been shown to have a synergistic effect, offering better activity and selectivity than their individual components [3]. However, the search for the suitable support, especially in terms of developing improved compatibility with the active nanocatalysts, translating to better reactivity and the selectivity of the overall catalytic process, still remains an area of active research. In this regard, a new class of predominantly sp^3-carbon-based materials - nanodiamond (ND) - has the potential of becoming a promising support materials especially given their recent reports on metal-free catalysis [4]. In view of their intrinsic inactive nature, surface oxidation (to form oxidized nanodiamond, ND_{ox}) is often required to generate necessary polar groups on the surface to facilitate superior immobilization of metal-based nanocatalysts. Following our continuing explorations in the field of heterogeneous catalysis, in the present work, anchoring of different metal-based-nanocatalysts on ND_{ox} and their catalytic prowess for a range of sustainable organic transformations is described along with their associated traits such as recyclability and leaching.



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IP5

Highly Active, Reusable, Self-Assembled Polymeric Palladium Catalyst at Parts per Million Levels for Cross-Coupling Reactions

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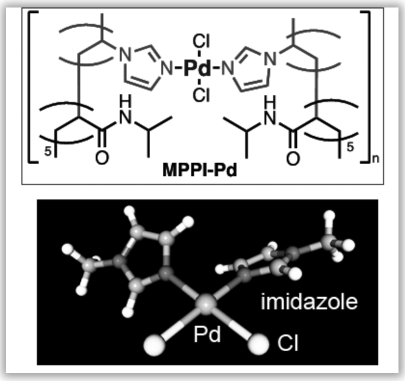
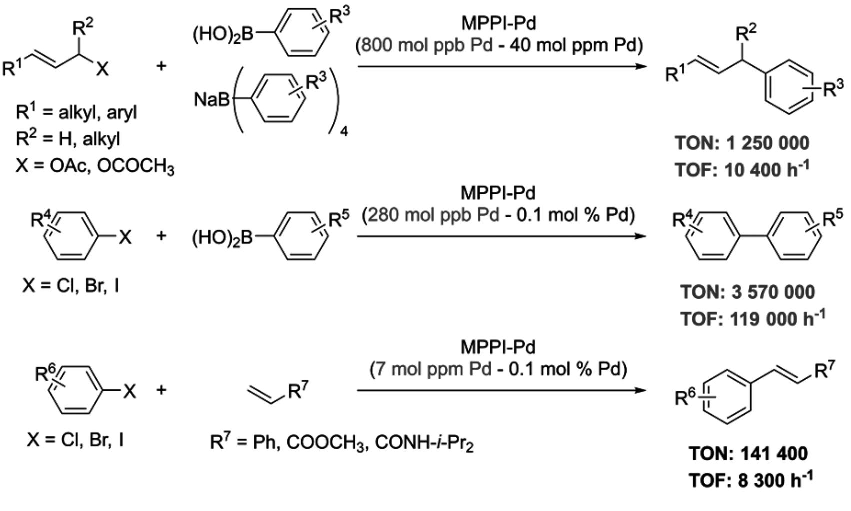
Keywords: Palladium, Polymer-supported catalyst, Cross-couplings, Parts per million Level, Self-assembly

Abstract

It is important to develop metalloprotein-inspired polymer-supported metal catalysts, ensuring catalytic activity, stability and reusability for safe, non-toxic, sustainable chemistry, and green organic synthesis. We have reported convoluted polymeric metal catalysts for organic transformation reactions, where a soluble linear polymer having multiple ligand groups is cross-linked with transition metals via coordinative complexation. Here, we report development of a highly active and reusable polymeric imidazole palladium catalyst MPPI-Pd. By using 0.28 mol ppm (0.000028 mol %) to 0.1 mol % of MPPI-Pd, the allylic arylation,[1] the Suzuki-Miyaura reaction,[1,2] and the Mizoroki-Heck reaction[3] proceeded smoothly to give the corresponding coupling products in high yield. MPPI-Pd was reused without loss of catalytic activity. Structure elucidation of MPPI-Pd also will be presented.





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IP6

Titanium(IV) salophen trifluoromethanesulfonate: An efficient and reusable catalyst for epoxidation of alkenes with sodium periodate

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Keywords: Titanium Schiff base, Alkene, Sodium periodate, Epoxidation

Abstract

Metal complexes with Schiff base ligands such as salen and salophen have extensive applications in the fields of synthesis and cataliysis and important transfer reactions [1]. These complexes can be used as biomimic model of metaloenzyme like cytochrome P-450 in epoxidation of olefins, oxygen transfer to heteroatoms, hydroxylation of aromatic hydrocarbons and oxidative degradation of environmental contaminants [2]. Titanium salophen have been used as catalyst for synthesis of acetates, TMS-ethers 1, 1-diacetates and tetrahydropyranyl ethers [3-6].

In this work, efficient epoxidation of alkenes with sodium periodate as an oxygen source in the presence of high-valent titanium (IV) salophen trifluoromethanesulfonate, [Ti^{IV}(salophen)$(OTf)_2$], is reported. In this catalytic system alkenes were converted to their corresponding epoxides in high yields at room temperature. The reaction parameters such as the amount of catalyst , kind of solvent and the amount of sodium periodate were optimized and 10 mol% of catalyst, CH_2Cl_2 as solvent and 2:1 molar ratio of sodium periodate to alkene were selected as optimized reaction conditions. It is noteworthy low amount of necessary catalyst and reusability of the catalyst are prominent environmental advantages of this heterogeneous catalyst.

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IP7

Green Catalytic Process for Ethylbenzene Oxidation to Acetophenone

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Keywords: Catalytic oxidation, Green process, Ternary metallic oxides, Ethylbenzene, Acetophenone

Abstract

Selective and efficient aerobic oxidation of hydrocarbon to oxygen-functionalizing compounds is of great industrial economic significance.[1] While, the traditional and commericial oxidation reaction process have some dreawbacks, such as high-pollutional oxidant, high energy consumption, harsh reaction conditions, and complexed seperation. For example, in the oxidation of ethylbenzene, acetophenone was produced with stoichiometric inorganic oxidants and homogenous cobalt catalyst which is difficent to separate.[2] Therefore, it is an important mission to develop green catalytic processs for the hydrocarbon oxidation to meet the demand of both industrial production and envirnment protection. Herein, a series of ternary MnNiCo oxides were prepared by a coprecipitation method, with them the ethylbenzene oxidation with molecular oxygen, an environmental friendly terminal oxidant, was performed in the absence of any additives, the conversion reached 60.4%, and acetophenone was produced with a high selectivity of 79.3%. The relation of structure and catalytic performance of the MnNiCo catalysts was discussed, the bulk structure was MnCo$_2$O$_4$ spinel structure, and the external was spinel with mixed valence elements and abundant oxygen vacancy, which causes the high catalytic activity and selectivity. The ethylbenzene oxidation to acetophenone with molecular oxygen over the ternary MnNiCo catalysts is a green catalytic preocess, and it is of bright environment-friendly prospect in industrial application.

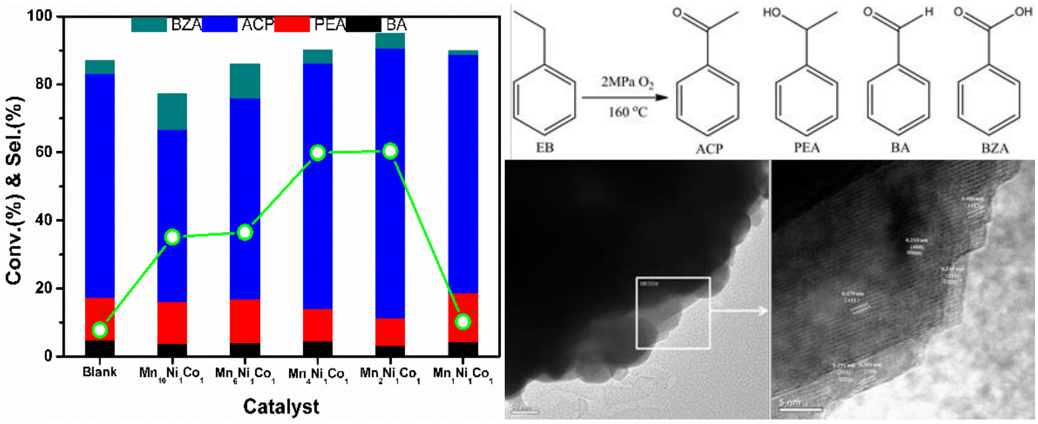

Fig.1 MnNiCo oxides activities for ethylbenzene oxidation and HRTEM image of MnNiCo oxides.

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IP8

Polymetallic catalyst and its application in the aqueous hydrodechlorination of Aroclor 1260

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Keywords: Used catalytic converters; *Klebsiella oxytoca* DSM 29614 ; Bio-generated catalyst; Polymetallic polysaccharide; PCBs;

Abstract

After aqua regia treatment of grinded exhausted catalytic converters and filtration, the solution was concentrated, neutralized and added to a broth of *Klebsiella oxytoca* DSM 29614 to produce nanoparticle metals-polysaccharide composite, (Met_xNPs-EPS = I), which was easily recovered, purified and might be used as a green polymetallic catalyst in water or in two-phase aqueos conditions. The % recovery of metals, originally present in the converter and now embedded in a peculiar polysaccharide structure, was fine-good. Here we describe the application of this composite as catalyst to treat polychlorinated biphenyls (PCBs) [1,2] in water. PCBs can be hydrodechlorinated with hydrogen using Pd-based catalysts that show a high potential for the destruction of such contaminants in water [3]. We explored different reaction parameters with this new catalyst (I) that contains Pd and other metals. Promising results, working at 1MPA of hydrogen and 60°C, were observed with significant removal of higher chlorinated congeners (Figure). These results improve strongly our recent data obtained working with bimetallic Pd,Fe-EPS [3] at 3MPa and 60°C, underlining possible cooperative effects among different metals.

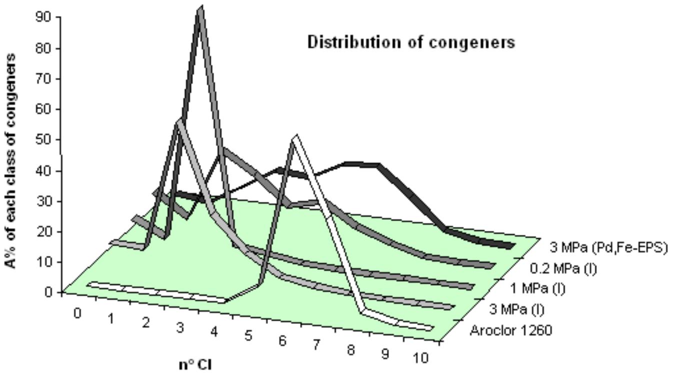

Figure. Distribution and area % of congeners in Aroclor 1260 in the different experiments

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IP9
The Development of Green Processes for Pharmaceuticals

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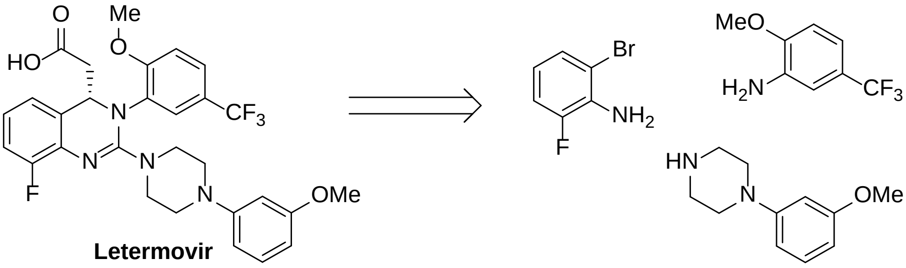
Keywords: Pharmaceuticals, Organocatalyst, Letermovir, Green Chemistry

Abstract

The discovery of innovative chemistry and the application of fundamental green chemistry principles go hand in hand during the development of a commercial process for the manufacture of pharmaceuticals. This presentation will cover some of the key strategies used to develop green processes for pharmaceutical agents and provide details from a recent case study. The discovery and development of an efficient and green commercial manufacturing process for a novel pharmaceutical agent (Letermovir) which is currently under development at Merck Research Labs for the treatment of cytomegalovirus will be reviewed. The identification of a novel, organocatalyst based, intramolecular asymmetric aza-Michael reaction, which is the cornerstone of the synthetic route, will be detailed in this presentation. The fundamentals of green-by-design process optimization and the impact on the development of an efficient, highly productive, low-waste manufacturing process will also be highlighted.



Letermovir
Anti-cytomegalovirus agent

Green Chemistry in China

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Chemical industry contributes greatly to the development of our society. However, many conventional chemical processes produce wastes and pollute environment. Sustainable development is one of the most important issues for humans and is a great challenge. The key points of green chemistry are producing environmentally benign products by using green feedstocks, atomic economy reactions, green catalysts, green solvents, and highly efficient processes, and the technologies should be economically viable. Development of green chemistry is an effective route for the sustainable development of chemical industry.

Over the past two decades, green chemistry has received extensive attention from academia, industry, and government in China. I would like to discuss green chemistry in China in my talk.

Oral Presentation

A. S. Elsayed Sayed
Faculty of Science Ain Shams University, Cairo, Egypt

Oral Presentation

A. Akhmetshina
Nizhny Novgorod State Techinacal University n.a. R. E. Alekseev

Dioxygenases as Green Biocatalysts for Organic Synthesis

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Microbial dioxygenases catalyze the dihydroxylation of aromatic rings to produce enantiopure *cis*-cyclohexadienediols. These materials have been extensively used by the organic synthetic community as valuable starting materials for the preparation of bioactive compounds. This allows for short and efficient chemical synthesis, that avoids the use of expensive chiral auxiliaries and hazardous metal catalysts to introduce chirality in the synthetic schemes. In this presentation, recent advances in the chemoenzymatic preparation of inosamines using the Toluene Dioxygenase (TDO) enzymatic complex will be presented. In addition, a novel enzymatic activity of TDO will be described: the biocatalytic transformation of benzyl azide to benzonitrile. Mechanistic studies of this reaction show the unprecedented ability of the enzyme to produce iron-nitrenoid species from benzyl azide. Further studies will determine if these species can be used as nitrene donors towards the biocatalytic amination of C(sp3)-H bonds and aziridine formation from olefins.

Oral Presentation

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New Challenges for Green Chemistry in Cultural Heritage

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Keywords: green chemistry, cultural heritage, sustainable development

Abstract

The 17 Goals recently approved by the United Nations make a close relationship between technological development and social needs. In this way basic sciences, economics and philosophy are established better than in the past.
This may appear like another one interdisciplinary field; however what the UN call for is actually the engagment of every one of us in bringing our own experience in our field of competence for common welfare.

When in Instanbul, I had the opportunity to visit the Military Museum, where I saw many bronze cannons exposed as military trophy around the garden. On the cannon surface the lion of the Republic of Venice has been melted together with the year of production and the manifacturer name.
It was very impressive and I thought about the different islands of the eastern Mediterrenean that were ruled by Venezia and that own architectural monuments of the Serenissima Republic where the cannons were taken from during many wars and conflict of cultures.

I suddendly realised that this can allows us to create a bridge between Venezia and Turkey, creating a common heritage that will link our historic memory to the presente development.

One possible way to do so is to use Green Chemistry as a mean to connect our technological development to the heritage restauration. The Italian Ministry for Resrch has already founded a research on innovation and safe compounds for restoration of cultural heritage.

This together with the action of UNESCO can be decisive to reach a turning point, not only for Venezia and the Mediterrenean area but also for the whole world, in a field not only of cultural interest but also of concrete intervention and social benefit.

Oral Presentation

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Chairperson of International Basic Sciences
Programme of UNESCO, Executive Director, The African Academy of Sciences (AAS), Kenia

Structural Biology for the rational design of greener catalysts

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Keywords: Biocatalysis and biotransformation, Bio-based materials, flow chemistry technology

Abstract

Enzymes are able of performing complex chemical tasks under physiological conditions, and are thus inherently green catalysts. However, they are also very fragile chemical entities, and strategies for improving their reuseability are contantly looked for. One strategy is to entrap them in solid matrices, which prevent leakage and denaturation and make the enzyme promptly reuseable. For this reason, immobilized enzymes are gaining great interest for industrial, medical and analytical applications.[1] Yet, in spite of such interest, characterization of these systems have so far relied only upon activity tests or microscopic investigations. We believe that structural biology may allow for a rational design of improved materials. We have demonstrated that these enzymes yield high quality SSNMR spectra, that can contribute to the understanding of the structural features in such systems in their artificial but functional environment [2].

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Oral Presentation

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University of Kabianga

Green chemistry in mineral processing: chemical and physical methods to enhance the leaching of silver while decreasing/replacing the consumption of cyanide

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Keywords: Mineral Processing, Cyanide, Mining, Noble metal leaching

Abstract

To achieve a sustainable, inclusive development, countries dependent on extractive activities (e. g., mining) require the development of improved processes able to increase profits without threatening their social and environmental stability. Mineral ores which are refractory (i. e., unresponsive to conventional processing methods) often have a higher consumption of energy and chemicals, which is particularly dangerous during leaching of noble metals, where cyanide is employed to extract metals from the mineral matrix. Our research focuses on developing novel strategies for mineral processing prior to (or during) leaching, so that the cyanide consumption could be decreased while simultaneously improving the extraction of metals. These methods can be chemical (e.g., oxidation of ores, dissolution of refractory materials) or physical (e.g. ultrasound-assisted leaching), and their success depend on the nature of the ores and the modification of their reactivity. By using advanced surface characterization techniques, we are able to understand the changes operating on the surface of the minerals during leaching, so that better strategies can be tested. In addition, we follow changes in the leaching solution during reaction to determine the rate of metal extraction and of cyanide consumption, as well as the maximum efficiency of a leaching process. This work introduces several of the green chemistry principles into mineral processing strategies, promoting the possibility of developing a more sustainable mining around the world.

Oral Presentation

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Oral Presentation

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Capture and valorisation of CO_2, a way to reduce carbon fingerprint

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Keywords: CO_2, Capture, Storage, Recycle and Use

Abstract

Stricto sensu, Green –or sustainable- chemistry means avoiding waste and pollution production, make environmental benign chemical synthesis along with the "12 principles of green chemistry"
But now that we are involved in the **Green Deal**, the role of CO_2 on the climate change prompts to consider this gas as a pollutant and to develop new and original methods to limit its presence.
One way to measure the impact of an individual on the environment is through the carbon footprint, the amount of greenhouse gases, and specifically CO2 emitted.
Current Kyoto-based approaches to reducing the earth's greenhouse gas problem involve looking for ways to reduce emissions. But these are palliative at best, and at worst will allow the problem to get out of hand. It is only through sequestration of atmospheric and emitted carbon that the problem can be solved, at least for the moment.
Three stages should be envisaged: Capt, Store, Use and Recycle.
Capture - Consists first to isolate it from its industrial sources: petrochemistry, iron industry, refineries.

Storage – This is mainly geological storage of CO2, and geochemical reactivity of CO2 with its surrounding should be better understood

Recycle and use - to make sense, the chain of unitary operations must not lead to emit more carbon than it is recycled. One can cite - use CO2 for its physicochemical properties - use of fuels derived from CO2 – reactions using CO2 as a C1 synthon.

These steps will be briefly described, and it will clearly appear that despite several promising routes, new and original approaches have to be developed.
What a challenge for our young and promising researchers…

Reference

Various authors, *L'Act. Chim.*, **2013**, 371-2, p. 23-106

Oral Presentation

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The Malta Conferences: Using Green Chemistry to Bridge Gaps Between Nations

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Keywords: Malta Conferences, Environment, Sustainability, Peace, Middle East.

Abstract

Science is an important tool for advancing the peace process among countries in conflict in general and in the Middle East in particular. The Middle East is a region of importance to the world because it has a source of energy that is a strategic resource: fossil fuel. This non-renewable source of energy is not only fueling economic and political conflicts, but its world-wide use is also placing at risk the sustainability of life on Planet Earth, by polluting the environment and contributing to climate change. Geopolitical borders are only lines on a map. The environment does not recognize these lines. Therefore, any work concerning the environment – especially air and water quality [1]- must be done in collaboration between nations. Science is an international language. A scientist from Bethlehem, Pennsylvania in the USA, and a scientist from Bethlehem, Palestine can communicate scientifically to one another without understanding each other's spoken language [2]. Building on the international language of science, seven major international conferences called the “Malta Conferences” and formally titled "Frontiers of Science: Research and Education in the Middle East - A Bridge to Peace.” In each of these conferences, scientists from 15 Middle East nations gathered with 6 Nobel laureates to discuss Green Chemistry as solutions to the problems of air and water quality, renewable energy sources, nanotechnology and material science, science education at all levels, and chemistry safety and security. The collaborations between these scientists have yielded results that are a cornerstone for a bridge to peace [3]. The same model can be applied to North and South Korea, India, and Pakistan and other nations in conflict.

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Oral Presentation

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Oral Presentation

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Perspectives for Greener Energy, Water Quality Improvement and the Reduction of Environmental Pollution

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Scientific topic: PhosAgro, UNESCO, IUPAC Symposium

Keywords: energy harvesting and storage, electrical energy, catalysis, reduction of pollution

Abstract

The movement towards greener energy sources, for energy harvesting, distribution, application and energy storage for pollution reduction will be discussed in the light of the Sustainable Development Goals. Current and new battery sources, fuel cells, photovoltaic cells and the use of electrical energy in catalytic and electrocatalytic processes will be addressed as well as the employment of less polluting reaction media such as ionic liquids and eutectic solvents. Such more energy-efficient processes lead to less toxic waste products and thence aid in ensuring and improving water quality. The development of simple continuous monitoring methods as remotely controlled diagnostic sensors in order to avoid the need for remediation and clean-up actions, now and in the future, will be presented and perspectives will be indicated.

The strategic role of Green Chemistry in the Italian Chemical Society (SCI)

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Keywords: Italian Chemical Society, Green Chemistry

Abstract

The Italian Chemical Society (SCI) considers strategic the development of an important emerging area such as the Green Chemistry. In fact, in the last years it has been created a variety of interdivisional groups in this field.

These groups are interdisciplinary with different divisions that involves all the main areas of chemistry and therefore the development of all the main themes of the Green Chemistry. Some of the main topics will be presented.

WEDNESDAY, THE 7TH OF SEPTEMBER

M15

Ring-Opening Metathesis Polymerisation of new Bio-based Monomers made from Furfuryl Alcohol and Itaconic Anhydride

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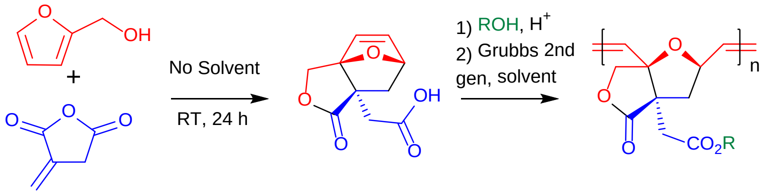
Keywords: Bio-based polymer, ROMP, itaconic anhydride, furfuryl alcohol, platform molecules, Diels-Alder

Abstract



Plastics are the largest output of the chemicals industry (at roughly 300 million tonnes/year) and consume more fossil resources than any other sector, aside from fuels. Therefore it is critical that any feedstocks for the production of bio-based materials are available on a large scale. Two ideal candidate platform molecules for biobased polymer synthesis are furfural[1] and itaconic acid,[2] hundreds of thousands of tonnes of which are already produced commercially from biomass yearly. Starting from furfuryl alcohol, which is easily made by reduction of furfural, and itaconic anhydride, we planned to make simple furfuryl itaconate esters, with the intention of polymerising these using standard free-radical chemistry.[3] However, we discovered that instead of the expected esterification an unusual, 100% atom-economical, tandem Diels-Alder and lactonisation took place to give us a single tricyclic oxanorbornene product. Esterification of this oxa-norbornene acid resulted in a monomer which could be polymerised using Ring-Opening metathesis polymerisation (ROMP).[4] To our knowledge this is the first time that an oxanorbornene with this type of substitution has been polymerised by ROMP. We have been able to demonstrate well-controlled, living polymerisation and produce a range of homo and copolymers using a variety of ester groups as well as copolymers with commercial norbornenes. The mechanistic aspects both of the tandem reaction to form the monomer, and the unusual polymerisation characteristics of this unexplored class of oxanorbornene-lactones are currently under detailed investigation, with early results showing some quite unusual behaviour.

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M16

Catalytic processes in the chemistry of lactic acid and PLLA

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Keywords: lactic acid, PLLA, biodegradable polymers, catalysis.

Abstract

The growing application of biodegradable biopolymers based on lactic acids demands the effective and sustainable methods for the manufacturing of both enantiomers of this important α-hydroxyacid. Since a couple of years, there is a large need for D-lactic acid especially as a monomer for PDLA or as a co-monomer for polymerization with L-lactic acid, since polymers containing both enantiomers show some special material properties in comparison to homochiral polylactic acid (PLA). Currently poly-L-lactic acid (PLLA) is dominating the market. Whilst L-lactic acid is readily available via fermentation in large quantities, the production of D-lactic acid is rather difficult and expensive.

Application of chemical and enzymatic catalysis opens new opportunities for the synthesis of both enantiomers of lactic acid. It allows to improve the overall costs of PLLA/PDLA production by transformation of the manufacturing waste into the valuable chemicals. At the other hand it offers an attractive and scalable approach to many C3-chemicals based on renewable resources. This concept could be applied for the creation of biorefineries on the basis of lactic acid.

Number of catalytic processes such as hydrogenation and epimerisation of lactides[1,2], metal and enzyme catalyzed stereoinversion of lactic acid esters [3] as well as carbonylation[4] were developed within this overarching concept and will be presented and discussed.

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M17

Characterisation and Application of Nanostructured Conducting and Redox Polymer Films Prepared in Deep Eutectic Solvents

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Keywords: conducting and redox polymers, nanostructured films, deep eutectic solvents, ionic liquids

Abstract

Deep eutectic solvents (DES) [1] have recently emerged as an alternative to room-temperature ionic liquids as electrolyte media for the preparation of modified electrodes, taking advantage of the ease of their preparation by simple mixing of two solid, low cost and biodegradable components. DES are formed by the interaction between a hydrogen bond acceptor and a hydrogen bond donor. Here, the quaternary ammonium salt choline chloride (vitamin B4) acts as hydrogen-bond acceptor mixed with alcohol hydrogen bond donors, ethylene glycol, glycerol or urea in a 1:2 molar ratio to give the DES ethaline, glyceline and reline, respectively. They have been used as media for the electrosynthesis of electroactive conjugated and redox polymer films. Such methodologies for producing polymer-modified and nanomaterial-modified electrodes have interest owing to the changes in the modifier film nanostructure induced by the DES polymerisation medium used in relation to ionic liquids or aqueous media. The changes can affect electrocatalysis, the available active surface area, and role as mediators in electrode reactions, important for application in catalysis, electrodeposition, sensors and biosensors.

Poly(3,4-ethylenedioxythiophene) (PEDOT)has been formed by electropolymerisation of the monomer EDOT in different DES and in the presence of conventional aqueous surfactants or $HClO_4$ media [2,3]. Characterisation of the assembly was done during and after growth by electrochemical voltammetric and impedance studies, scanning electron microscopy and the quartz crystal microbalance. The best performing DES medium, acidified reline in the presence of $HClO_4$, was applied successfully with excellent results and compared with aqueous media for the simultaneous quantification of the biologically relevant ascorbic acid, dopamine and uric acid.

Electroactive redox polymers, exemplified by poly(neutral red) and poly(methylene blue), were formed by electropolymerisation on glassy carbon electrode supports in pure DES and in DES-aqueous mixtures. Polymer growth and properties have been compared with those formed in purely aqueous media or in ionic liquids, e.g. [4], in the context of electrochemical sensing applications.

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M18

Electric insulating resin with high heat resistance derived from woody lignin obtained by steam-explosion

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Keywords: Lignin, Hardener, Eposy resin, Thermosetting

Abstract

The application of lignin extracted from steam-exploded woody biomass to epoxy resins, which are widely used as insulating materials in modern electric and electronic equipment, has been explored. In our previous study [1]-[3], the glass transition temperatures (Tg) of hardened epoxy resin containing lignin from softwood were over 200°C—higher than those of commercially available epoxy resins hardened with petro-derived phenol resin. The correlation between lignin properties and the properties of epoxy resin hardened by lignin obtained from softwood and hardwood has also been reported. Stem-exploded lignin could be applied to a copper-clad laminate and molding compound. In order to be used as a heat resistant insulating material, the resin should have both heat resistance and electrical insulating properties, not only high Tg. Here, we report thermal durability and electrical properties such as electric resistance and electrical breakdown voltage of epoxy resin hardened by steam-exploded lignin. The thermal durability of epoxy resin hardened by steam-exploded lignin was classified as Class F, which is defined in Japanese Industrial Standards (C2143). Both the Class F thermal durability and electrical breakdown strength of 154 kV/mm are almost the same as those of hardened epoxy resin by petro-derived phenol resin. These results show that woody lignin, obtained from wood via a steam-explosion process, is a promising raw material for insulation in modern electric and electronic equipment.

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M19

Green Chemistry for biopolymer valorisation.

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Keywords: Biopolymer, Valorisation, Chitosan, Process development

Abstract

The chitin and chitosan market worldwide has shown tremendous growth, propelled by the expansion in the application domain. The market is projected to be more than 70 thousand metric tons by the year 2015. The global market for chitin derivatives is expected to reach $63 billion while the global chitosan market could exceed $21 billion by the year 2015, as stated by Global Industry Analysts, Inc.[1] Among Chitin derivatives, chitosan is projected to offer the highest growth potential. The major source of chitin in China is shrimp and crab and most of the chitin produced in this region is hydrolysed to glucosamine.

The effort to establish a chitosan manufacturing industry in South Africa must be considered holistically and coupled to the local crayfish industry. Operators supplying the crayfish tails to the US market currently either crush the waste shells and discards them at sea or lands these shells and sells them to the local market that uses the shells as a flavoring at low cost. The most economically viable areas for chitosan manufacturing lie in the coastal towns of South Africa which forms part of sensitive ecosystems. How can chemistry contribute to enabling environmentally friendly, benign manufacturing in eco-sensitive regions?

The production of chitosan is prone to natural variation, depending on the source material as well as process parameters [2]. Thus, specifications can differ greatly from one vendor/supplier to another. The demand for a reliable source of high quality chitosan is rapidly increasing as new value added products enters the market. At the same time the growth of value added chitosan based products are limited by the availability of a sustainable supply chain. The process chemistry for bulk chitosan manufacturing is not very environmentally friendly. Green technologies for chitosan modification have increased in recent years and now face the challenge of economic viability. Our intention is to establish a process technology base and an IP portfolio in modified chitosan for applications in chromatography, water purification, catalysis, biomedical and cosmetics [3].

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M20

Isosorbide-based Methacrylate and Its Crosslinked Soybean Oil-based Thermosets: Synthesis, Modification and Characterization

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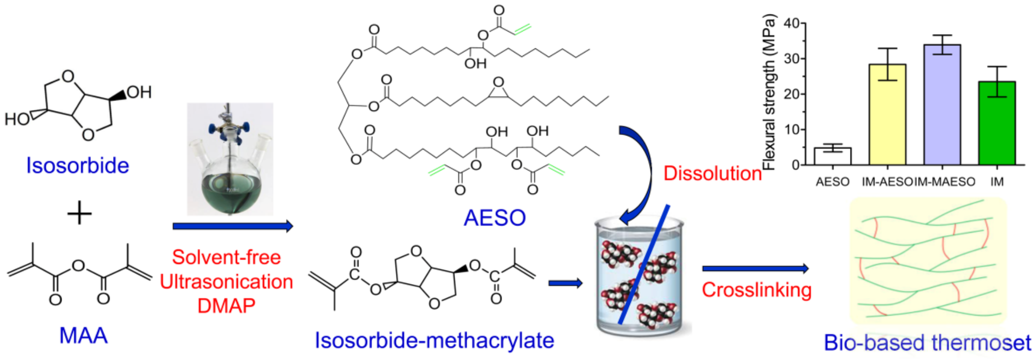
Keywords: Isosorbide, Bio-based crosslinking agent, Acrylated epoxidized soybean oil, Thermosetting resin, Mechanical properties.

Abstract

A rigid bio-based monomer, isosorbide-methacrylate (IM), was synthesized from isosorbide with methacrylate anhydride (MAA) by a solvent-free, ultrasonic-assisted method and then was used as a crosslinking agent for acrylated epoxidized soybean oil (AESO) to formulate a soybean oil-based thermosetting resin with high performance.The chemical structure of the obtained IM was characterized by ^{1}H NMR, ^{13}C NMR and ATR-FTIR. The solubility of IM was evaluated by mixing IM with various chemicals including AESO and unsaturated polyester. The formulated IM-AESO blend was further modified with MAA to impart the resin (IM-MAESO) with higher degree of unsaturation through replacing the hydroxyl groups of AESO with methacrylate groups. Rheological analysis indicated that both IM-AESO and IM-MAESO resins have much lower viscosity and activation energy than the pure AESO due to the incorporation of IM as a diluent. The curing kinetics of the resins was discussed by applying the Kissinger's theory and the Crane equation, which indicates that the AESO resins with IM have high polymerization rate and degree of curing. The cured soybean oil-based networks show much higher flexural strength, flexural modulus, storage modulus, and glass transition temperature than the neat AESO network due to the incorporation of IM resulting in a higher crosslinking density. Furthermore, the MAA modification gives rise to the crosslinking degree and hence stiffness of the IM-MAESO resin as a result of the increase in unsaturated degree of MAESO.In summary, a series of bio-based thermosetting resins with superior processability and high performance were successfully developed and could beused as the matrices for fiber-reinforced composites.

Graphic abstract:



M21
Structure-Property-Function Relationships of Biosynthetic, Biodegradable, and CO_2-Based Polymers

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Keywords: Biosynthetic polymer, Biodegradable polymer, CO_2-based polymer

Abstract

Aliphatic biodegradable polyesters may be classified into natural, semi-natural, and synthetic ones. Poly((*R*)-3-hydroxybutyrate) (PHB) is a purely natural polyester because it is synthesized and decomposed by microorganisms. A semi-natural polyester, polylactide (*i.e.*, poly(lactic acid), PLA) is artificially synthesized from carbon-neutral sources. Poly(ethylene succinate) (PES) and poly(butylene succinate) (PBS) are now produced from petrochemicals, however, being expected to be prepared from carbon-neutral substances in the future. In addition, poly(ethylene carbonate) (PEC) and poly(propylene carbonate) (PPC) can be synthesized directly from carbon dioxide and hence regarded as CO_2-based polymers.

To establish structure-property-function relationships of a given polymer, first of all, it is required to elucidate the most fundamental physicochemical information of the polymer. Therefore, we have investigated conformational characteristics and configurational properties of PHB [1], PLA [2], PES [3], PBS [3], PEC, and PPC by the refined rotational isomeric state (RIS) scheme combined with *ab initio* molecular orbital (MO) calculations on their model compounds. We have designated the methodology as *ab initio* statistical mechanics [4] and have characterized a number of polymers thereby.

The *ab initio* statistical mechanics has been applied to aromatic and aliphatic polyesters to yield their bond conformations, chain dimensions, thermodynamic parameters, dipole moments, molar Kerr constants, *etc*. Our study on PHB [1] has successfully elucidated its solution properties, crystal structure, thermal properties, and interactions with a PHB depolymerase (see Figure 1). The methodology, combined with the Bernoulli or Markov stochastic process, has predicted conformation- and configuration-dependent properties of poly(L-lactide) and poly(DL-lactide) synthesized with stereospecific polymerization catalysts [2]. The similar approach has been applied to synthetic biodegradable polyesters, PES and PBS [3]. Furthermore, selective affinities ofthe biodegradable polyestersto depolymerases have been satisfactorily interpreted in terms of their conformational characteristics and interactions with the enzymes.

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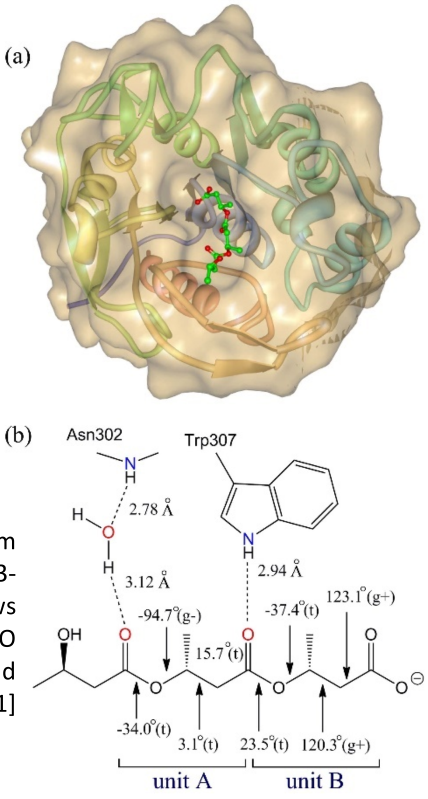

Figure 1.(a) Crystal structure of a PHB depolymerase extracted from *Penicillium funiculosum* and complexed with a trimeric (*R*)-3-hydroxybutyrate (HB) substrate[5]. (b) The schematic diagram shows dihedral angles (conformations) of the skeletal bonds and N...O and O...O distances of the hydrogen bonds. The HB chain adopts the most stable and metastable conformations. This picture was extracted from reference [1] according to the reuse rule of Nature Publishing Group.

P1

The Future of Green Chemistry to Bring About Transformative Change

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The redesigning of the material basis of our society and our economy is required to be able to sustain our civilization. The current unsustainable trajectory that society is on needs to be replaced. There needs to be a fundamental transformation in the way that we think about the materials that we design and use including the materials used to generate, store, and transport our energy. Those who benefit financially from our current products, processes, and systems will likely resist change if possible. What needs to be done such that the science and innovation that green chemistry has and continues to produce can be used to bring about the transformational changes in the timeframe required? That question will be explored in this talk.

P2

Towards automation of chemical process route selection based on data mining

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Keywords: Big Data, Network Chemistry, Route Selection, Green Metrics, Sustainability Assessment

Abstract

In a globlaised, reasearch intensive economy industrial actors are challenged by a constant demand to evaluate new, potential synthesis routes to new or existing targets, adapt to changing supply chains or identify better, more sustainable feedstocks. This demand creates a necessity to develop and evaluate scenarios increasingly frequently in order to stay competitive. At the same time the 21st century has seen the advent of large scale databases, such as Reaxys, SciFinder or ChemSpider, storing large amounts of chemical and reaction data. Leveraging these data could provide potential savings in scenario generation. In 2005 it was first demonstrated that it was possible to convert a predecessor of the Reaxys database into a network (called the Network of Organic Chemistry, or NOC) by storing all its species as nodes and all reactions contained within it as edges connecting these nodes according to the products and reactants involved [1]. Such a network representation allows a superficial search for synthesis routes based on connectivity though crucially suffers from some drawbacks in that it crucially neglects reaction information. Nontheless it allows the user to get a quick overview of a certain area of chemistry by allowing the identification of all papers that relate to the potentially relevant reactions and space. When using the network for the purposes of synthesis planning and scenario generation it is of great importance that the suggested routes are not merely superficially connected but provide some insight into the underlying chemistry and reaction conditions.

This is one of the first works trying to combine analysis of the Network of Organic Chemistry with route scoring based on sustainability considerations to provide meaningful criteria. To this end a case study of conversion of waste limonene into benzoic acid as a chemical intermediate was studied. Analysis of the network structure yielded 232 unique synthesis paths consiting of three or less reactions. A subset of these paths was analysed using a combination of exergetic efficiency, mass-based indicators, health, safety and environmental impacts through solvents, industrial reliability of the proposed reactions and the principles of redox economy. The results of these methods were analysed using multi-criteria decision making to come up with a ranking of the process options. Though questions around data availability remain, the methodology was able to evaluate the synthesis route options successfully in an automatable manner as a proof-of-concept, demonstrating the usefulness of the approach and adding an important dimension of analysis to the network providing potentially large time savings in the initial stages of sustainability analysis, by allowing a fuller leveraging of the datasets contained in Reaxys. The authors gratefully acknowledge RELX Intellectual Properties SA’s support in making the Reaxys data available to them.

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P3

Two Decades of Green Chemistry Progress, not only for the Environment but for Education, through the US Presidential Green Chemistry Challenge Awards

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Keywords: Education, Green Chemistry, Sustainability

Abstract

The US Presidential Green Chemistry Challenge Awards [1] began in 1996. Through 2015, a total of 104 awards have been given to companies and academics. The chemistry described in these awards represents outstanding examples of green chemistry covering all areas of chemistry. The awardees encompass a wide range of industries from small businesses, to the largest chemical companies on the planet, as well as faculty from across the US. The content of these awards offers a treasure trove of chemistry for academics to blend into the curriculum at all levels for both science majors and courses outside the chemistry curriculum. These awards provide powerful examples which companies can use educate their employees and emulate. The awards can also be used to illustrate to the public how chemistry can be part of the solution to move toward sustainability, not part of the problem. Green Chemistry is chemistry that we can all live by and learn form.

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P4

Sustainable Chemistry: Strategies and Initiatives of the German Environment Agency (UBA)

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Keywords: Sustainable Chemistry, ISC_3, Concept, Criteria and Indicators, Chemical Leasing

Abstract

The German Environment Agency developed based upon an analysis of approaches, guidelines, programmes with respect to Sustainable Chemistry. The concept for Sustainable Chemistry aims at a better understanding of the objectives and key aspects characterizing Sustainable Chemistry, and to make the application of these principles measurable.

The German Government is currently constructing an International Sustainable Chemistry Collaborative Centre (ISC3). The ISC3 will promote a holistic concept for Sustainable Chemistry as well as technical developments in Sustainable Chemistry i.a. through exchange and presentation of best practice examples. The ISC3 will rise awareness in industry, science and politics as well as in public perception by networking with initiatives and stakeholders.

The tool Parameters for Sustainable Chemistry (PSC) is a set of quantifiable indicators for Sustainable Chemistry. This PSC set of indicators is designed for companies, consultants and other evaluators in the field of sustainability. The result of the evaluation is a first quantitative assessment how e.g. companies that produce, use or trade chemicals perform in terms of sustainability or whether measures implemented have led to more sustainability. Companies may apply PSC to different areas such as products, processes, trade, company site or entire company.

The guideline “Criteria for Sustainable Chemicals” is a tool for producers and operators evaluating sustainability through a set of criteria applicable to substances and mixtures. The assessment criteria encompass e.g. green house gas potential, resource demand, (eco-) toxicity, mobility and persistence in the environment as well as responsibility in the value chain. The guideline helps producers and operators to green their chemical portfolio as well as their internal processes. The guideline was recently updated and amended by the feature to assess also mixtures and the electronic, free instrument SubSelect was developed based on key elements of the guideline.

The business model of Chemical Leasing is an instrument to put sustainable chemistry into practice: the profit does not depend on the quantity of chemicals sold but on their best economical use per service unit. It is the purpose of such an approach to decrease the quantity of chemicals used, save costs, reduce resource consumption, and ensure best performance and safety management practices. Chemical Leasing is chaperoned by challenging sustainability criteria. Currently, sub-criteria and indicators are developed to help Chemical Leasing business partners to comply with the sustainability criteria.

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P5

Evaluation of nitration of aromatics with nitric acid in fluorinated alcohols with literature methods by green chemistry metrics

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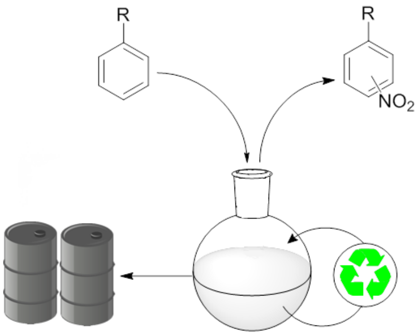
Keywords: Green chemistry metrics, nitration, template catalysis, fluorinated alcohols

Abstract

Aromatic nitration is one of the most basic reactions in organic chemistry and has great importance in industry especially for preperation of fine chemicals, dyes, agrochemicals and plastic. Reason for this lies in simple transformation of nitro group into wide variety of functional groups [1]. Even though there is strong drive for development of new methods following green chemistry, classical method with concentrated sulfuric acid as activator is still most often used. Low price and easy availability of sulfuric acid are difficult to match even though classical method produces a lot of waste acid, has poor selectivity and dangerous and corrosive reaction conditions.

We developed new method for aromatic nitration where nitric acid is activated by fluorinated alcohol which works as template catalyst. Template catalyst work similar like an enzyme by providing complementary charge to transition state and thus lowers energy barrier [2]. To understand how the method fulfils requirements of Green chemistry we made evaluation of literature methods for nitration of aromatic molecules by calculating green chemistry metrics (atom economy, E-factor…) [3]. Methods were also compared by the cost of reagents needed to carry out reaction.



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P6

NEW CHEMISTRY: EMBRACING THE HUMAN ELEMENT

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Keywords: New Chemistry, Ethics, Curiosity, Systems, Green Chemistry

Abstract

In the twentieth century, chemistry's linear profit-driven model made profound discoveries — and consequently large amounts of toxic waste and byproducts — which greatly contribute to the modern challenges humanity faces. This oversight provoked the adoption of practices and principles such as green chemistry and green engineering as a way to practice high-level chemical experimentation without acting unsustainably.

With the growing integration of green chemistry and engineering in industry and academia, Paul Anastas' talk *Green Chemistry Next* highlighted the lingering issue of "preventing getting stuck in a metric driven loop" [1]. We began to seek out why this might happen, realizing the necessity to re-ask "What does it mean to be chemists, members of society, and human?" In response to these questions, we took a humanistic approach and began to address key components needed to help chemists rise to the challenges in the new era of chemistry.

New Chemistry is intended as a guide to allow society and chemists to prosper and grow sustainably, by acknowledging the human element and finding ways to cooperate with it rather than control it. New chemistry encourages a shift away from shareholder and consumer desires as the primary driving force behind research, instead impressing ethical guidelines that assist chemists in devising their new role in society as environmental and social stewards. These guidelines help them to ultimately embrace green chemistry and engineering principles, and avoid reverting to the linear thinking, which caused these problems in the first place.

The introduction of curiosity as a core component of new chemistry allows for continual expansion and intellectual stimulation of the individual, leading to growth in fundamental research and subsequent applied research opportunities, and making innovative breakthroughs inevitable. These components are essential for tackling the increasingly complex problems humanity faces, such as those recently noted by George Whitesides at Harvard: public health, mega-cities, climate instability, and dissipative systems [2].

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IP10

Green Chemistry in Fragrances – Success and Challenges

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Abstract

Green Chemistry and Sustainability play an important role in the Flavor & Fragrance Industry[1]. With more than 4000 ingredients the complexity is high. Nearly 80 % are single aroma molecules, individually produced by a broad range of different organic reactions. In some areas fragrance chemistry has been the driver of new developments, like e.g. photo- or macrocyclic chemistry. More than 60% of these ingredients are used by the entire industry but at quantities below 1 ton/annum.

Even though the quantity of a perfume oil in the final product is often less than 1% (e. g. a laundry detergent) it has a high visibility to the final consumer, as the perfumer is a driver of sensory preference and perceived function. Many ingredients have been well-established on the market for years and produced with conventional chemical synthesis. New catalytic methods, raw materials from renewable resources and more environmentally friendly products are changing the industrial environment of the fragrance industry.

We will report on new catalytic processes for well-established products and new products from renewable feedstocks on the basis of actual examples.

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IP11

Valorization of mango kernel waste using an enzymatic fractionation process

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Abstract

Mango processing waste, as a “low cost” feedstock for recovery of bioactive compounds, has attracted much attention in recent times (Banerjee et al, 2016; Dhingra & Kapoor, 1985; Kaur, Singh, Sandhu, & Guraya, 2004). Kernels comprise up to 10-12% of the total waste generated after fruit processing; and have been found to be rich in bioactive lipids, polyphenols and starch. In previous studies, large quantities of organic solvent, such as hexane, have been used for the selective extraction of lipids from dried kernels (Dhingra & Kapoor, 1985; Rukmini, 1984). Water as a green solvent helps in recovery of polyphenolics but is not effective for the recovery of hydrophobic and more complex components. In this study, an enzymatic fractionation method was developed to breakdown the complex kernel matrix using amylase and glucoamylase. Lipids released into the aqueous medium after enzymatic hydrolysis formed a stable emulsion. After the extraction of lipid in the first stage with the help of stirring with hexane and centrifugation, sugars and polyphenolics were quantified in the aqueous phase. Compared to conventional soxhlet process where hexane is used in 1:20 (solid:solvent) and 11.5±1.4% lipid yield was obtained, in this alternative study, 8.4-10.8% lipid yield was obtained with varying concentrations of enzymes. Quantity of hexane required to recover lipid from the top phase was found to be 1:5 (solid:solvent). Reducing sugars, primarily glucose were obtained in the aqueous phase. The experiments were conducted on fresh kernels which saved the cost of drying significantly and simplified downstream processing operations.

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IP12

Nanocrystalline Cellulose-templated Mesoporous ZSM-5 for Direct Conversion of Cellulose to Hexitols

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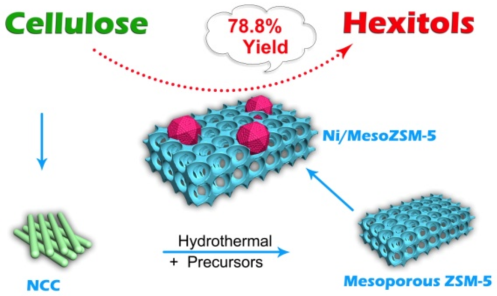
Keywords: Cellulose, biomass conversion, mesoporous ZSM-5, nanocrystalline cellulose

Abstract

Efficient utilization of cellulose is of scientific significance andgreat challenge for both fundamental and industrial studies[1,2].Herein, we synthesized MesoZSM-5 zeolites by usingnanocrystalline cellulose as template for the first time, andreported the exciting performance of the corresponding nonnoblemetal catalysts (Ni/MesoZSM-5) for efficientconversion of cellulose to hexitols. By modulating the ratio oftemplate to precursor, MesoZSM-5 supports were producedwith tunable pore structure and acidic sites. With thecooperation of active Ni sites and acidic sites of MesoZSM-5,hexitols were obtained with a high yield of around 60% in thedirect conversion of commercial microcrystalline cellulose(MCC). The corresponding correlation between structural characteristics and catalytic performance was established. Thiswork provides a new way for the efficient utilization of cellulose, as well as gives rise to a sustainable templating methodfor the synthesis of mesoporous zeolite[3].



Direct conversion of cellulose to hexitols with high yields was achieved over NCC-templated Ni/mesoporous ZSM-5 catalysts

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IP13

Sequestration of metallic ions and silver nanoparticles in aqueous media using immobilized chitosan derivatives

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Keywords: Sequestration, chitosan, water treatment, nanoparticles, metals.

Abstract

Nanomaterials are currently used commercially due to their specific properties. In 2011, the production and consumption of silver nanoparticles (Ag NPs) were estimated to 320 tons/year and would increase. Ag NPs are interesting due to their high surface/mass ratios that confer high reactivity. Ag NPs are largely used in several consumer products (*e.g.* textiles) notably for their antibacterial properties and will likely be found in wastewater, then in the receiving environment. Metallic ions are also largely used industrially. The development of a green product capable to sequestrate those released contaminants is therefore needed. We have developed some cationic supports composed of immobilized chitosan derivatives. The cationic supports were characterized by spectroscopic methods. Sequestrations of citrate-coated Ag NPs (120 $\mu g.L^{-1}$) were realized in various conditions such as in water, in synthetic seawater, with addition of humic acid, anionic and neutral surfactants, hydrosulfide ions and municipal wastewater. Supports and Ag NPs were characterized by microscopic methods. With addition of hydrosulfide ions, the percentage of sequestration increased up to 100%. The efficiency of sequestration was correlated with the zeta potential of Ag NPs. The immobilized chitosan derivative recovered a large portion of silver regardless to the speciation (Ag NP, Ag_2S or Ag^+).

IP14

Facile HMF formation from glucose in water over Phosphate/TiO_2 with water-tolerant Lewis acid catalyst

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Keywords: Biomass conversion, HMF, TiO_2, water-tolerant Lewis acid

Abstract

The reaction mechanism for the formation of 5-(hydroxymethyl)furfural (HMF) from glucose in water over TiO_2 and phosphate-immobilized TiO_2 (phosphate/TiO_2) with water-tolerant Lewis acid sites was studied using isotopically labeled molecules and ^{13}C nuclear magnetic resonance measurements for glucose adsorbed on TiO^2.[1-4] Scandium trifluoromethanesulfonate ($Sc(OTf)_3$), a highly active homogeneous Lewis acid catalyst workable in water, converts glucose into HMF through aldose−ketose isomerization between glucose and fructose involving a hydrogen transfer step and subsequent dehydration of fructose. In contrast to $Sc(OTf)_3$, Lewis acid sites on bare TiO_2 and phosphate/TiO_2 do not form HMF through the isomerization−dehydration route but through the stepwise dehydration of glucose via 3-deoxyglucosone as an intermediate. Continuous extraction of the evolved HMF with 2-sec-butylphenol results in the increase in the HMF selectivity for phosphate/TiO_2, even in highly concentrated glucose solution. These results suggest that limiting the reactions between HMF and the surface intermediates improves the efficiency of HMF production.

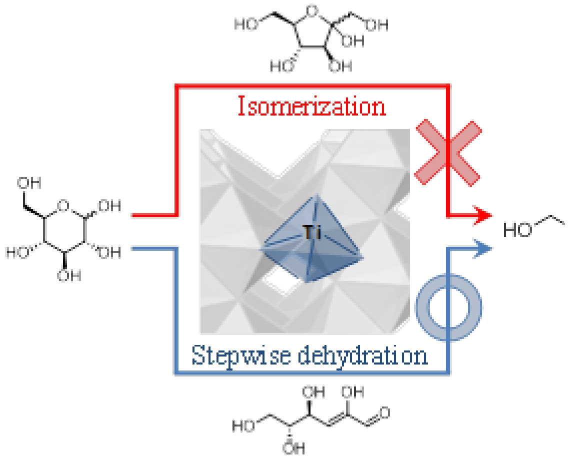

Figure. Schematic illustration of reaction pathway for gkucose to HMF transformation over phosphate/TiO_2 with water-tolerant Lewis acid sites

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IP15

Study of the aggregation of bio-sourced emulsifier in vegetable oils Towards a mechanism involved in oleo-eco-extraction

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Keywords: Aggregation, Surfactants, Small Angle X-ray Scattering, Oleo-eco-extraction.

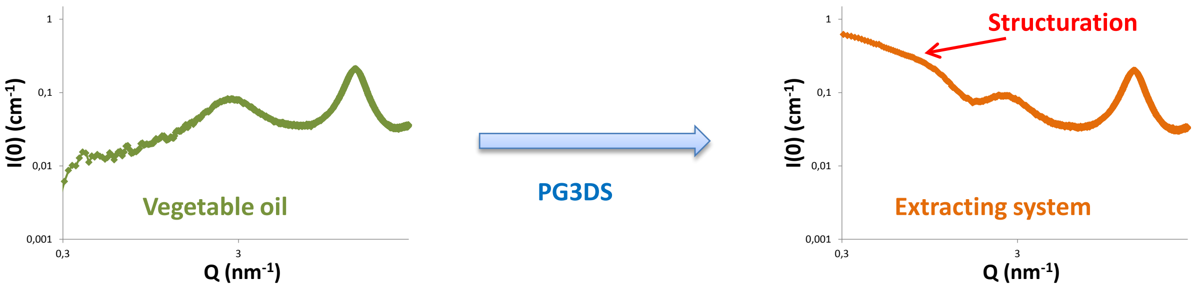
Abstract

Most antioxydants used in cosmetic and food formulations are currently extracted from plants by maceration processes. These processes consist in immersing vegetable solids in a solvent such as hexane, acetone or dichloromethane. In this way the targeted molecules are solubilized in the liquid phase. The drawback is that these methods are generally known to be harmful to the environment due to the use of synthetic solvents.

In order to reduce the environmental impacts, a new type of process, namely "oleo-eco-extraction", was developed and patented by OLEOS Cie. Oleo-eco-extraction is based on six principles: (i) the use of renewable plant resources (ii) the use of alternative systems as biosourced solvents (iii) the reduction of the waste production and the promotion of the production of co-products (iv) the reduction of the energy consumption (v) the reduction of the number of unit operations (vi) the prevention of contamination and the production of a biodegradable pure product.[1] The use of green solvents as vegetable oils is the major evolution towards making an environmentally friendly process.

One way to improve the recovery of polyphenols by eco-oleo-extraction from olive leaves, a family of antioxydants, is the use of an extractant in the vegetable oil. The polyglyceryl-3-diisostearate (PG3DS) was used as surfactant. The extraction by these systems is dependent on the aggregation in the solvent phase.

A method based on the combination of experimental investigations (SAXS, VPO…) and molecular simulation was applied on model extraction systems.[2] This innovative approach allows to bring new information about the supramolecular structures. The influence of various parameters (with or without water and phenolic coumpounds) on the structuration of oil phases was investigated and shed light on the physico-chemical mechanisms involved in the extraction.



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IP16

A Precise Understanding of Organocatalytic Properties of Imidazolium-Based Ionic Liquids; Catalytic Processes involve *N*-heterocyclic carbenes or not?

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Keywords: Imidazolium-based ionic liquids, *N*-heterocyclic carbenes (NHCs), and cellulose

Abstract

Along with a growing importance of sustainability in modern chemistry, chemists need to promote a shift from petroleum-based chemistry to bio-based one. In this context, chemical utilization of biomass has been spotlighted. Despite a number of bio-renewable compounds including amino-acids, terpenes, fatty acids, to mention a few, cellulose obtained from wood-biomass should be one of the most promising chemical feed-stocks because wood-based biomass would be free from instinctive competition with foods for human-beings.[1]

Although utilization of cellulose had been suppressed for long years due to its poor solubility in many common solvents, the integration of ionic liquids (ILs) into modern green chemistry provided a new frontier in the field of the cellulose chemistry. The striking feature of ILs is a distinctive and unique chemical property of dissolving cellulose under mild conditions without harming its structures. In addition, since ILs are, in most cases, organic compounds, a design and synthesis of ILs are straightforward to be reached, leading to a blooming of ILs featuring unique functionalities. Recently, we have envisioned to employ imidazolium-based ILs (Im-ILs) as not only a solvent for cellulose but also organocatalysis for organic transformation reactions.[2] As a matter of fact, the cellulose modification reactions in Im-ILs underwent smoothly to afford modified cellulose derivatives with facile reactivity. To be precise, cellulose was subject to transesterification reactions (TERs) with isopropenyl acetate (IPA) in 1-ethyl-3-methyl imidazolium acetate (EmimOAc) as a reaction medium and a catalyst for the TERs. An organocatalytic property of Im-ILs are rationally expected to be either 1) molecular recognition events by both anions and cations of ILs or 2) spontaneous generation of *N*-heterocyclic carbenes (NHCs) from parental Im-ILs. In spite of a discrete advantage of the organocatalytic properties of Im-ILs, the organocatalytic behavior of Im-ILs have not been studied in detail. In this presentation, we give insights into the organocatalytic nature of Im-ILs for the TER of cellulose with IPA. In addition, the mechanistic understanding of IL-catalyzed TERs successfully optimized the reaction conditions for cellulose modification reactions in Im-ILs.

Acknowledgment: This research was promoted by COI program "Construction of next-generation infrastructure using innovative materials～Realization of a safe and secure society that can coexist with the Earth for centuries～ supported by MEXT and JST. This study was also supported in part by an Advanced Low Carbon Technology Research and Development Program(ALCA) of the JST and the Cross-ministerial Strategic Innovation Promotion Program (SIP) from the JST.

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E1

Visible-light Induced Carbon-carbon bond formation from CO_2 with Dye Molecule-biocatalyst Hybrid System

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Keywords: CO_2 utilization, Biocatalyst, Photoredox system, C-C bond formation

Abstract

Recently, CO_2 utilization technology including the artificial photosynthesis has received much attention. In this research field, CO_2 is used as feedstock for fuels, chemistry and polymers. In catalysts for the CO_2 conversion, some biocatalysts for CO_2 utilization have received much attention. For example, malic enzyme (ME) catalyzes the reaction of malic acid to pyruvic acid and CO_2 with $NADP^+$, and catalyzes the reverse reaction of pyruvic acid and CO_2 to malic acid with NADPH. Thus, ME is also attractive biocatalyst for the carbon-carbon bond formation from CO_2. Some research on the visible light-induced malic acid from pyruvic acid and CO_2 with the system consisting of an electron donor (D), a photosensitizer (P), an electron mediator (C), ferredoxin-$NADP^+$ reductase (FNR), $NADP^+$ and ME as shown in Fig. 1 (system 1) are reported. As this system is very complicated, however, it is necessary to simplify by novel electron mediator (PV^{2+}) as shown in Fig. 1 (system 2).

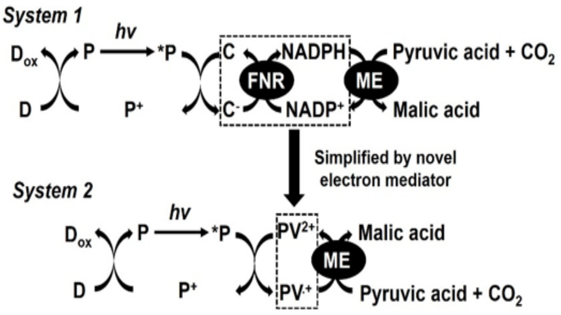

Fig. 1. Visible light-induced malic acid from pyruvic acid and CO_2 with ME

In this work, the visible-light induced malic acid synthesis from pyruvic acid and CO_2 with ME using the photoreduction of phenylviologen derivatives (Fig. 2) with water soluble tetraphenylporphyrin tetrasulfionate (H_2TPPS) in the presence of triethanolamine (TEOA) as an electron donor is developed.

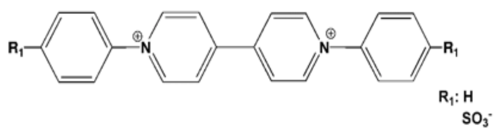

Fig. 2. Chemical structure of phenylviologen

When a sample solution containing TEOA (0.2 M), H_2TPPS (40 □M), PhV^{2+} (0.4 mM), pyruvic acid (6.0 mM) and ME (4.0 units) in CO_2 saturated Bis-Tris buffer (pH 8.0) was irradiated, oxaloacetic acid (main product) and malic acid were produced. Thus, the visible light-induced photoredox system for carbon-carbon bond formation from CO_2 with ME using PhV^{2+} as an electron mediator.

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E2

Enhanced water oxidation activity on core-shell $NiCo_2S_4$@$NiCo_2O_4$ nanoneedles

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Keywords: Water oxidation, core-shell, $NiCo_2O_4$, $NiCo_2S_4$

Abstract

The water oxidation half reaction plays a critical role in efficient solar energy conversion and is also a bottleneck to overcome in developing sustainable energy sources. The reaction is complicated with transfer of four electrons and four protons which makes it sluggish in kinetics, and a large overpotential (η) is usually needed to facilitate the reaction [1]. Up to date, it is still urgently needed to search for efficient electrocatalysts to accelerate the reaction kinetics, reduce the overpotential and improve the current density, especially that composed of low cost earth-abundant elements, such iron, nickel, cobalt and manganese etc., so that large scale solar energy conversion will be commercially achieved in the near future [2].

Spinel Co-Ni oxide based materials are promising stable and earth-abundant water oxidation catalyst in alkaline solution. However, the activity was still low and needed to be improved. In this work, considering the much higher conductivity of the $NiCo_2S_4$ and the drawbacks of instrinct low surface area and non-porosity [3], core-shell $NiCo_2S_4$@$NiCo_2O_4$ nanoneedles (CSNNs) was designed and fabricated on the conductive substrate Ni foil in order to improve the catalytic performance of $NiCo_2O_4$. The core-shell $NiCo_2S_4$@$NiCo_2O_4$ CSNNs was prepared by means of a facile hydrothermal reaction in sodium sulfide solution with Ni-Co compounds as precursor. By carefully adjusting the hydrothermal treatment time, $NiCo_2S_4$@$NiCo_2O_4$ CSNNs with different shell thickness was obtained. The electrochemical water oxidation investigation revealed that an optimal $NiCo_2S_4$@$NiCo_2O_4$ CSNNs structure could be prepared by sulfurization for 8 h, which exhibited the best water oxidation performance. The overpotential needed to produce 10 $mA.cm^{-2}$ catalytic current for the optimal $NiCo_2S_4$@$NiCo_2O_4$ CSNNs was about 290 mV, which was much smaller than that of most reported spinel Ni-Co oxide catalyst. And the Tafel slope for the optimal $NiCo_2S_4$@$NiCo_2O_4$ CSNNs was measured as about 66 mV/dec. The mechanism for the excellent water oxidation performances was discussed in detail by investigating the electron transfer resistance, electrochemically active surface area (ECAS) of catalysts and the different chemical state of the surface adsorbed oxygen. Impressively, the $NiCo_2S_4$@$NiCo_2O_4$ CSNNs after sulfurization for 8 h exhibited better electrical conductivity, larger ECAS and bigger oxygen vacancies ratio than other electrodes, being a promising water oxidation electrocatalyst.

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E3

Ni-complex / g-C_3N_4: A low cost and environmental friendly photocatalytic system for hydrogen evolution under visible light irradiation

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Keywords: photocatalysis, water splitting, hydrogen evolution, g-C_3N_4, metal complex

Abstract

One of the ways to produce environmental friendly energy is to use photocatalytic water splitting system. In order to make this technology feasible it is preferable to prepare low-cost photocatalyst with high activity and stability. A graphitic carbon nitride (g-C_3N_4) is a suitable candidate for photocatalytic water splitting system under visible light irradiation [1]. The photocatalytic activity of pristine g-C_3N_4 is negligible due to the fast recombination of photogenerated holes and electrons. It is necessary to use cocatalyst to enhance the photocatalytic activity for hydrogen or oxygen evolution. A Pt nanoparticle is known to be effective cocatalyst for this system but there is the effort to replace them by non-noble metal cocatalysts due to high cost.

In the present study we will show that it is possible to prepare photocatalytic system with high stability without using any expensive technology. We have investiged the effect of Ni complex loading as a non-noble metal-based cocatalyst for an alternative to Pt on the photocatalytic activity for g-C_3N_4. The injection of electrons from g-C_3N_4 to Ni-complex sites will improve the activity.

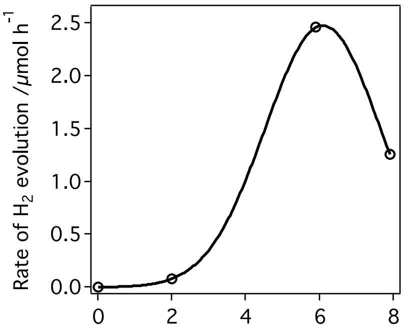

Figure 1 The rate of H_2 evolution on Ni-mercaptoethanol complex / g-C_3N_4 prepared with different mass ratio of Ni (λ > 420 nm).

A g-C_3N_4 was synthesized by a simple procedure. A urea was heated at 550 °C for 4 h to form g-C_3N_4. Ni-mercaptoethanol complex was prepared from Ni(II)acetate and 2-mercaptoethanol. Ni-complex solutions were just mixed with g-C_3N_4 particles without any additional treatment.

Figure 1 shows the rate of H_2 evolution in the presence of a triethanolamine as the electron donor on Ni-mercaptoethanol complex / g-$C_3N_4$with different mass ratio of Ni to g-C_3N_4. The photocatalytic activity of g-C_3N_4 was improved by loading of Ni-complex and showed maximum at 5.9 wt% Ni-loading. Non-noble metal-complex / g-C_3N_4 could be a promising candidate for further studies to achieved higher photocatalytic activity.

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E4
Solar Light Metal-free Arylations from Arylazo Sulfones

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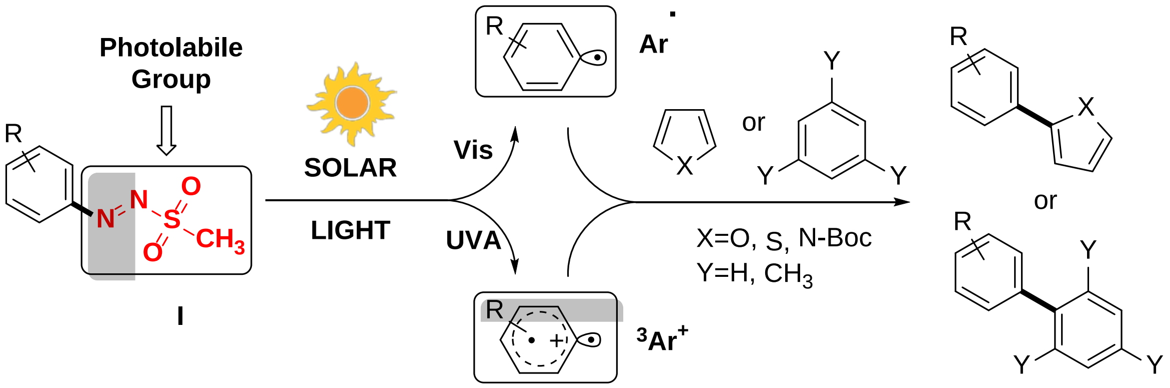
Keywords: Solar Photochemistry, Metal Free Processes, Photochemical Activation

Abstract

Sunlight (visible) induced photochemical reactions are becoming an important approach in sustainable organic synthesis. [1] We report herein the use of Arylazo sulfones as valuable substrates in solar induced metal-free arylation procedures with no need of a (photo)catalyst or other additives to promote the reaction.

Arylazo mesylates (**I**, Scheme 1) are thermally stable derivatives of aryl diazonium salts [2] bearing a photolabile coloured moiety that generates highly reactive intermediates upon exposure to visible (solar) light. Indeed, aryl radicals ($Ar^\bullet$) and triplet aryl cations ($^3Ar^+$) can be selectively generated at will as arylating agents by tuning the photochemical conditions (Visible light for the former ones and UVA light for the latter ones). [3] When photolysis is carried out in acetonitrile-water mixture in the presence of □□ bond trap thiophene, *N*-Boc-Pyrrole) or alkenes, the corresponding arylated products are formed in satisfactory yields (see for instance biaryls and heterobiaryls in Scheme 1). [3]



Scheme 1.

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E5

Enhanced Photoelectrocatalytic Oxidation activity of TiO_2 /carbon aerogel electrode with High Percentage of Exposed (001) Facets in Degradation of Bisphenol A

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Keywords: Bisphenol A, {001} TiO_2, High percentage of facets, Photoelectrocatalytic oxidation

Abstract

The photodegradation of bisphenol A (BPA), a representative endocrine disrupting chemical, has become ubiquitous in the environment. It was carried out in the presence of the landfill leachates, air, dust and waters [1]. This study proposes an photoelectrocatalytic method for the degradation of bisphenol A (BPA) in water based on a novel Nanocrystalline {001} TiO_2/carbon aerogel (CA) photoelectrodes (H-{001}TiO_2/CA), which possesses nearly 100% percentage of exposed {001} facet and excellent photoelectrocatalytic oxidation performance. The photoelectrode was fabricated by loading nano-sized (50-60 nm) anatase {001} TiO_2 [2] on a CA substrate via electrophoretic deposition. Through comparision of M-{001}TiO_2 (the {001} facet percentage is 68%) and L-{001}TiO_2 (the {001} facet percentage is 15%), it is confirmed that the largest photocurrent density and electron carrier concentration (9.05×10^{18} cm^{-3}) was obtained on the H-{001}TiO_2. When H-{001}TiO_2/CA, M-{001}TiO_2/CA and L-{001}TiO_2/CA photoelectrodes were treated with BPA (10 mg/L), the highest BPA removal of nearly 100% in 6h was observed on H-{001}TiO_2/CA, indicating the greatly promoted photoelectrocatalytic oxidation activity. It was resulted from the high percentage of active facets that obtained on nano-sized particle with high specific surface area. The degradation kinetics and intermediates on the H-{001}TiO_2/CA was determined by HPLC and LC–MS in detail. Possible mechanism of the PEC degradation of bisphenol A was further explored [3].

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E6

Niobium oxides and clay modified with Nb as photocatalysts for environmental applications.

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Keywords: niobium oxide, clays, photocatalysts, environmental-catalysis

Abstract

The aim of this study was preparing catalysts based on niobium oxides, natural clay and clay modified with niobium oxide, and characterize them by different physico-chemical techniques and test their catalytic properties in the removal of Rhodamine B (RhB, $C_{28}H_{31}ClN_2O_3$) in water under UV radiation [1]. Fort these purposes a natural clay (montmorillonite) was treated with NaCl (1 mol.L^{-1}), niobium oxide was synthesized by precipitation with NaOH (5 mol.L^{-1}) of $NH_4[NbO(C_2O_4)_2.H_2O].xH_2O$. The clay modified with Nb was prepared by *in situ* precipitation in basic media of the oxy-hydroxide of Nb, in the presence of clay suspension at two pH: 8 and 10. All samples were calcined at 500ºC, 5ºC.min^{-1} in air stream, the samples were named as: Clay_NaCl, Clay/Nb/pH8, Clay/Nb /pH10, and niobium oxide. The photocatalytic tests were performed using a RhB solution (10mg.L^{-1}) prepared with distilled water and a determined quantity of each photocatalyst, in a batch reactor (open to atmospheric O_2) of Pyrex glass, at constant temperature (25 °C) and under UV radiation (provided by six UV lamps, 253.7 nm, 15 watt) exposed directly to the solution. The catalysts were characterized by X-Ray diffraction (XRD), UV-visible diffuse reflectance spectroscopy (DRS), Energy Dispersive X-ray Spectroscopy (EDX), Scanning Electron Microscopy (SEM), Temperature programed reduction (H_2-TPR) and Adsorption-Desorption of nitrogen (BET). The results of characterization showed that the niobium oxide resulted in a crystalline heterostructure composed by Nb_2O_5 (hexagonal phase) and $Na_2Nb_4O_{11}$ (monoclinic phase). All clays of this work have montmorillonite clay ($Al.Si_2O_6(OH)_2$) and magnetite (Fe_3O_4), as major phases. Crystalline structures related to niobium oxide in the samples of Clay modified with Nb, were not found. The results obtained in the photocatalytic tests showed that the heterostructure niobium oxide (Nb_2O_5-hexagonal/$Na_2Nb_4O_{11}$) synthesized is a good photocatalyst for degradation of RhB, removed up to 95 % of the dye at natural pH conditions (pH 6-7), and 1g$_{cat}$.L^{-1} under UV radiation. His removal efficiency is mainly due to its activation under UV radiation, since the contribution by the adsorption process was very low. The addition of niobium to clay enhanced the photocatalytic activity of the clay. The decreasing order for the effectiveness of the catalysts was: niobium oxide> Clay/NbpH8> Clay/NbpH10> Clay NaCl. The natural clay does not have any significant photocatalytic activity, however the addition of niobium oxide in the clay notably increased its photocatalytic activity, which is of interest for several applications.

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E7

Quantitative chemical state analyses of visible light response nitrogen doped titanium dioxide photocatalysts

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Keywords: Visible light photocatalyst, nitrogen doped titanium dioxide, XAFS, EELS

Abstract

Photocatalytic reactions at the surface of titanium dioxide (TiO_2) under UV light irradiation have been attracting much attention due to their practical applications such as environmental cleaning. Recently, it was found that the doping of nitrogen into TiO_2 contributed to narrowing of the band gap, thus providing a visible-light response [1]. Previous studies demonstrated that nitrogen doping generated new optical absorption bands in the visible-light region and the absorbance evolved with increasing nitrogen. On the other hand, absorbance may not be linearly proportional to the photocatalytic activity [2], and it is thus important to understand the chemical state of doped nitrogenmost effective for the visible-light response.

The N K-edge XANES spectrum of the photocatalytic active nitrogen doped TiO_2 showed a characteristic double-peak at 398 and 401 eV, and the XANES spectrum of the inactive photocatalyst a distinct single peak around 401 eV. These features of the XANES spectra were well reproduced by theoretical simulations based on the model where an O atom in TiO_2 were replaced by N ((N)s) for the active photocatalyst, and that of substitutional NO_2 ((NO_2)s) for the inactive photocatalyst [3]. The (N)shad proven to be indispensable for band-gap narrowing and photocatalytic activity, and the optimal nitrogen concentration for generating the (N)s was evaluated to be less than 1.8 atom%.

We also succeeded to visualize these two different nitrogen species in TiO_2 by introducing modern mathematical treatments to energy-filtering TEM. This advanced nanosized mapping clearly showed that the spatial distributions of both (N)s and (NO_2)s species in TiO_2 are the important key to generate visible-light response of a TiO_2 photocatalyst. Furthermore, the quantitative XANES/ELNES analysis of (N)s and (NO_2)s suggested that some nitrogen species other than (N)s, such as (NO_2)s also absorb the visible light. Thus, the absorbance in the visible-light region is not necessarily the indication of the visible-light responsiveness of a photocatalyst.

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THURSDAY, THE 8TH OF SEPTEMBER

E8

Sustainable Carbon Dioxide Capture and Conversion Processes

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Keywords: Carbon Dioxide, Organic Superbases, Methane, Metal Nanoparticles, Ionic Liquids

Abstract

Carbon dioxide emissions resulting from the consumption of carbon-based fossil fuels is universally accepted as the cause of global warming. As worldwide fossil-fuel consumption is bound to increase, so will carbon emissions, from their current level already above 30Gt/year. Carbon capture and sequestration (CCS) is currently under scrutiny at large pilot-plant level as a mitigation strategy for the CO_2 emission problem and global warming. Carbon dioxide utilization has also been proposed, but the sheer size of carbon emissions imposes that only the transformation of CO_2 into fuels may have any real potential as an alternative to sequestration.

In this context, our group have developed efficient methods for CO_2 capture and utilization using sustainable synthetic strategies [1,2].

Herein, we reported two recent approaches:

a) ***CO_2 Capture:*** Novel systems, based on highly abundant saccharides, D-Mannose, D-Glucose, β-Cyclodextrin, Alginic Acid and Mannitol in combination with an organic superbase, Tetramethylguanidine (TMG) or 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) have been tested [3]. In the D-mannose series the highest result was obtained with a D-mannose:DBU ratio eq. = 0.625 (13.9 wt% CO_2 uptake). A more effective stirring system, designed to overcome the high viscosity of the products, allowed the use of a D-glucose:DBU = 1:1 with 11.5 wt% of CO_2 uptake). Additionally a DSC thermal study was performed in order to study stability/reversibility of the CO_2 loaded systems.

b) ***CO_2 Utilization:*** The efficient transformation of carbon dioxide into fuels can be an excellent alternative to sequestration. We developed a CO_2 hydrogenation process to methane in imidazolium-based ionic liquid media, using ruthenium nanoparticles prepared in situ as catalyst system [4]. The best yield of methane (69%) was achieved using 0.24 mol% ruthenium catalyst (in [omim][NTf_2], 1-octyl-3-methylimidazolium bistrifluoromethanesulfonylimide, at 40 bar of hydrogen pressure plus 40 bar of CO_2 pressure, and at 150^{o}C.

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E9

One-pot microwave assisted catalytic transformation of Waste Frying Oil into glycerol-free Biodiesel

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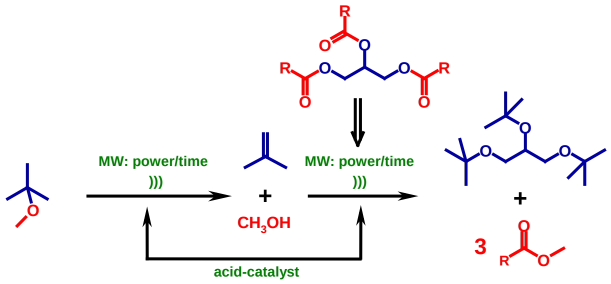
Keywords: Biofuels, Heterogeneous catalysis, Microwave, Waste Frying Oil, Sustainability

Biofuel production has increased in recent years and some commodities like corn, sugar cane or vegetable oil can be used either as food, feed, or to make biofuels. An alternative to overcome the *"Food versus Fuel"* dilemma is to use only non-food crops as feedstock for biofuel production.[a] However, the long-term sustainability for biofuels can be accomplished by exploiting alternative feedstocks from non-arable land. In this contest our attention is focused to the WFO (waste frying oils) from household and industrial sources.[b] Recently, We have reported a catalytic *one-pot* microwave assisted transformation of vegetable oils into a mixture of FAMEs (fatty acid methyl esters) and glycerol ether derivatives, using the commercially available MTBE (methyl *t*-butyl ether) as single source both as transesterification and transetherification reagent.[c,d] The present study is an attempt to adapt the already developed protocol to the transformation of WFO. It is necessary to note that the high temperature of the frying processes and the water from the foods accelerate the hydrolysis of triglycerides, and it increases the FFAs (Free Fatty Acids) content in the oil. Usually, vegetable oils with high content of FFA are not preferred for biodiesel production because they need a pretreatment to convert the FFA to the corresponding methyl esters.[e] Preliminary analysis on the received WFO showed a quantity of FFAs 12 times major to the same oil before its use. When a sample of WFO and MTBE (1:4), in presence of the selected catalyst*, was submitted to the microwave radiation, we observed a complete conversion into the corresponding mixture of FAMEs and glycerol ethers derivatives. Interesting to highlight a complete conversion of FFAs to FAMEs and, as desired, a negligible trace of glycerol was detected.[f]There are several advantages making this process very attractive, among which the WFO could be directly transformed, without any preliminary treatment, the obtained mixture, which is without glycerol, only needs to be separated from the catalyst, through a simple filtration, and it may be used directly in the energy chain.



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E10

Ionic liquid assisted biomass pretreatment for biofuel production

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Keywords: Ionic liquids, Lignocellulosic biomass, Biofuel, Value added chemicals

Abstract

Lignocellulosic biomass, a rich source of cellulose, is one of the most promising raw materials for the production of biofuels and other value added chemicals [1]. An efficient pretreatment of lignocellulose is required in order to deconstruct its highly complex structure and assist enzymatic hydrolysis [2]. Ionic liquids (ILs) are increasingly being explored as potential solvents for the biomass pretreatment because of better solubility of lignocellulosic biomass, compared with conventional solvents [3,4]. In this study both aprotic and protic ILs have been used in order to pretreat lignocellulosic biomass. Among various aprotic ILs, [EMIM][Ac] was selected in this study as it is environmentally benign and known to breakdown the biomass effectively, thus increasing its enzymatic digestibility [5,6]. In order to produce biofuel at an industrial scale, the process of biomass pretreatment needs to be optimised for various pretreatment parameters such as biomass loading, biomass particle size and pretreatment time along with the recovery of the IL. In this study readily available castor stalk (CS), which is rich in cellulose content, was used as the feedstock for the process optimisation of biofuel production. For the very first time, this study demonstrated significantly higher enzymatic digestibility, up to 96%, even at relatively larger particle size and higher biomass loadings. Furthermore, the present investigation was also extended to include biomass pretreatments using protic ILs. Protic ILs are relatively cheaper, easy to synthesize and distillable. Some protic ILs have been reported to dissolve lignin efficiently [7]. In this study, the protic ILs, N,N-dimethylethanolammine formate and pyrollidinium formate were effective in the pretreatment of CS, given high digestibility, comparable with [EMIM][Ac], providing additional options for biomass pretreatment using ILs. Similarly, protic ILs were shown to have negligible effect on the subsequent fermentation, if any residues remain in the biomass.

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E11

Towards New Development in Renewable H_2 Fuel Generation from Water Splitting: Tandem Catalysis and Organic Hydrogen Carriers

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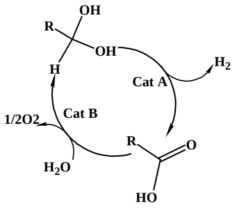
Keywords: water splitting, hydrogen fuel, tandem catalysis, Liquid organic hydrogen carrier

Abstract

The continuity and reconversion of the current energy supply are major challenges increasingly faced by modern civilization. The present massive exploitation of energy resources and the consequent negative impact on the environment is a resulting growing concern. Fossil fuels such as coal, natural gas, and petroleum provide about 90% of the energy used today by developed countries. Renewable and sustainable sources are the only alternative to this rising global problem. Towards this end, the generation of hydrogen fuel from water splitting is an active field of research [1]. However, the separation of the gas mixtures generated by the photocatalytic water splitting is the bottleneck for an efficient industrial hydrogen production plants. The development of a catalytic system that is able to generate pure hydrogen gas from water in industrial scale, provide a solution. However, water splitting also implies oxygen gas evolution in turn requiring a highly expensive and potentially hazardous gas [2]. We have developed and proposed a tandem catalytic cycle based on oxidation and reduction of a carbon carrier, releasing pure H_2 in one step and re-hydrogenation using water (releasing oxygen) in the subsequent step. In this presentation, we will disclose our preliminary results on the utilization of partially oxidized low molecular weight hydrogen carriers in an overall water splitting cycle.



Hydrogen carrier in an overall water splitting cycle

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E12

Catalytic aromatization of natural gases over hierarchical bifunctional Ga/HZSM-5 nanosheets for propane aromatization

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Keywords: Hierarchical zeolite, Galloaluminosilicate zeolite, Natural gas

Abstract

Natural gases (i.e., methane, ethane, propane, etc.) have been discovered in large quantities throughout the world. The conversion of natural gases to high value-added chemicals can be more economically sustainable. One technique for converting natural gases has been achieved by a zeolite -based process as green catalyst (i.e. non-toxic, environmentally friendly). Herein, we have been successfully prepared H-galloaluminosilicate (MFI) zeolite nonosheets by using a tetrabutylphosphonium ion (TBPOH) in a one-pot reaction via a hydrothermal synthesis. A molecular highway mesoporous structure has been created due to the house-of-card assembly of nanosheets[1,2], resulting in a decrease of the microporous diffusion length and an increase of the external surface area. The obtained samples were characterized by means of X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), N_2 sorption technique, NH_3 Temperature Programmed Desorption (NH_3-TPD) and ^{27}Al NMR spectroscopy. Because of the benefits of bifunctional metalloaluminosilicate zeolites compared with an aluminosilicate zeolite, for example, the presence of Ga active sites leads to high selectivity of the dehydrogenation and reduction of a coke formation, the catalytic performances of the H-galloaluminosilicate (MFI) zeolite nonosheets can be greatly improved for the conversion of natural gas in terms of the activity and the stability of catalysts.

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E13

Ionic Liquids as novel electrolytes for energy applications

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Keywords: ionic liquids, non-aqueous electrolytes, green solvents

Abstract

Ionic liquids, compounds composed entirely of ions and liquid per definition below 100°C, have gained popularity over the past 10 years and have become products of industrial interest, instead of just being lab curiosities. Their large electrochemical and thermal stability combined with their low vapor pressure and incombustibility lead to new and safer electrochemical devices, such as batteries and supercapacitors, altogether. In this regard, new electrolytes based on ionic liquids (ILs) are promising alternatives to organic solvents [1].
In the cases where the viscosity of the pure IL is too high, we can use eutectic mixtures in order to increase performance (Figure 1).

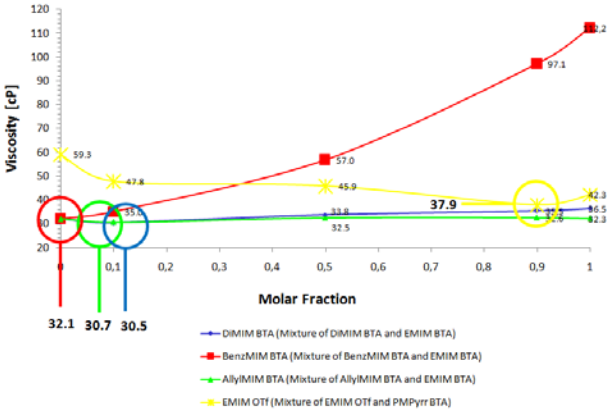

Figure 1 Effect of mixing on conductivity of selected ILs

Although the use of ILs in batteries is still in the R&D stage, it turns out that the IL has a mjor role in the SEI formation process. For supercapacitors, IL as electrolyte has already been commercialised and stabilities of up to 8 000 000 cycles are possible [2]. Therefore, we will present our latest results for Ionic Liquids as novel electrolytes in these kind of devices.

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E14

Thermally stable electrolyte for Li ion batteries at high Li ion concentration

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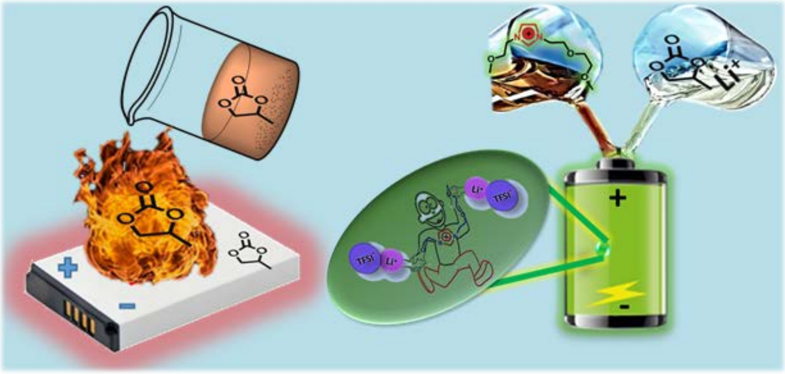
Keywords: Thermally stable electrolyte, Li ion battery, Microwave synthesis, Li ion transportation, Ionic liquid

Abstract

Tuning of the constituent ions and the substituent on imidazolium core alters the physicochemical properties of ionic liquids. Ether-siloxane substituent on imidazole effect on its ILs has been established for low viscosity and improved thermal properties even for high molecular weight ionic liquids.[1] In other direction we explored ionic liquids were applied as additives to vegetable oil in MQL machining of AISI 1045 steel. Because metalworking fluids as a lubricants are a major cause of health hazards apart from being sources of environmental pollution, thus necessitating research in minimum quantity lubrication (MQL) for machining.[2] In this study we investigated ether-ether and ether-siloxane functionalized ILs with TFSI anion and their mixtures with propylene carbonate as electrolyte in lithium-ion battery. The synthesis of these ILs are performed under microwave irradiation and devolped method for kilogram scale in microwave condition. The electrochemical stability and conductivity of these novel ILs were analyzed by electrochemical studies. The application of these ILs as an electrolyte was studied in presence of high concentration of LiTFSI and ether-ether IL was shown to possess high electrochemical stability window (ESW) of 5.9 V and good conductivity of 2.2 mS/cm with different temperature. The electrochemical stability and conductivity was further complimented by self-diffusion of constitute ions using pulsed gradient spin-echo (PGSE) NMR, viscosity and thermal properties.[3]



Thermally stable electrolyte for Li ion batteries

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Ed1

Promoting green chemistry education in Africa: interplay of local and global perspectives and cross-field challenges

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Wide-ranging green chemistry education in Sub-Saharan Africa is still largely to be designed. This offers valuable opportunities to articulate the design in such a way as to take into account a variety of perspectives: local and regional characteristics, continental characteristics and worldwide needs and trends.

The presentation outlines and discusses the main criteria that are currently being explored for possible incorporation into a comprehensive project: the importance of offering information about green chemistry since learners' first encounter with chemistry; the type of information that is relevant for non-chemistry-major tertiary students taking chemistry courses, and the approach to its presentation; the importance of incorporating green chemistry components in all the courses for chemistry major students, to better highlight its cross-field nature (across the various chemistry specialisation areas); adequate emphasis on the interplay of local, regional, continental and global perspectives in all the occasions in which green chemistry is presented to learners; the importance of maximising learners' active engagement, so that the information on green chemistry has a lasting impact on future chemistry professionals and on future citizens in general; and the search for opportunities and options to spread information to the public. Each of these aspects is analysed in detail, and concrete examples are provided to substantiate the analysis through extensive illustration.

Ed2

Green Chemistry Experiments with Small-Lab Kit

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Abstract

While hands-on experiments can help students to better understand the theory of chemistry, organic chemistry laboratory, typically involved flammable solvents and toxic chemicals combined with the normal requirements for heating to carry out the traditional experiments, can create potentially dangerous situations for students and harmful to environment. This paper describes options to perform experiments in line with green chemistry concepts such as pollution prevention, safety, efficiency and use of environmentally benign solvents, using the Small-Lab Kit, invented in Thailand. As the prevention green chemistry concept can be referred to as "molecular-level pollution prevention", such new approach of conducting experiments will tremendously reduce the overall risk associated with organic chemistry laboratory. A case study on the hydrolysis of methyl salicylate in a local medicinal ointment, a household chemicals familiar to the students, will be illustrated as an example. The students have learnt several laboratory technics as well as the green chemistry concept due to the design of Small-Lab Kit, which enables saving chemicals, water, energy and experimenting time, and greatly reducing the amount of waste.

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Ed3

Sustainable processes in the chemistry department: from green chemistry education in the laboratory to environmentally friendly engineering designs

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Keywords: Green Chemistry Education, laboratory practicals, energy-saving design

Abstract

Ever since the twelve principles of green chemistry have been formalised [1] have chemists had the impetus and reference for their pursuit to develop sustainable products and processes. Scientists, not only in chemistry and chemical engineering, have naturally thought about more environmentally benign reactions and design solutions beforehand, although the motivation might have been as diverse as a financial stimulus, an indefensible waste problem or an improved awareness of energy consumption. This appreciation of a possibility of a better future for all has incensed also chemistry to respond with a mindfulness for limited resources and driven green topics in research and education.

However, in order to retain attention and to advance consciousness about environmental solutions and green chemistry a concerted effort is crucial. In this presentation, different angles will be highlighted, starting with undergraduate laboratory instruction, to innovative construction design solutions as well as raising awareness through policies and committee work.

Examples from chemistry education include classical approaches like teaching green metrics, *e.g.* atom economy and reaction efficiency, via different reaction trajectories (*e.g.* organo-catalytic versus organometallic catalysis to stoichiometric), to various improvements through simple changes in the apparatus reactions are performed in (*e.g.* sonication, microwave, mechano-chemistry versus standard heating) and a choice of recyclable over less favourable products with the same or comparable properties.

Cases in the area of design solutions include energy efficient, solvent recycling and water saving laboratory equipment (*e.g.* recirculating [2], air-cooling or Peltier condensers) implemented in our teaching and research laboratories as well as innovative engineering solutions that significantly reduce the carbon-footprint of our department.

Lastly, the presentation will discuss the various stages at which we think it is important to engage people to secure their full and continued support, emphasising outreach, undergraduate and postgraduate education, and how departmental committees influence faculty policies.

To conclude, green ideas from the basic undergraduate laboratory to policy briefs, green chemistry is centre-stage in Chemistry at the University of Southampton and goes beyond faculty borders. Pinnacles from the previous years' accomplishments will be appraised.

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Ed4

Green Chemistry Education for the next generation of scientists in Mexico, via the Biopolymeric Materials Project (BIOPMAT)

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Keywords: Green Chemistry Education, Biopolymers, Materials, Waste, Sustainable

Abstract

Even in our days the sustainable development culture has not yet being embraced by mexican scientists, so from 2008 and on we have been working on the Biopolymeric Materials Project (BIOPMAT). BIOPMAT: is a project that circumscribes within the world trend denominated "Green Chemistry". Of course, the Project is a real one in its early stages, but already useful to diseminate knowledge on Green Chemistry and sustainable development.

Collaborating in BIOPMAT, senior and young chemists as well as students get involved and learn how using agricultural and marine wastes one can produce biopolymers with two expected outcomes : 1) the development of high value-added materials which are an alternative to petroleum-based polymers, and 2) the solution to a highly complex environmental problem such as agricultural and marine wastes.

The project BIOPMAT International dimension:

Since it was launched in 2008, BIOPMAT has attracted an international group of scholars interested or already working in the field of biopolymers, an area that we consider as stated before, of great importance for the sustainable future of our country, and have been interacting with our group during 2 international conferences designed, celebrated and chaired by us in Mexico (Veracruz 2008; Puebla 2010) and they are willing to continue exchanging ideas and sharing knowledge with us in the third Edition of the conference next year, when we will be exploring ways of further collaboration and at the same time educating ourselves and all the conference participants for a greener, more sustainable future.

We thank the authorities of the University of Veracruz, for the economical support provided since the beginning of this project.

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IP17

Functional Group and Phytochemical Analysis of Seeds, Flowers and Leaf of *Moringa oleifera* Plant.

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ABSTRACT

Moringa oleifera, a highly valued medicinal plant and vegetable was used for this study and the functional groups of its seeds (fresh and dry), flowers and leaf were analysed using Fourier Transform Infra-red (FT-IR) spectrometer while some of its phytochemical constituents were analysed by standard methods. The various band signals obtained for the seeds indicated hydroxyl (–OH) and amide (N-H) with a wave number of 2600 – 2400cm^{-1}, imino (=N-H) functional groups appearing at 3350 – 3320cm^{-1}; aromatic tertiary amine (-C=N) within 1380-1340cm^{-1}, methoxy (C-O) and aromatic (-C=C-) groups at 2852.70 and 1615 – 1500cm^{-1}respectively. The flowers and leaves indicated the presence of the following functional groups and their frequency ranges (cm^{-1}) which includes; O-H stretching vibrations (3790-3390), C-H stretching (2953-2752), N-H stretch (1643-1514),C=N symmetric stretching (2723-2351) bending, N=O symmetric stretching (1460-1305), C-N stretch (1265-1033),C=O stretching (1651-1566) and C=C bending (1033-721). Some phytochemical analysis of *M. oleifera* seeds showed that saponins, alkaloids and cyanogenic glucosides were higher in the in dry seeds (7.7, 8.76 and 1.76% respectively) than fresh seeds (5.4, 5.12 and 0.16% respectively) while flavonoid was observed to be slightly higher in fresh seeds (4.76%) than in dry seeds (4.64%). The leaf analysis shows it to contain saponin 5.0%, flavonoid 5.42%, alkaloid 5.36% and cyanogenic glycoside 3.3% while the saponin, flavoniod, alkaloid and cyanogenic glycoside in flowers are 3.20%, 7.12%, 1.55% and 2.6% respectively.

Keywords: *Moringa oleifera1*, functional group2, FT-IR spectrometer3, spaponin4 and cyanogenic glycosides5.

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IP18

Magnetically recoverable catalysts: separation technology meets green chemistry

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Keywords: Magnetic separation, catalyst, recycling, noble metals

Abstract

Catalytic routes applied for the synthesis of complex organic molecules is highly desired but yet hindered by both high costs and difficulties in catalyst separation and recycling. Catalyst separation from product streams remains an issue for almost any manufacturing process. The nature of the catalyst material and the time and energy consumed usually determine which separation process will be chosen. Once the use of conventional separation methods like centrifugation or filtration became widespread, the use of magnetic separation was not always obvious, though if some part of a mixture is intrinsically magnetic, then magnetic separation is often the best choice [1]. Each separation method has its own limitations of cost, efficiency, or generation of secondary waste, but magnetic separation meets most of the criteria of green chemistry. Magnetic separation generally offers high efficiency and specificity when compared with equivalent centrifugation or filtration; it is fast, low-energy consuming and minimizes the prodution of waste. The preparation of magnetically recoverable catalysts relies on the choice of a magnetic support and a catalyst immobilization strategy. Iron oxides, silica-coated iron oxides or carbon-coated iron oxides are the most used catalyst supports. The functionalization of the surface of magnetic nanomaterials is an important step in the design of supported catalysts, because it allows the immobilization of a wide range of molecular catalysts, biocatalysts, organocatalysts, and metal nanoparticles. Here we will present the design of magnetically recoverable catalysts prepared by the ligand-assisted immobilization of metal nanoparticles (Rh, Pd, Ru, etc.) on magnetic supports containing silica, ceria and titania for application in green reaction, as exemplified by selective hydrogenations, where the catalysts were recovered and reused in successive reaction with neglegible metal leaching (Figure 1).

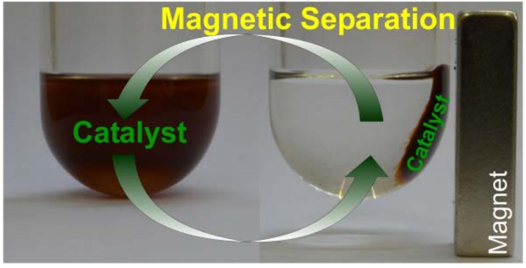

Figure 1. Magnetic separation

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IP19

Synergy between ionic liquids and water that favours process efficiency

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Keywords: hydrated Ionic liquids, carbon dioxide capture, microalgæ, extraction of lipids

Abstract

A remarkable explosion in the ionic liquid literature (*ca.* 5000 papers per year) has resulted in many inconsistencies even in the definition of an ionic liquid. Twenty years ago, when our factual database and theoretical understanding were very limited, the common definition of an ionic liquid was a liquid, consisting entirely of ions, which melted at *ca.* 100 °C. This dates back to a paper published in 1914, by Paul Walden [1], who stated about the first recognised ionic liquid ethylammonium nitrate, "The general picture of these organic salts at low temperatures (below, or around 100 °C) thus corresponds to the experiences made with inorganic (single, non-complexing) molten salts at much higher temperatures approximately between 300 and 600 °C)". In parallel, a class of solvents related to ionic liquids, known as deep eutectic solvents, was developed by Abbott [2]. These contain molecular components, typically one anion, one cation, and two moles of a Lewis base; in some cases their structure may contain the molecular components tightly bound to either of the ions (this closely resembling ionic liquids in many of their properties, and if the binding is tight, they may actually be ionic liquids), in others the molecular components may be essentially free. Ohno [3], has shown that "hydrated ionic liquids" (*i.e.* ionic liquids containing a small amount of water) have different properties from both simple ionic liquids, and aqueous salt solutions. Our own work has demonstrated that phosphonium carboxylates, in the presence of small amounts of water, capture carbon dioxide more efficiently (both physically and chemically) than any reported simple ionic liquid [4]. In a related project, hydrated tetrakis(hydroxymethyl)phosphonium chloride, $[P(CH_2OH)_4]Cl$, was successfully used for the extraction of microalgæ lipids for biodiesel production [5].

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IP20

Synthesis of Bio-Based Thiophene Derivatives with Supported Ionic Liquids in a Fluidised Bed Reactor

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Keywords: supported ionic liquids, biorefinery, bio-derived thiophenes, platform chemicals, 2,5-dimethylfuran

Abstract

Commodity chemicals remain dependent on fossil fuels, with more than 5 % of crude oil used for chemical production.[1] Meanwhile, climate change and fossil fuel depletion drive the development of integrated biorefineries. Cellulose, a renewable feedstock, can be converted into intermediates such as 5-HMF and 2,5-DMF.[2] However, the furan ring conversion to other heterocycles has been explored to a lesser extent, limiting the potential range of applications.

Thiophenes are valuable building blocks in pharmaceuticals, agrochemicals and conducting polymers.[3] The reaction of open-chain precursors with a sulfur source is the principal route to thiophenes whereas the heterogeneous recyclization of furans is also possible.[3,4] Nonetheless, prolonged heating in acidic media, high temperatures and catalyst deactivation remain a challenge. Ionic liquids are excellent media for biomass transformations,[2,5] providing novel options for end-to-end applications in biorefining, though their ability to catalyze thiophene synthesis has not been reported.

We investigate the immobilisation of ionic liquids onto solid porous supports for the economic synthesis of thiophenes from bio-based furans. A series of acidic ionic liquids were screened as catalysts for the synthesis of 5-HMF and 2,5-DMF thiophene analogues. Supported ionic liquids provide a solution to mass transport issues arising from the high viscosity of the acidic medium whilst achieving continuous processing. A spouted bed reactor was designed and constructed to study the effect of several reaction parameters of the bio-derived thiophene synthesis. H_2S was chosen as the reactant gas as it is readily available as an industrial by-product.

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IP21

Synthesis of 1,5-benzodiazepines and 3-amino-2-alkenones

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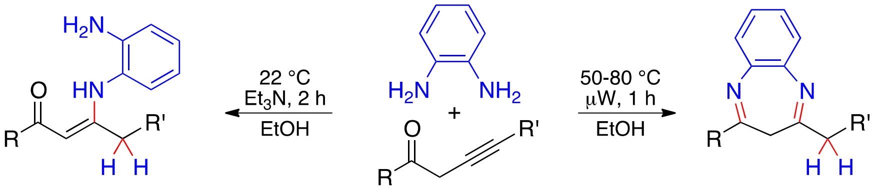
Keywords: 1,5-Benzodiazepines, 3-Amino-2-alkenones, Microwave-assisted Synthesis, Hydroamination

Abstract

Diazepines are known for their pharmaceutical applications and commercial success.[1] Derivatives of this seven-membered ring system exhibit a wide range of biological activities. Among them, the 1,5-benzodiazepines have received less attention than other homologs.[2] An example of active 1,5-benzodiazepines includes the widely prescribed antioxidant and anticonvulsant medication, Clobazam.[3] Due to their potential in pharmaceutical or materials chemistry, new synthetic methods for producing new homologs of benzodiazepines are of considerable interest.[4]

Reaction of alk-3-yn-1-ones with *o*-phenylenediamines provides an effective method with high atom economy for the synthesis of diversely substituted benzodiazepines and conjugated enaminones. This microwave-accelerated reaction proceeds in ethanol in the absence of a catalyst and leads to benzyl-substituted 1,5-benzodiazepines with good yields (70-92%). A room temperature protocol with the same set of reagents (stabilized with triethylamine) leads to enaminones (3-amino-2-alkenones, 70-99%). The tautomer formed and the regio- and stereochemistry of the process is confirmed by the X-ray crystallographic structure determination of 2-(4-methylbenzyl)-4-phenyl-3*H*-benzo[*b*][1,5]diazepine and (*Z*)-3-[(2-amino-4,5-dimethylphenyl)amino]-4-(4-*tert*-butylphenyl)-1-(4-chlorophenyl)but-2-en-1-one.[5]



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IP22

Hydrogen peroxide in cyclic peroxides synthesis

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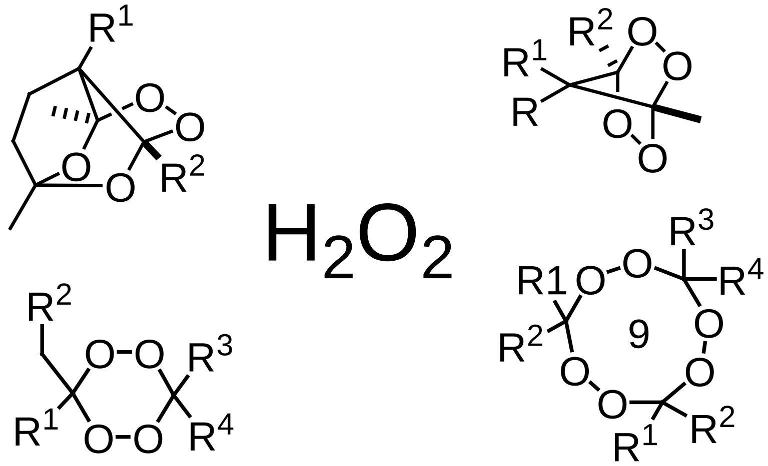
Keywords: hydrogen peroxide, cyclic peroxide, medicinal chemistry, carbonyl compounds

Abstract

In the last decades, organic peroxides have received considerable attention from chemists and drug design experts, which is associated with a need in the search for drugs for the treatment of parasitic diseases, such as malaria and helminth infections. Considerable progress has been made in the design of effective peroxide antimalarial drugs. Some synthetic peroxides exhibit activity equal to or higher than that of artemisinin. Peroxides having antitumor or growth-regulatory activity were also documented. In our work we developed new and green methods for synthesis of various types of peroxides using hydrogen peroxide and carbonyl compounds.



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IP23

Selective hydrogenations using Ni-, Ru- and NiRu-nanocatalysts in ionic liquids

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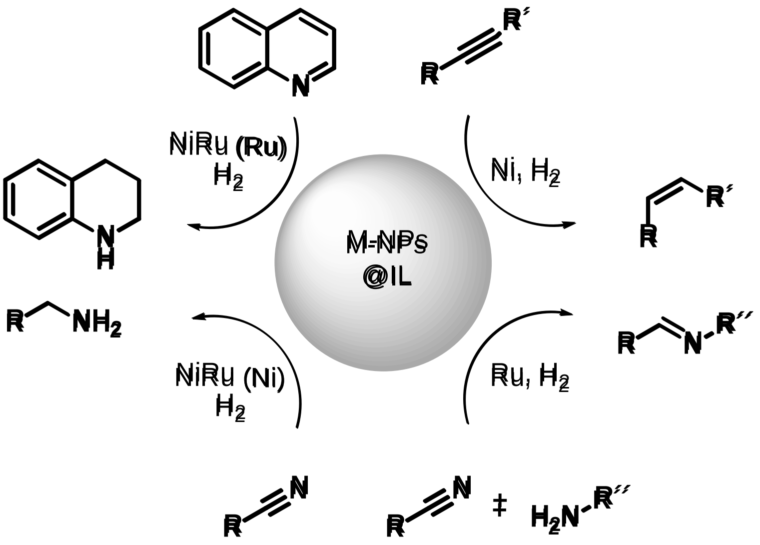
Keywords: metal nanoparticles, ionic liquids, selective hydrogenation, multiphase reactions

Abstract

Selective hydrogenation reactions of various double and triple bonds like alkynes,[1] nitriles or heteroaromatic bonds,[2] is highly desirable as the possible products represent *Z*-alkenes, secondary imines or primary amines as well as partially hydrogenated heteroarenes, like 1,2,3,4-tetrahydroquinoline from quinoline. These products are important compounds as they found appliance for the agrochemical industry or the production of fine chemicals and pharmaceuticals.



Scheme 1:Selective hydrogenation reaction of double and triple carbon and heterobonds using monometallic Ni-, Ru- and bimetallic NiRu-NPs in ILs.

In our current studies we found catalyst systems which are easily tunable on the one hand by the composition of the metal nanoparticle (NPs) and by selective poisoning of the metal surface with ionic liquids (ILs) on the other hand. For example Ni-NPs are selective catalysts for the hydrogenation of alkynes to Z-alkenes,[1] and nitriles to primary amines.[2] Contrary Ru-NPs convert nitriles under hydrogenative conditions to secondary imines.[3] Interestingly, bimetallic NiRu-NPs embedded in ILs are suitable for the partial hydrogenation of nitriles and heterocycles. The latter ones were not possible to hydrogenate with simple Ni-NPs but with Ru-NPs. Thus the bimetallic NiRu-NPs exhibit a two fold reactivity for these substrates. However, the typical selectivity towards imines for ruthenium is suppressed in presence of nickel, but the activity to hydrogenate heteroarenes belongs to ruthenium.

Moreover, we found also for the synthesis of the bimetallic NiRu-NPs that the ILs induce simultaneously the decomposition of organometallic precursors $[Ru(2\text{-methylallyl})_2(COD)]$ and $[Ni(COD)_2]$ which has been applied so far only for monometallic NPs.[4] Thus the IL plays a three-fold role: stabilizing agent, selectivity controller, and complex decomposer. These simple catalyst systems allow various selective hydrogenations depending on the used NPs, ILs and reaction conditions, exhibiting recycability with high activity and selectivity in biphasic systems.

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IP24

Recycled 3D Printed Photocatalytic Active Supports for NO_x Abatement

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Keywords: 3D photocatalytic reactors, NO_x abatement

Abstract

The removal of NO_x (NO + NO_2, pollutants very frequently found in the atmosphere) from air can be effectively achieved in reactors based on TiO_2 heterogeneous photocatalysis. A variety of reactors have been developed based on the immovilization of TiO_2 in a convenient support (glass, metal, etc.) [1,2]. Additionally, 3D-printing supported by computer-aided design (CAD) can be a very versatile fabrication system to partially or fully produce bench scale reactors. The use of plastic filaments obtained from recycling processes makes it a powerful tool to build green, low-cost and ready-to-use reactors. In this work, a polyethylene terephthalate (PET) 3D-printed support coated with TiO_2 was used to efficiently remove NO in a laboratory photocatalytic gas reactor.

A PET multi-channel square cell monolith was printed with a CHIMAK LEON 200 3D printer using a commercial recycled transparent PET filament and then coated with TiO_2 (AEROXIDE® TiO_2 P25) by wet impregnation as described in Ref. [3]. This photocatalytic support was fitted in a continuous gas flow device to set up a photocatalytic reactor and then used to evaluate the photocatalytic removal of NO. Irradiation was performed with three black-light tubular UV lamps (λ_{max} = 351 nm). A 40 ppm continuous NO current was introduced in the system by a flow controller using clean air as carrier with a total flow of 200 mL min^{-1}. O_2 and NO_x concentrations were monitored with a Horiba P250 air monitor. Each irradiation cycle lasted 10 min.

A 10% of adsorption over the active support in the dark and a 55% removal of NO (measured as NO_x) under irradiation have been observed. A removal efficiency of 25% was achieved after five cycles of irradiation, suggesting the formation of strongly attached NO_3^- on the surface of the photocatalyst.

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IP25

Green chemistry in mineral processing: chemical and physical methods to enhance the leaching of silver while decreasing/replacing the consumption of cyanide

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Keywords: Mineral Processing, Cyanide, Mining, Noble metal leaching

Abstract

To achieve a sustainable, inclusive development, countries dependent on extractive activities (e. g., mining) require the development of improved processes able to increase profits without threatening their social and environmental stability. Mineral ores which are refractory (i. e., unresponsive to conventional processing methods) often have a higher consumption of energy and chemicals, which is particularly dangerous during leaching of noble metals, where cyanide is employed to extract metals from the mineral matrix. Our research focuses on developing novel strategies for mineral processing prior to (or during) leaching, so that the cyanide consumption could be decreased while simultaneously improving the extraction of metals. These methods can be chemical (e.g., oxidation of ores, dissolution of refractory materials) or physical (e.g. ultrasound-assisted leaching), and their success depend on the nature of the ores and the modification of their reactivity. By using advanced surface characterization techniques, we are able to understand the changes operating on the surface of the minerals during leaching, so that better strategies can be tested. In addition, we follow changes in the leaching solution during reaction to determine the rate of metal extraction and of cyanide consumption, as well as the maximum efficiency of a leaching process. This work introduces several of the green chemistry principles into mineral processing strategies, promoting the possibility of developing a more sustainable mining around the world.

IP26

Efficient Removal of Lead-Contaminated Water Using Papaya Peel Activated Carbon Biosorbemt

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Keywords: Activated carbon, papaya peel, adsorbent, lead, agrowaste

Abstract

Papaya (*Carica papaya*) is a tropical fruit cultivated widely in equatorial and subequatorial countries in Central America, Africa and Asian tropical countries. In this study, the efficiency of papaya (Carica papaya) peel (PP) and its relative activated carbon (AC-PP) to adsorb Pb (II) from wastewater was studied. The chosen material was modified using various methods to improve the surface characterization and the cation exchange capacity (CEC) as adsorbents. The proposed adsorption process was investigated in batch process with respect to initial pH, concentration of adsorbent and metal ions as well as time evaluating isotherm and kinetic parameters. Utilization of papaya peel to produce carbon active can produce two-fold benefit, i.e. minimization of papaya peel waste volume and new activated carbon source for heavy metal removal from wastewater. It was observed that Pb(II) uptake is pH-dependent and optimum biosorption of Pb(II) ion using AC-PP was obtained in the basic solution with 93.22 % removal efficiency whereas the removal efficiency using pristine papaya peel powder was only 85.33 %. Overall, the efficiency of the Pb(II) uptake process using AC-PP was more than 40% higher than the values reported for most crop-based adsorbents, confirming its potential for use in wastewater treatment processes. Based on the research results, it is well proved that when the proper condition are provided, papaya peel waste can be employed as an effective and economically feasible biosorbent to remove Pb(II) from wastewater.

IP27

Development of polysaccharide-based composites for multifunctional application

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Keywords: Polysaccharides, Fuel Cell, Carbon Nanotubes, Drug Delivery

Abstract

Natural polysaccharide based materials meet unique number of properties such as biocompatibility, biodegradability, non-toxicity, stimuli-responsive characteristics which make them prospective for multifunctional applications. Growing energy consumption and depletion of nonrenewable resources turn the polymer science towards eco-friendly polysaccharide-derived materials as alternative. Polysaccharides are now being considered as prospective materials for multiple applications including energy storage, water purification, biomedical and many more other fields.

This research concerned mainly, energy storage and biomedical applications. We developed an effective polymer electrolyte membrane for fuel cells using polysaccharide of microbial origin and polyvinyl alcohol to construct the material. Obtained polymer films were characterized using AFM, DMA and DRS methods. Besides, the samples were tested in fuel cell prototype and showed results competitive to commercial polymers. The method of chemical modification of xanthan was also developed using the phosphorous anhydride (V) and ortophosphoric acid as modifiers. After modification hydrogels gel were obtained and investigated via dielectric and relaxation spectroscopy method. The hydrogels obtained were partially cross-linked and contained additional acidic groups. Results of DRS investigation of modified hydrogels demonstrated considerably high levels of ionic conductivity up to $1{,}5\times10^{-2}$ Sm/cm.

Considering biocompatibility of the polysaccharides we developed the hydrogels which can be used for transdermal drug delyvery. The cross-linked xanthan composites filled with multiwalled carbon nanotubes were synthesised. In this research, we used hydroxyl-containing MWCNT as carriers for ciprofloxacin and hydrogels of xanthan polysaccharide as polymer matrix. The cytotoxicity of xanthan hydrogel was evaluated via MTT assay using HEK cell line. The viability of the cells was higher than 80%. The adsorption capacity of MWCNT was evaluated in concentration range from 0.01 mg/mL to 0.1 mg/mL during 5 days. It was shown that equilibrium was achieved after 2 days and the adsorption capacity for the highest concentration was 0.8 mg/mg.

IP28

Mustard carbonates: the effect of the leaving group

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Keywords: Dialkyl Carbonate, Alkylation; Halogen-free, Neighboring effect, Mustard carbonate anisotropic electrophiles

Abstract

The substitution of a chlorine atom with a carbonate moiety in mustard compounds has led to a new class of molecules, namely mustard carbonates that retain the reactivity of the well-know toxic iprites, but are safe for the operator and the environment [1].

In this work, we report the further development in mustard carbonates chemistry.The influence of the leaving group on the anchimeric effect of sulfur mustard carbonates has been investigated both in autoclave and neat conditions. Results have led to enhanced selectivity of the anchimerically driven alkylation, as well as, to the improved and more accessible reaction conditions [2].

On the basis of the best results obtained the greener and efficient one-pot method of anchimericlly aided alkylation through syntesis of 2-(methylthio)ethyl ethyl carbonate ***in situ*** has been developed.

Besides, a new family of half-mustard carbonate anisotropic electrophiles has been synthesized and their reactivity with aromatic nucleophiles has been investigated.

The selectivity between two possible products deriving from the nucleophilic attack on the anysotropic mustard carbonates has been shown to depend on the intensity of the electron-withdrawig effect (combination of –I and –M effects) of substituent on an aromatic nucleophile in the para-position.

This is remarkable example of how Green Chemistry can domesticate toxic compounds and open the way for their potential application in both preparative and industrial chemistry.

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IP29

Environmental Friendly Epoxidation of Propylene (HPPO process) Catalyzed by Hollow Titanium Silicalite Zeolite at Pilot Scale

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Keywords: Environmental friendly, HPPO, Epoxidation, Propylene, Hollow titanium silicalite

Abstract

Propylene epoxidation with hydrogen peroxide (referred to as HPPO process) catalyzed by TS-1 zeolite is the most promising green technology to prepare propylene oxide (PO) in industry. It overcomes many drawbacks in the traditional PO preparation methods, such as co-oxidation and chlorohydrination routes, which usually need long reaction pathway and produce large amount of low value-added side-products/wastes. Herein, the commerical hollow titanium silicalite zeolite (HTS) has been employed as catalyst, and the responding HPPO process has been carried out by SINOPEC in a fixed-bed reactor at 1.0 kt/a scale. It is demonstrated that rising reaction temperature favors increasing the turnover frenquency (TOF) of H_2O_2 but reducing the selectivity of PO, due to the accelebrating of major and side reactions simultaneously. Moreover, increasing the CH_3OH amount and the WHSV of H_2O_2 is in favor of enhancing the TOF of H_2O_2 and the selectivity of PO, but adding capital cost and energy consumption as well. Through large amount of working, the optimized epoxidation conditions are confirmed and illustrated as follow: T is 40–50 °C; molar ratio of CH_3OH/H_2O_2 is 5–15, and the WHSV of H_2O_2 is more than 1.2 h^{-1}. After the epoxidation of propylene carried out over 6000 h, the TOF of H_2O_2 is 30.9–32.2 mmol g^{-1} h^{-1} and the PO selectivity is 96–99%, respectively, which are very close to the catalytic performance of fresh HTS zeolite(as shown in Fig.1). The PO product from this plant is at 99.97% purity, and it has already been used as an intermediate to synthesize chemicals.

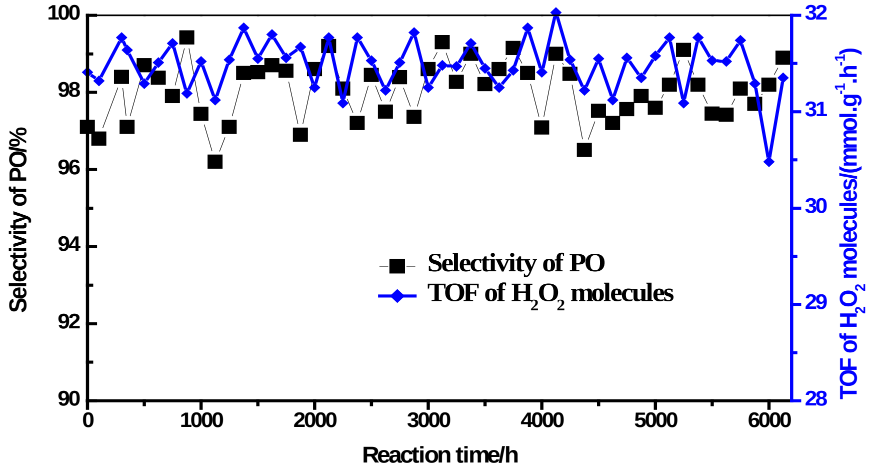

Fig.1 The TOF of H_2O_2 and the selectivity of PO in HPPO process catalyzed by HTS

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ABSTRACT POSTER PRESENTATIONS

GREEN MATERIALS

M101

Organo functionalised mesoporous magnetitemagnetic nanoparticles as an adsorbent to remove heavy metal ions

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Organo functionalised mesoporous Fe_3O_4magnetic nanoparticles on solid supports for the removal of heavy metal cations in waste water has been synthesized. It is applied as an efficient and economical adsorbent for green removal of lead (II) ions from water.

A core-shell magnetic nanostructure was prepared by performing hydrolysis in alkaline solutions using tetraethylorthosilicate (TEOS) and functionalising the silica coating with a terminal linker which was further modified with organic molecules.

The process of modifying was confirmed by High Resolution scanning electron microscopy, High Resolution Transmission Electron Microscopy (HR-TEM), Fourier transform infrared spectroscopy and X-ray diffraction. Structural studies showed that the Fe_3O_4 core were cubical in shape with a uniform mesoporous shell. The structural integrity of the materials was not comprised during the surface modification.

It is applied as an efficient and economical adsorbent for green removal of lead (II) ions from water.Magnetic nanoparticles were strongly influenced by an external magnetic field and resulted in the separation from the aqueous media within 1 minute. To its adsorption capabilities, the effect of dosage of adsorbent, contact time, initial pH and initial concentration of lead ion are scrutinized. Owing to high adsorption capacity of these catalysts, lead ion can be removed considerably, up to 80 %, and the adsorption reaches equilibrium within 10 minutes under optimized conditions. Regeneration and reusability of these catalysts studied and were able to regenerate without significant adsorption capacity loss.

M102

Synthesis of Silica Aerogel Powders using Water-Glass under Ambient Pressure Drying and itsCombination with Fiber Webs

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Keywords: Aerogel, Water-Glass, Powders, Blanket, Ambient Drying

Abstract

Silica aerogels have attracted more attention due to their unique properties and their potential applications as well as thermal and acoustic materials, adsorbents, catalyst supports, radioactive waste confinement[1]. Silica aerogels were synthesized using water glass under ambient pressure drying(APD). Silicic acidic solution was prepared by reacting between water glass with inorganic acid. Sol-gel polymerization of silicic acidic solution was preceded by the addition of alcohol solvent for gelation to form network structure.The gelation was occurred at very fast time within a few minute. The subsequent surface modification and solvent exchange simultaneously was carried out in organic reagent such as trimethylchlorosilane, reacting with surface hydroxyl group to give silylated hydrogel and also isoprophylalcohol and hexane for displacement of pore water in the wet gel during 3-5hrs. The aerogel powders can be obtained by APD for 2-3hrs the hydrophobic gel[2]. For fabrication of aerogel blanket, the hydrophobic gel produced during aerogel powders processes combined with existing fiber webs like glass fiber and polyester and ceramic fiber. The fiber webs included hydrophobic gel also was dryed under ambient pressure for 2-3hrs similar to powders processes. The aerogel blanket can be fabricated with ease using water glass under APD [3]. Physical properties of aerogels were analyzed to show BET specific surface area, pore size and pore volume, microstructure and thermal conductivity.

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M103

A rapid and Ecofriendly Reversed Phase High Temperature Liquid Chromatography Method For Simultaneous Determination of some Sulfonamides in Complex Matrices

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Keywords: HPLC, High temperature liquid chromatography, retention mechanisum, sulphonamides Green chromatography

Abstract

A simple and sensitive high-performance liquid chromatography-UV detection method was developed for the simultaneous determination of sulfonamides compounds

The method is based upon a hybrid ODS X-Bridge C18 column with two different mobile phases depending on the use of low percentage of organic modifier from acetonitrile as water rich mobile phase and pure water at high temperature (superheated water liquid chromatography).High temperature used to reduce retention in stationart phase, increase mass transfer and decrease. Different pramerters as flow rate and different percentage of acetonitrile also studied. The developed method was validated in terms of accuracy, precision, linearity, reproducibility limit of detection, limit of quantitation and solution stability. In addation, the sulphonamides removed by using CNt and graphene under optimum condation of high temperature liquid chromatography

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M104

Gutmann´s Donor Numbers Correctly Assess Solvent Effects on the Kinetics of SNAr Reaction in Ionic Liquids

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Keywords: Ionic Liquids1, Organic Chemistry2, Solvent Effects3, Gutmann Numbers4, Anion Effect5

Abstract

We report an experimental study on solvent effects on the model S_NAr reaction between 1-chloro-2,4-dinitrobenzene and morpholine in a series of pure ionic liquids (IL). A significant catalytic effect is observed with reference to the same reaction run in water, acetonitrile and other conventional solvents. The series of IL considered include the anions, NTf_2^-, DCN^-, SCN^-, $CF_3SO_3^-$, PF_6^- and FAP^- with the series of cations 1-butyl-3-methyl-imidazolium ($BMIM^+$), 1-ethyl-3-methyl-imidazolium ($EMIM^+$), 1-butyl-2,3-dimethyl-imidazolium (BM_2IM^+) and 1-butyl-1-methyl-pyrrolidinium ($BMPyr^+$). The observed solvent effects can be attributed to an “anion effect”. The anion effect appears related to the anion size (polarizability) and hydrogen bonding (HB) abilities to the substrate. These results have been confirmed by performing comparison between rate constants and Kamlet-Taft solvatochromic parameters and rate constant with Gutmann like donicity numbers (DN). The best correlation between rate constant and DN emphasizes the major role of charge transfer from the anion to the substrate, which is consistent with effective HB effects, with the anion acting as HB acceptor.

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M105

Biodegradable Composites Containing Natural Polymers of Different Origin

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Keywords: Synthetic and natural polymers, Properties, Morphology, Biodegradation

Abstract

A creation of new biodegradable materials based on synthetic and natural polymers, which can undergo decomposition and be transformed under environmental conditions into harmless for nature compounds, attracts a great attention of a large number of researchers. Such systems are of interest due to the constantly rising volumes of synthetic polymers resulting in environmental pollution and necessity of their utilization, as well as the nonrenewable consumption in long-term perspective of the petroleum world stocks, which is the main raw material for production of the synthetic polymers. Nowadays the most widespread approach to production of biodegradable materials is based on introduction into synthetic polymer the components of plant origin, which serve as nutrient medium for microorganisms initiating the polymer destruction under action of environment. For production of the biodegradable composites of particular interest among natural polymers are constantly reproducing and representing almost inexhaustible source of raw materials polysaccharides (cellulose, starch, chitin, chitosan).The large-tonnage synthetic polymerspossess high mechanical characteristics, but are stable to action of microorganisms, whereas natural polysaccharides have low mechanical parameters, but are biodegradable, therefore, the production of blends based on them is a rather simple and inexpensive method of modification of the initial polymers allowing one to combine the properties of each of the components. Such materials can be successfully applied in food industry and packaging production. Among the polymers based on natural raw materials, a special place is also occupied the polylactide (PLA) which is close by its properties to the synthetic polymers. However PLA is not so widespread due to its high cost and low biodegradability. The production of PLA blends with polysaccharides allows one to eliminate ultimatelythese disadvantages and such way to expand the possible application fields of the materials based on PLA. In the present work the compositions of low-density polyethylene with polysaccharides were obtained under the action of shear deformations that allows one to obtain more homogeneous composites in comparison with the traditional methods. With the use of numerous physicochemical methods the mechanical, thermophysical properties, morphology, water absorption, and biodegradability were studied. It was established that the properties of the composites based on natural polymers (polysaccharides and polylactide) as well as LDPE with polysaccharides depends on blend composition and polysaccharide nature.

Acknowledgments

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M106

Catalytic Transformations of Novel Ionic Polymer-Supported Palladium Metal Nanoparticles

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Keywords: Nanoparticle, Ionic polymer, Catalysis, Suzuki coupling reaction

ABSTRACT

Metal nanoparticles are increasingly used in catalysis due to their high surface area and increased density of surface active sites compared to bulk metal.[1] Ionic liquids have been shown to stabilized nanoparticles towards aggregation and also, in some cases, to enhance the catalytic activity or selectivity.[2] In this project cross-linked ionic copolymers were prepared by radical polymerisation of imidazolium-functionalised styrene monomers together with styrene carrying a neutral pyrrolidinone derivative designed to interact with metal nanoparticles.

The ionic polymer was loaded with $PdCl_4^{2-}$ by anion exchange and then hydrogenation produced a Pd (0) loaded polymer which was characterized by TEM, microanalysis, ICP-OES, XPS, XRD, SEM, and TGA-DSC.These palladium-immobilised ionic polymer-supported nanoparticles were demonstrated to be active catalysts for Suzuki cross coupling reactions.

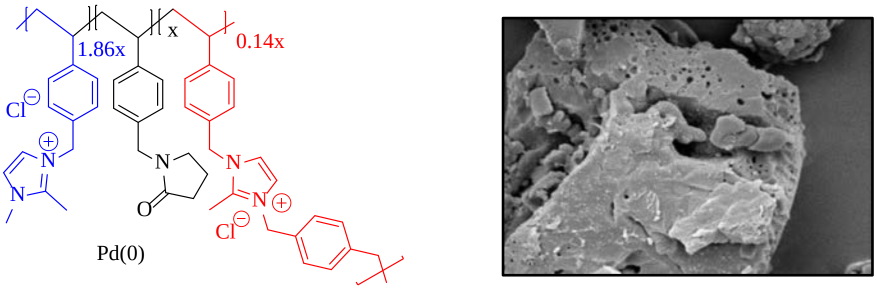
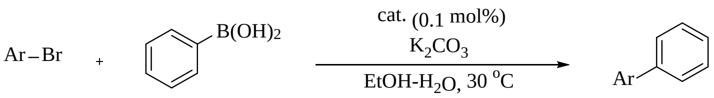


Figure1: The structure and SEM image of the palladium loaded ionic polymer.



Scheme1: The general conditions for Suzuki coupling.

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M107

Preparation of hydrophilic polymer coated magnetic silica nanoparticles with aptamer for pre-concentration of pathogen from food samples

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Keywords: Silica nano-particles, Aptamer, Pre-concentration, Detection.

Abstract

Nucleic-acid aptamers have attracted intense interest and found wide applications in detection of pathogen from various biological samples. Also, sensitivity of pathogen detection sensors is very important due to rapid growth capacity of microorganisms. They are small in size, chemically stable and cost effective [1,2]. In this study, magnetic particles were synthesized in two steps. Fe_3O_4 particles were prepared using $FeCl_3$ and $FeCl_2$ in basic solution with precipitation method. In the second step, Fe_3O_4 particles were coated using 3-(triethoxysilyl)-propylamine (APTES). Then, the APTES functionalized magnetic particles was grafted with polyethylene glycol methacrylate (PEG-MA) macromonomers by atom ransfer radical polymerization (ATRP) [3]. Subsequently, glycidyl methacrylate (GMA) was also grafted as secondary block polymer. The epoxy groups of the magnetic silica particles was used for immobilization of aptamers. The coating of the APTES and grafting with polymer onto the magnetite particles was confirmed by ATR-FTIR in the one-bounce ATR mode. A vibrating sample magnetometer was employed to measure the magnetic properties of the magnetic and silica coated magnetic particles. As expected, both samples exhibited ferromagnetic behavior, and the saturation magnetization values of magnetic and silica coated magnetic particles were 87.6 and 68.3 emu g^{-1}, respectively. In addition, the coating efficiency of the silica grafted magnetic beads was about 83%, and it was calculated by weighting the magnetic nanoparticles before and after coating with silica layers. The determined free amine group of the APTES coated magnetic silica particles was about 3.4 mmol. The mesoporous silica coated magnetic particles were used for construction of aptamer gated biosensor. The magnetic pre-concentration system can efficiently capture cells about within10 min, feeding captured bacteria to a QCM flow cell system showed specific detection of *Brucella melitensis* at 100 CFU/mL from milk. Regeneration of the QCM crystal surface with NaOH solution allowing the sensor crystal to be used several times.

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M108

Biobased *Janus* molecule for the facile preparation of water solutions of few layers graphene

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Keywords: Serinol derivative, *Janus* molecules, Few layers graphene

Abstract

Biobased Janus molecule was prepared through the Paal Knorr reaction between 2-amino-1,3-propandiol and 2,5-hexanedione: 2-(2,5-dimethyl-1H-pyrrol-1-yl)-1,3-propanediol (serinol pyrrole, SP) was obtained with water as the only byproduct, yield of 96% and atomic efficiency of 85% [1-2]. The reaction was performed in the absence of solvent and catalyst.

Such serinol derivative, SP was used for preparing stable water solutions of carbon allotropes [3]. In fact, hydroxy groups in SP are suitable for the interaction with polar surroundings and the pyrrole ring can interact with carbon allotropes containing sp^2 carbon atoms. High surface area nano-sized graphite (HSAG), endowed with high shape anisotropy and with about 35 graphene layers stacked in crystalline domains, was used as the carbon allotrope. Green methods, such as ball milling and heating, were adopted for the preparation of the adducts. The reaction with SP did not alter the order in the graphitic layers, as shown by wide angle X-ray diffraction analysis and raman spectroscopy.

Stable water solutions of HSAG/SP adducts (about 15% by mass of SP) were prepared, in concentration range from 0.1 to 10 g/L. Centrifugation at 9000 rpm allowed to isolate adducts with few stacked graphene layers, as revealed by high resolution transmission electron microscopy.

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M109

Electrochemically Grown Bismuth (III) Oxide Nanoparticles on Gold as Sensors for Quantification of Methimazole

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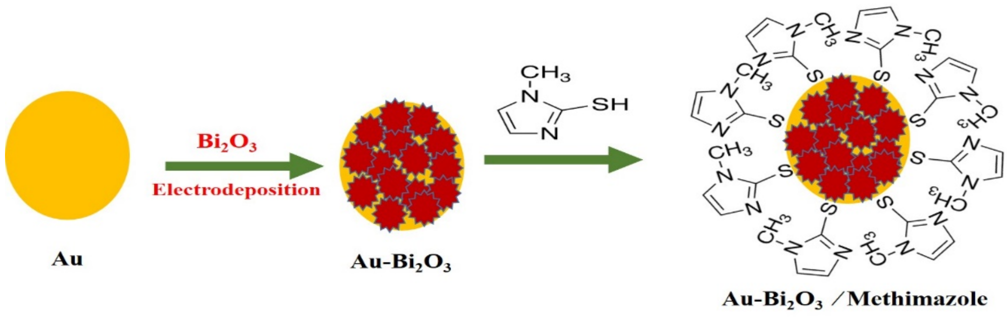
Keywords:*Bismuth (III) Oxide, Nanostructure, Methimazole, square wave voltammetry, differential pulse voltammetry, validation*

Abstract

Bismuth (III) oxide modified gold electrode was fabricated succesfully using a electrochemical method and characterized by cyclic voltametry (CV), potential-controlled electrochemical deposition, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), photolüminesans (PL) and UV visible spectroscopy techniques. The ease of fabrication, excellent electrochemical performance and high electroactive surface area are the promising features of the fabricated sensor. This modified electrode was used for the detection of methimazole in pharmaceutical formation in 1 mM $K_3[Fe(CN)_6]$containing 0.1 M KCl. The fabricated sensor can be used for sensitive and selective determination of many pharmaceuticals owing to their sensitivity, specificity, speed response and low cost of analysis.

In this study, Bi_2O_3/Au nanostructure sensor was fabricated and a validated square wave and differential pulse voltammetric procedure was developed and successfully applied to the estimation of methimazole in tablet samples. Bismuth (III) oxide is nontoxic and has excellent chemical inertness and biocompatibility. Nanosized bismuth (III) oxide shows greater advantages and novel characteristics than regular sized particles, such as the much higher specific surface and greater surface free energy, which are favorable for the biomolecules adsorption[1]. These have been succesfully used for the preparation of sensor sor biosensors, with good stability and easy to fabricate[2].



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M110

Preparation and characterization of an imprinted polymer for selective removal of Cr(VI) from aqueous medium

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Keywords: Molecular imprinting, Functional polymer, Removal, Cr(VI).

Abstract

There are many methods to remove Cr(VI) from industrial wastewater, including precipitation, membrane separation, adsorption. The adsorption process is the most popular method to remove Cr(VI) from aqueous solution due to low-cost, easy operation, and regeneration capability. Several adsorbents have been used as adsorbents for removal of Cr(VI), such as activated-carbon, chitosan, synthetic polymer, microbial biomasses. Cr(VI) species are highly soluble oxides (i.e., chromate (CrO_4^{2-}), hydrochromate ($HCrO_4^{-}$) and dichromate ($Cr_2O_7^{2-}$) anions) [2]. Cr(VI) anions species are strong oxidants, which act as carcinogens, mutagens and teratogens in biological systems [2]. The specificity of adsorbent can be improved by molecular imprinting technique (MIP). Resent years, molecular recognition-based separation techniques have received much attention in environmental technology for removal of toxic heavy metal ions, because MIP adsorbents have high selectivity to their target metal ions. Ion-imprinted polymers are similar to MIP, but they recognize metal ions after imprinting and retain all virtues of MIP [1-3].

The Cr(VI)-MIP and non-imprinted (NIP) microbeads were synthesized in the presence of the template molecule, Cr(VI), which results in the formation of recognition cavities complementary to the template molecule. An imidazole group containing monomer, N-methacryloyl-3-aminopropyl)imidazole (MAAPI), was used as the functional monomer. Initially, Cr(VI)-MAAPI complex was prepared and polymerized with ethyleneglycoldimethacrylate (EGDMA) in the presence of an initiator "azo-iso-butyronitrile" via suspension polymerization. The MIP and NIP microbeads were characterized by Zeta-sizer, FTIR, SEM and BET method. The effect of initial concentration of Cr(VI), the adsorption time, adsorbent dosage, medium pH, and selectivity in binary solution were studied using MIP and NIP imprinting microbeads. The maximum sorption of Cr(VI) ions onto MIP and NIP beads was about 87.5 and 41.6 mg/g, respectively. Adsorption studies of U(VI), Cr(III), Cu(II), and Cd(II) ions were investigated in binary system using MIP microbeads. The satisfactory results demonstrated that the obtained Cr(VI)-MIP microbeads showed an appreciable binding specificity toward Cr(VI) than those of the other tested metal ions. Moreover, the reusability of Cr(VI)-MIP microbeads was tested for several times and no significant loss in adsorption capacity was observed.

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M111

Ball milling as an effective method to prepare magnetically recoverable heterometallic catalysts for 1-phenylethanol oxidation

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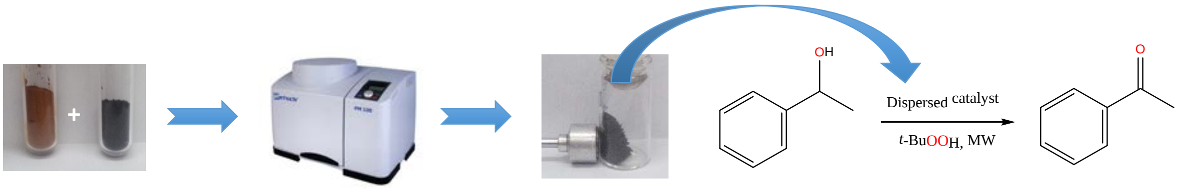
Keywords: Mechanochemistry, Composites, Heterometallic catalysts, Alcohol oxidation

Abstract

Heterometallic double Fe_2O_3-$CoCl_2$, $CoCl_2$-V_2O_5, MoO_3-V_2O_5, and triple CuO-Fe_2O_3-$CoCl_2$ 3d metal dispersed systems were prepared by a simple and solvent-free mechanochemical method, *i.e.*, ball-milling and characterized by scanning electron microscopy (SEM), field emission gun scanning electron microscopy (FEGSEM), energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM). They catalyse the microwave-assisted solvent-free oxidation of 1-phenylethanol to acetophenone with *tert*-butyl hydroperoxide (*t*-BuOOH) as oxidant, used as a model reaction. In most of the heterometallic systems a significant improvement in the catalytic activity was observed in comparison to homometallic ones. For the tested catalytic systems and experimental conditions, the CuO-Fe_2O_3-$CoCl_2$ and Fe_2O_3-$CoCl_2$ systems exhibit the highest activity with maximum 78% yield and TON 39 after 1 h. The possibility of magnetic recovery of the catalysts was demonstrated for the Fe_2O_3-$CoCl_2$ (3:1) system.



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M112

Conversion of carbon dioxide to methanol and others environmentally friendly compounds: A comparative electrocatalytic activityof two different modified electrodes.

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Keywords: Carbon dioxide; Modified electrodes; Tetraruthenated porphyrins; Electrochemical impedance.

Abstract

Electrochemical reduction of carbon dioxide (CO_2) to useful chemical materials is of great significance to the virtuous cycle of CO_2. However, some problems such as high overpotential, high applied voltage and high energy consumption exist in the course of the conventional electrochemical reduction process [1]. The electrochemical reduction of CO_2 is a promising process for this aim and depending on the number of electrons transferred; it is possible to obtain several reduction products, being the most interesting involve the transfer of more than two electrons the most interesting those that involve the transfer of more than two electrons (methane, methanol and ethanol) [2]. To obtain these products, electrocatalysts based on transition metals complexes containing multiple metal centers have been utilized to achieve multielectron transfers [3,4].

This work describes the electrochemical reduction of carbon dioxide in neutral aqueous solution mediated by tetraruthenated metalloporphyrins (Co(II), Ni(II) and Zn(II)) in Nafion and PVC as a support. The comparative aspects of the two polymeric matrices are expressed in terms of the electrocatalytic character of these modified electrodes such as overpotential and turn over numbers.These modified electrodes are able to reduce at -600mV approximately showing enhanced reduction current and a decrease in the required overpotential compared to bare glassy carbon electrode. Controlled potential electrolysis at experiments they were carried out at -1000mV, in order to extreme conditions. Verifies the production of formic acid, formaldehyde and methanol at potentials where reduction of solvent is plausible demonstrating some selectivity toward the carbon dioxide ion. Measurements of electrochemical impedance show the presence of one active site for GC/Nf/CoTRP (CoTRP) and three for GC/PVC/CoTRP (GC;PVC; CoTRP) those who acted individually. This information corroborates the high values of TOF obtained for GC/PVC/CoTRP.

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M113

Molecular and Macroscopic Bistability in Valence Tautomeric Complexes with Structurally Flexible Chains

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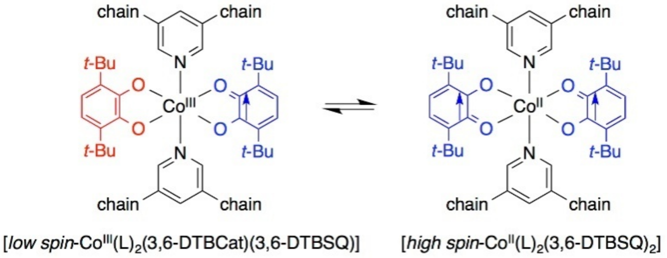
Keywords: Valence tautomerism, Bistable molecule, Stimuli-responsiveness, Cobalt complex, Dioxolene

Abstract

Development of molecular-based systems that sensitively respond to external stimulus such as heat, light, and magnetic and electric fields has attracted considerable attention.[1] They have great scientific and technological potential as molecule-based devices, i.e., low-energy driven switches, memories, information storages, and sensors in environment. Valence tautomerism (VT) is the property to show reversible exchange between two or more tautomers differing in their charge distribution. In particular, a family of cobalt-dioxolene complexes of [*low spin*-$Co^{III}(L)_2$(DTBSQ)(DTBCat)] undergoes reversible VT shifts to [*high spin*-$Co^{II}(L)_2(DTBSQ)_2$]. $DTBSQ^{\cdot-}$ and $DTBCat^{2-}$ refer to monoanionic di-*tert*-butylsemiquinonato and dianionic di-*tert*-butylcatecholato forms, respectively, and L is a nitrogen-containing auxiliary ligand (Scheme 1). The most prominent feature of VT interconversion is that the two tautomers are related by an intramolecular single-electron transfer between DTBCat and the Co^{III} ion as well as a spin change from a *low-spin* Co^{III} form ($S = 1/2$) to a *high-spin* Co^{II} form ($S = 3/2$ with two $S = 1/2$).

We reported that VT complex functionalized with long alkyl chains and VT behavior synchronized with a macroscopic phase transition.[2] These studies revealed that introduction of alkyl chains lead to flexible assembled structure and the synchronic bistability of molecular VT interconversion and macroscopic phase transition. These data promise us the rationally designable bistability by combining VT core with long chains. This presentation reports new VT complexes with structurally flexible chains and its molecular and macroscopic bistability.

Scheme 1. Valence tautomeric bistability



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M114

Selective oxofunctionalization of cyclohexane bysolar simulatedphotocatalysts

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Keywords: Solar photocatalysis, Oxofunctionalization, Bismuth oxyhalides, Doped titanium dioxide

Abstract

The photocatalysis by semiconductors has been mainly applied for total removal of recalcitrant pollutants. However, these unselective systems could become selectives choosing the appropriate reaction conditions or catalysts.

This work studied the selective oxofunctionalization of cyclohexane by solar simulated photocatalysis at room conditions. For this purpose, five titanium dioxide–based photocatalysts (Fe-doped and N-doped) and three bismuth oxyhalides photocatalysts (BiOCl, BiOBr and BiOI) were synthesized and characterized (XRD, Band gap, SEM and BET surface area).

The titanium dioxide–based photocatalysts showed the highest cyclohexanone/cyclohexanol (Chone/CHol) ratio (4.49 - 87.50). Both, BiOCl and BiOBr showed similar Chone/CHol ratios (1.92 and 1.27 respectively). Even more, the BiOI showed the lowest ratio for Chone/CHol (0.23).

The Chone/CHol ratios and yields dependence on the physical properties of the photocatalysts were studied. In this analysis only a relationship between bandgap and cyclohexanol yield was observed. In this way, titanium dioxide–based photocatalysts and BiOXs exhibits different behavior to conversion yield of cyclohexane to cyclohexanol. TiO_2-based photocatalyst shows an exponential dependency (r = 0.89) for the cyclohexanol yield when the bandgap increase reaching a maximum value = 5.22 ± 1.83 μmol m^{-2} g. On the other hand for BiOXs photocatalysts, the cyclohexanol yield depends linearly with bandgap (r = -0.94). BiOI reached the maximum cyclohexanol yield (16.5 ± 1.3 μmol m^{-2} g). In addition, was determined that the production of cyclohexanone by BiOCl and TiO_2 was not correlated with the oxidation of cyclohexanol.

Acknowlwdgement

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M115

Determination of radical intermediaries ofselective oxofunctionalization of cyclohexane by *in situ* EPR experiments

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Keywords:EPR, Oxofunctionalization, dioxide–based photocatalysts, oxyhalides photocatalysts.

Abstract

The selective oxofunctionalization of cyclohexane by solar simulated photocatalysis have been studied. For this purpose, five titanium dioxide–based photocatalysts (Fe-doped TiO2, N-doped mesoporous TiO2) and three bismuth oxyhalides photocatalysts (BiOCl, BiOBr and BiOI) were employed. Significant differences were observed for the selectivity of ciclohexanol and ciclohexanone production by different photocatalysts.

The high selectivity for cyclohexanol production by BiOI photocatalyst (cyclohexanol / cyclohexanone = 4.35) is highlighted. The selectivity was related to band gap of the photocatalyst.

With the aim to investigate the formation of radical species from the oxidation of cyclohexane in early stages of the reaction, in situ EPR measurements were performed. The spin trapping technique was performed, using, N-tert-Butyl-α-phenylnitrone (PBN) as spin trap. The reaction was carried out in an quarz tube inside the EPR cavity irradiated by a metal halide lamp.

In all the systems (except using BiOI as photocatalyst) only one triplet signal (aN= 13.6 G) was observed. This was assigned as cyclohexyloxy (C6H11O•) or cyclohexylperoxy C6H11OO•. For cyclohexane oxidation by BiOI, as photocatalyst, two signals were observed. Two partially overlapped triplets with hyperfine coupling constants of 13.6 G and 8.1 G. The first signal was assigned to C6H11O• (or C6H11OO•). The second signal was assigned to PhCON(O•). This is an oxidation product from PBN. Its formation has been associated as evidence of •OH radical. The production of •OH radical by BiOI photocatalyst could be related with the higher yield and selectivity for cyclohexanol production. The bandgap of the photocatalysts could be related to lamp spectrum, because the bandgap of BiOI (at 678nm) is in the edge of the emission region of the metal halide lamp (340 nm to 670nm). The low radition intensity could be related to the •OH radical production. In order to determine this effect, a new experiment was performed using an infrared lamp ranging from 550 nm to 780 nm, with a maximum emission at 625 nm. In this condition the PhCON(O•) adduct was observed. Accordingly, the •OH radical do not depend of the intensity of the radiation but rather of the properties of the BiOI photocatalyst.

Acknowlwdgement

The financial support for this work was granted by CONICYT National Doctoral Fellowship 21130450, FONDECYT 1160100 and FONDAP Solar Energy Research Center, SERC – Chile 15110019.

M116

Self healing capability of advanced lime mortars

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Keywords:engineered self-healing, lime mortars, sustainability

Abstract

The use of smart materials, like advanced lime mortars with self-healing capability in structural restoration of historical masonry buildings, would not only give relevant answers to demands of conservation, but would improve durability and chemical-physical-mechanical compatibility. Among the materials used in construction, self-healing ones have been widely studied, such as cement binders polymers, asphalts; but the issue of implementation and engineering of this capacity in lime mortars has been not yet but seldom investigated [1]. This work proposes a system for the evaluation of self-healing capability with reference to traditional and advanced lime mortars. The idea underlying in this work is hence twofold: first a mortar is created with a part of the lime protected by an impermeable coating surface, able to make it inert during the phases of setting and hardening; then, when the material is subjected to an external stress, the protective layer of the treated lime granules should undergo a rupture which will trigger another step of setting and hardening in the material made dormant by the same treatment. Several types of granules "protected" with different truly innovative synthetic "coatings" have been investigated. The study deals with the verification of the behavior of the capsules in relation to their resistance to the mixing process, as well as their efficacy in breaking upon damage and activate the self-healing process. For the sake of comparison the performance of a mortar containing 3% of a commercially available crystalline admixture, will also be analyzed [2]. Strength development was continuously monitored: i) After a proper curing time: damage induced by loading the specimen to a compressive strength prescribed fraction; ii)After the pre-cracking stage: specimens placed in water for different durations; iii) At the end of ii) stage the post-conditioning phase starts in which specimens, after a microscopy observation of the healed cracks, were re-tested. UPV test, optical microscopy observation and SEM analyses complemented the investigations. The effectiveness of repairs is evaluated through the recovery of mechanical strength, comparing the compressive strength values of the samples made of lime mortar and that of specimens with the healing triggering additions. Results clearly show that the compressive instantaneous average compressive strength of the mixes with self-healing agents capsules is only quite lower than the resistance of the reference mortar, but once the coating is broken, paves the way to the development of the self-healing capacity.

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M117

Structural peculiarities and catalytic properties of perovskite $(Gd,Sr)_{n+1}Fe_nO_{3n+1}$ for the olefins production

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Keywords:olefin, selectivity, hydrocarbons, perovskites

Abstract

Studied in this work the catalytic properties of complex oxides of nanostructured perovskite gadolinium ferrite and strontium $GdFeO_3$, $SrFeO_3$ + x, $GdSrFeO_4$, $Gd_{2-x}Sr_1$ + xFe_2O_7 against selectivity in the hydrogenation of olefins of carbon monoxide. Nanodispersed layered perovskite ferrites synthesized by the ceramic and sol-gel technology. Methods: radiographic, microscopic, spectroscopic photonic - established the presence of a single phase perovskite-like structure for all the samples; ferrites obtained by ceramic technology are submicrocrystalline state and sol-gel method - in nanocrystalline and have a porous structure.

By Mossbauer spectroscopy revealed that in complex ferrites obtained by ceramic technology, the iron atom is in a magnetically ordered state Fe^{+3}. Mossbauer spectras of solid solutions synthesized by the sol-gel technology, has shown that in samples $GdFeO_3$ iron is in the Fe^{+3} in two fields of different symmetries and complex oxides $GdSrFeO_4$ and $Gd_2SrFe_2O_7$ - along with Fe^{+3} in the three fields of various symmetries. There is Fe^{+4} with oxygen vacancies.

The catalytic activity in the hydrogenation of carbon monoxide was studied in flowing catalyst installation at atmospheric pressure and the component ratio [CO: H2] = 1: 1, 1: 2, 1: 4, followed by chromatography (Crystal 5000) analysis of the reactants and products.

The experiments and analysis have shown that the activity of gadolinium ferrite and strontium is comparable with the previously studied ferromanganese nanosystems. The main product is a C_1-C_4 hydrocarbons, olefin selectivity (C_2H_4 and C_3H_6) at a temperature of 673 K was 30-35%. The specific catalytic activity (Wi – velocity of reception the i-th product of reactions to 1gr. on catalyst mol / h * ga.f.) And selectivity in the hydrogenation of CO increased in number $SrFeO_{(3-x)}$, $GdSrFeO_4$, $Gd_{2-x}Sr_1$ + xFe_2O_7, $GdFeO_3$, there was a correlation between the number of perovskite layers n = 1,2,3, ..., ∞ and Wi. The state of heterovalent iron with oxygen vacancies, probably favorable for the formation on the surface of active atomic hydrogen surface redox processes and activation of CO, which leads to the formation of C * and CH_x radicals.

This work was supported by the Russian Foundation for Basic Research (№ 14-03-00940 A).

M118

Constructioning and introduction of green catalytic processes at the production enterprises as the mechanism of ensuring chemical safety at the international level

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Keywords:olefin, selectivity, environmental , green policy

Abstract

Improving the quality of life, the protection of public health, the environment is the main objective of development of industrial production, including chemical and petrochemical, and introduction of innovative products. Also, necessary to consider that any industrial production has the potential to technogenic danger-mechanical, radiation, chemical or biological [1]. The special place among the technological dangers is chemical. The problem of chemical safety is to protect people and the environment, where the risk of negative effects of dangerous chemical agents is reduced to an acceptable level, in modern conditions is becoming increasingly important and should be a priority for environmental law. Legislative consolidation of these measures requires the improvement of the normative legal regulation and public administration, first of all through the preparation and adoption of the basic Federal Law "On Chemical Safety" in Russia. However, regional problems can not be solved excluding the causes and consequences of a world scale. A large number of environmental conventions are a diverse mosaic of international agreements covering certain geographic regions and their limits a range of activities or substances. But such approach complicates environmental protection. To eliminate defects of international legal regulation to allow the new framework convention which would be reflected totality innovative mechanisms for the prevention of environmental pollution.Currently, the framework for the creation of mechanisms of protection against chemical pollution is the green chemistry. Following one of its prinitsip it is possible to receive unsaturated hydrocarbons (C_2H_4, C_3H_6), using the technological emissions of the production enterprises containing the carbon oxides.

As a result of the work was created catalytic nanosystems based on nanopowders iron and manganese matrixed in oxides substrate (Fe/Al_2O_3, Fe/SiO_2, Fe/ZrO_2, $MnOx/SiO_2$, $Fe\text{-}MnOx/ZrO_2$, $Fe\text{-}MnOx/Al_2O_3$, $Fe/ZrO_2\text{-}SiO_2\text{-}MnOx/SiO_2$) and iron oxides of complex of gadolinium ($GdFeO_3$, $SrFeO_3+x$, $GdSrFeO_4$, $Gd_{2-x}Sr_1+xFe_2O_7$) for utilization of greenhouse gases with hydrogen at atmospheric pressure. The selectivity of the process for unsaturated olefins amounted to 42%. In articles [2],[3], the reaction mechanisms described in detail extending with the catalysts described above. The successful results show that this utilization of greenhouse gases industrial production technology must be fixed in law and implemented in the industrial enterprises, along with the same rate as the required payment of environmental tax.

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M119

Nonhazardous Solvent Systems for Processing Perovskite Photovoltaics

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Keywords: Perovskites, Photovoltaics, Nonhazardous Solvents, Ink Engineering, Solution Processing

Abstract

Hybrid organometallic halide perovskites have rapidly become a front runner in the area of cost-effective semiconducting material for thin film photovoltaics, attaining certified 22.1% in power conversion efficiency for single junction solar cells [1,2]. Methylammonium lead halide perovskites, i.e., $CH_3NH_3PbI_3$, are solution processable, have a controllable direct band gap, [3] are tolerant to defects, [4,5] and combine a sharp absorption edge and high diffusion length with low absorption depth [6]. This combination of characteristics makes this material especially attractive for solar energy solutions. Replacing toxic solvents with nonhazardous solvents is now one of the key challenges for industrial scale commercialization of thin film perovskite photovoltaics. Here, nonhazardous solvent/alcohol/acid systems are presented for the single-step deposition of pinhole-free perovskite layers with combined lead halide precursors of $Pb(CH_3CO_2)_2{\cdot}3H_2O$, $PbCl_2$, and CH_3NH_3I. Comparable performance to standard hazardous inks is achieved: devices with 15.1% power conversion efficiency are demonstrated and maintain 13.5% tracked for 5 min at maximum power point. Blade coated 4 cm^2 solar modules fabricated with highest performing device ink attain 11.9% in power conversion efficiency.

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M120

Highly efficient and selective synthesis of quinolines catalyzed by Copper doped carbon aerogels

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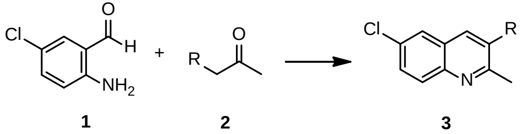
Keywords: Quinolines, Friedländer Condensation, Nanostructures Carbon Aerogels

Abstract

The development of new catalytic technologies based on the use of green porous catalytic systems still constitutes a challenge with industrial repercussion; among them highlight the carbons, low cost materials acting as catalysts or catalytic supports meeting the requirements for green and sustainable chemical technologies. In this context, nanostructured carbon aerogels are one of the most promising new carbon forms due to the versatility of their surface properties. Carbon aerogels offer the advantage of controllable porosity with high catalysis capacities [1]. These materials are traditionally prepared from the carbonization of organic aerogels commonly prepared by polymerization of resorcinol (R) with formaldehyde (F) in aqueous (W) solutions. The characteristics of the gels depend on the different variables such as R/F, R/W, and R/C reactant ratios and the solution pH.

In other way, Friedländer condensation is considered as an economic atom reaction which proceeds through cascade reactions between 2-aminoaryl carbonyl structures with other carbonyl compounds exhibiting enolizable hydrogens. It is the simplest synthetic approach for the preparation of substituted quinolines (Scheme 1) [2]. These nitrogen heterocycles are an important class of compounds present in many natural products with wide application in pharmacy industry.



Scheme 1. Synthesis of quinolines **3** from 2-aminoaryl aldehyde **1** and carbonyl compound **2**.

Our interest is focused on the development of new carbon aerogels doped with Cu(0) nanoparticles able to promote the Friedländer condensation. We communicate for first time the synthesis of quinolines **3**, from 2-amino-5-chlorobenzaldehyde **1** and substituted carbonyl compounds **2**, catalyzed by carbon aerogels, under solvent-free and mild conditions. Remarkably, in all the investigated cases, the corresponding quinolines were obtained with total selectivity and in high yields. The explored carbon aerogels were found to be environmental-friendly alternative and efficient catalysts for Friedländer reaction.

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M121

The use of selected agro-based biomass waste for remediation of wastewaters

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Keywords: Biomass materials, Adsorption, Wastewaters, Heavy metals, Dyes

Abstract

Various wastewater treatment methods have been reported and many of them pose serious technological and technical problems. Most of the methods have various demerits such as incomplete pollutant removal, high capital investments and operation costs, high energy consumption and low selectivity. Adsorption is a recent technology that is gaining popularity as it is perceived to be relatively rapid, reversible, economical and environmentally friendly. The technology utilizes naturally occurring waste materials (biomaterials and agricultural by-products) for the removal pollutants from wastewaters [1]. This work explores the potential applicability of raw and modified biomaterials such as marula seed husk biomass, *Moringa oleifera, Opuntia ficus indica* and agricultural by-products such as *Zea Mays* [2*]* and *Vigna unguiculata* [3] biomass for the adsorption of selected heavy metals (Pb(II), Cd(II) and Ni(II)) and dyes (methylene blue and methyl red). The biomass materials were applied either as raw or as magnetite and biopolymer derivatives [1,4,5]. The results revealed interesting transformations of the biomass materials as characterized by FTIR, XRD and SEM-EDS techniques. The effectiveness of the biomass materials as adsorbent materials was evaluated based on the maximum adsorption capacities following adsorption isotherm modelling. The results from the studies show that biomass materials may be used as a low-cost, eco-friendly and effective adsorbents to remediate environmental wastewaters.

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M122
Fabrication of Biomass ResinUsingChicken Feathers

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Keywords: Chicken feather powder,Biomass resin, Hot press,HPLC analysis, Cystine quantification

Abstract

We have found that fibroin resins can easily be obtained through silk powder resinification prepared from mechanically crushed silk fiber using a hot press. By the same method, we have also fabricated keratin resins using powders obtained from wools comprising keratin proteins. These biomass resins outperform polycarbonate (PC) and denaturated polyphenylene ether in terms of glass transition temperature, three-point bending strength, Young's modulus, and Vickers hardness. In particular, the thermal conductivity of the fibroin resin was remarkable compared to that of other commodity resins that show values as high as that of high-density polyethylene resins. Moreover, the thermal expansion coefficient of the keratin resin was considerably small compared with those of metals such as copper and aluminum.Notably,both resins can be recycled after being mechanically crushed.

In this study, we resinified the powder of chicken feathers that had been crushed by a ball mill in the same way as the wool powder without using any cross-linking agents or plasticizing agents. So far, the feather powder has been resinified using glutaraldehyde as a cross-linking agent. It was reported that by heating the powder under a pressure of 9.3 MPa until it reached 95 °C, fibers with a bending strength of 52 MPa and a Young's modulus of 3.8 GPa were obtained [1]. Additionally, when a plasticizing agent such as glycerin was added to the crushed feather powder in aluminum foil, keratin films were fabricated by heating to only 160–180 °C under pressure [2].

We utilized the powder of chicken feathers crushed using a ball mill and collected only that with fiber lengths in the range 106–250 μm by sieving. Thereafter, this powder was pressurized in a hot press at 31.2 MPa at a given temperature. We then dried the samples under a vacuum for three days at 100 °C. Uniform resins were obtained when the temperature exceeded 190 °C. However, the glass transition temperature was 176.8 °C, the thermal expansion coefficient was 39×10^{-6} °C^{-1}, three-point bending strength was 66 MPa, Young's modulus was 3.3 GPa, and Vickers hardness was Hv27. Compared with wool resin, the glass transition temperature was lower, thermal expansion coefficient was larger, and the three-point bending strength, Young's modulus, and Vickers hardness were lower. However, compared with PC, all properties except for the three-point bending strength were similar.

We performed HPLC analysis of hydrolyzed solutions prepared by treating the chicken feather powder and resin with methanesulfonic acid. The wool resin contained a high quantity of hydrophilic amino acid with a water contact angle of 66°, whereas the chicken feather resin contained a high quantity of hydrophobic amino acid with a water contact angle of 81°. According to the HPLC analysis, cysteine (1/2 cystine) present in the wool powder was 1.5% (8.3%) and that in the chicken feather powder was 1.6% (4.7%). In contrast, cysteine (1/2 cystine) present in the wool resin was 2.0% (7.0%) and that in the chicken feather resin was 2.8% (2.1%). This means that in both cases, the cysteine content increased as the powder resinified and the 1/2 cystine content decreased. In addition, the amount of 1/2 cystine content present in the resin was higher for the case of the chicken feather. Evidently, the mechanical characteristics of resins depend on the amount of cystine they contain.

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M123

Citrullus lanatus Rind: aPotent and Low-cost Biosorbent forCd(II) Sequestration from Aqueous Solution

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Keywords: Biosorption, Cadmium, Heavy metals, Wastewater treatment, Watermelon rind

Abstract

To investigate the performance of *Citrullus lanatus*(watermelon) rind as a biosorbent for Cd(II) removal from aqueous solution, batch studies were performed under differentpH, biomassdosage, initial Cd(II) concentration, and salinity. Various desorbing agents (i.e. HCl, HNO_3 and citric acid)were applied to desorb Cd(II) from the surface of *C. lanatus* rind. Equilibrium and kinetic studies were also carried out to characterize the biosorption process.Due to the bias of linear regression, the equilibrium data were non-linearly simulated by six isotherm models, namely the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich (D-R), Redlich-Peterson (R-P)and Sips models. It was found that the Cd(II) uptake was highly dependent on pH, and positively correlated to the initial concentration, but negatively to salinity, with theexperimental maximum uptake(q_{max}) of 104.1mg-Cd(II)/g-biomass at pH 7.0. The desorption results revealed 0.1 M HNO_3 as the best desorbing agent, withthe elution of 93% of the laden Cd(II) from *C. lanatus* rind in 3 h.The Sips model provided the best simulation to the equilibrium data with a predicted q_{max} of 100.3 mg-Cd(II)/g-biomass, implying a heterogeneous adsorption surface upon *C. lanatus* rind.The kinetic study showed an extremely rapid Cd(II) uptake with 92.1%of Cd(II) adsorbed within 5 min at 298K. Characterization of *C. lanatus* rind by theFourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS), before and after Cd(II) loading, indicated the involvement of hydroxylic, carboxylic, amino and ether groups in the Cd(II) biosorption. The binding energy shifts in the XPS spectra suggested the potential mechanisms of ion exchange and complexation. Accordingly, *C. lanatus* rind is a potent biosorbent for Cd(II) with a high adsorption capacity and a remarkably rapid uptake, suggesting its great potential in practical application.

Acknowledgement

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M124
Fabrication of High Strength Biomass Resins Using Vietnamese Silk

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Keywords: Vietnamese Silk Waste, Fibroin Protein, Silk Powder, Biomass Resin, Three-Point Bending Test

Abstract

Though China is supplying a much bigger quantity of raw silk, Vietnam is the world's sixth producer of raw silk after India, Uzbekistan, Thailand and Brazil.

An author has found that fibroin resins can be easily obtained through resinification of silk powder consisting of fibroin proteins alone by heating and putting pressure using a hot press.The fibroin resins had a glass transition temperature of 180 ℃, a three-point bending strength (Young's modulus) of more than 100 MPa (4.5 GPa), and a heat conductivity of 0.44 W/(m.°C).

This study aims to fabricate fibroin resins using the silk powder of yellow silk thread made from Vietnamese domesticated silkworms and that of Eri silk thread made from Eri silk worms, both of which were obtained not by dissolving but by crushing.

In order to get the raw material, we crushed the thread of yellow silk, Eri silk and Chinese white silk (which was used for a comparison) using a planetary ball mill (an alumina cup: 500ml, an alumina ball : φ20 mm, φ15 mm, 3.2kg) and obtained silk powders with a fiber length of －50 μmr. Next, we filled stainless-steel jigs of φ20 mm with these powders in order to fabricate silk resins by a hot press.The condition of resinification is as follows: we applied heat to the materials with a pressure of 31.2 MPa until the temperature reached a fixed level and then cooled them. Evaluation of resin properties was carried out after drying was conducted for three days at 100°C ina vacuum. The density of these materials were 1.35 g/cm^3 for the White's, Yellow's and 1.42 g/cm^3 for Eri silk.

The temperature which evenly resinified the whole specimen was 150 °C in all cases. Furthermore, no resins showed any temperature-dependent properties in terms of three-point bending strength from this range of temperature until 180 °C. However, there was a dependent property in terms of drying hours. The longer the drying time became, the bigger the three-point bending strength. In addition, three-point bending strength increased in the following order : Eri silk＜yellow silk＜white silk. For example, when the temperature of resinification was 180°C and the drying time was seven days, three-point bending strength was 127 MPa for white silk, 112 MPa for yellow silk and 98 MPa for Eri silk. Three-point bending strength of each fiber was much bigger compared to polycarbonates. On the other hand, Young's modulus and micro-Vickers hardness increased with higher resinification temperatures and longer drying time. Young's modulus and micro-Vickers hardness became bigger in the following order : Eri silk＜white silk ≦yellow silk. For example, when the resinification temperature was 180 °C and the drying time was seven days, Young's modulus and micro-Vickers hardness of yellow silk and white silk were two times bigger compared to those of polycarbonates. Regarding to TMA result, the glass-transition temperature were higher in the following order: yellow silk ＜white silk＜Eri silk. In particularly, for the highest resinification temperature and longest drying day, the glass-transition temperature were 188.5^{o}C, 191.8^{o}C and 206.4^{o}C for yellow silk, white silk and Eri silk, respectively.

M125

Facile chemical conversion of cellulose into thermoplastic polymers using organocatalytic function of ionic liquids

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Keywords: Cellulose, Ionic liquids, Thermoplastic polymers

Abstract

Cellulose has attracted attention as a replacement for the raw material of the existing plastics because it is a renewable resource and the largest ever amount of plant resources. If the cellulose of plant origin can be applied as a plastic material, the sustainable development can be expected. However, cellulose is hardly dissolved in general organic solvents due to the strong inter- and intramolecular hydrogen-bonding. Recently, it was founded that some of the ionic liquid could dissolve the cellulose in the mild conditions and ionic liquid could reusable green solvent. Takahashi and co-workers also reported that the ionic liquid, such as 1-ethyl-3-methylimidazolium acetate (EmimOAc), could promote the transesterification reaction of cellulose to give the cellulose acetate with the quantitative yields. In this study, we focused on the such modification reaction for the synthesis of the degree of substitution (DS)-controlled cellulose acetate butyrate (CAB) as the biorenewable thermoplastic. The thermal properties of the CAB were measured by thermogravimetric analysis/differential thermal analysis (TG/DTA) and differential scanning calorimetry (DSC).

CAB was synthesized from cellulose using isopropenyl acetate, vinyl butyrate, and EmimOAc at 80°C in the argon atmosphere. The structure of the obtained product was analyzed by ^{1}H NMR and ^{13}C NMR measurement. From the ^{1}H NMR spectrum, the characteristic signals due to the butyryl groups were observed at the region of 0.75 to 1.25 ppm, the acetyl groups at 2.0 ppm, and the proton of the cellulose backbone at region of 3.5 to 5.5 ppm. Similarly, in the ^{13}C NMR spectrum of the product, the characteristic signals due to the carbonyl carbon of acetyl groups were observed ranging from 169 to 171 ppm and the carbonyl carbon of the butyryl groups ranging from 172 to 173 ppm. These results indicate that the obtained products were CAB with the various DS of the acetyl and butyryl groups. From the evaluation of the thermal properties by TG/DTA and DSC measurement, the glass transition temperature (T_g) of the obtained CAB was decreased with the increasing the DS values of the butyryl groups.

The synthesis of CAB was succeeded with the well-controlled DS as the cellulose-based thermoplastic using the ionic liquid of EmimOAc as the solvent and the catalyst. Furthermore, the thermoplastic properties could be controlled by changing the value of DS of the acetyl and butyryl groups in the obtained CAB.

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M126

Novel Through-porous Particle Applied to HPLC

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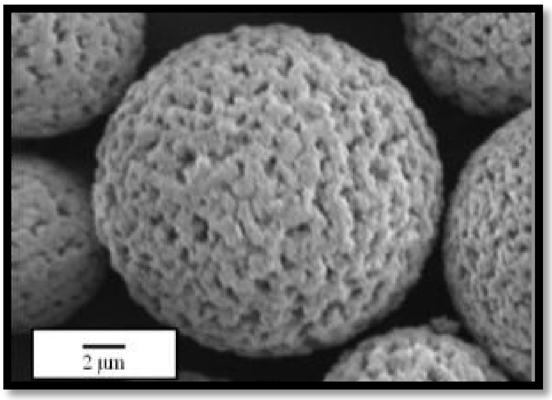
Keywords: Monolith, Phase separation, Porous, Particle, Emulsion

Abstract

‘Through-porous particle’ is a novel porous material, having co-continuous structure with through-pores and skeletons like a monolithic (co-continuous) structure[1]. It is expected to be used as a chromatographic medium, an adsorption medium and a support of catalyst in solid-phase synthesis, etc. In this study, we succeeded in preparation of novel porous particles with variety of materials such as silica, polystyrene-divinybenzene, polyacrylic resin and poly epoxy resin, etc. These particles synthesized using emulsion polycondensation accompanied by gelation and phase separation based on spinodal decomposition, have homogeneous through-pores, which can be controlled in the range of ca. 0.1 ~ 100 μm. Furthermore, the particle size can be controlled in the range of ca. 10 ~ 100 μm. We assessed pore characterization and chromatographic properties obtained with a column packed with the through-porous silica to compare with conventional particle-packed column.



Through-porous particles

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M127

Concentration-dependent apparent partition coefficients of ionic liquids possessing ethyl- and bi-sulphate anions

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Keywords: Ionic Liquids, Apparent Partition Coefficient, Aggregate Formation, Hydrogen Bonding

Abstract

Ionic liquids (ILs) are modified structurally to enhance their biodegradability. Bio-degradability of ILs is essentially based on the compositions of cation and anion. Imidazolium-based ILs are known to be the class of bio-degradable ILs. However, ILs should also be explored predominantly on the basis of modification of the anion. Studies have shown that the substitution of the halide-based anion by the alkyl sulfate anion, improves their biodegradability by 54%.[1] The alkyl sulfate anion-based IL are commonly used in the petrochemical field for extraction processes,[2] alternatives to the routine hydrodesulfurization,[3] and can be synthesized efficiently as well as in a halide-free form at low costs. The present study deals with the concentration dependent apparent partition coefficients, log *P* of the ethyl sulfate ($EtSO_4^-$) and bisulfate (HSO_4^-) -based ionic liquids. It would be of great significance to explore the analysis for the further implementation of alkyl sulfate based ILs as solvents in extraction processes. Our study demonstrates the concentration dependent apparent partition coefficient (log *P*) of HSO_4^- and $EtSO_4^-$-based ILs. The log *P* values of the $EtSO_4^-$-based ILs vary linearly with the concentration of the IL, whereas a flip-flop trend has been obtained for the HSO_4^--based ILs. The different behavior is observed due to the difference in hydrogen bond accepting, basicity and possibility of aggregate formation of these anions.[4] This study also emphasizes the effect of hydrophobicity of anions on the log *P* values. The order of the hydrophobicity of the anions is $[HSO_4]^- < [EtSO_4]^- < [BuSO_4]^-$.

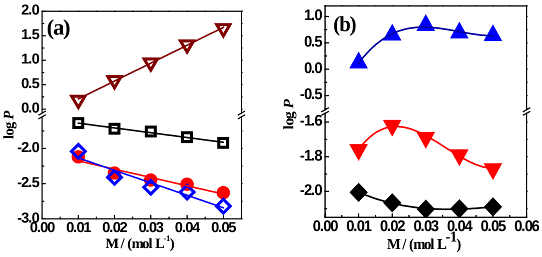

Figure 1. Variation of log *P* with concentration (a) for $[EMIM][EtSO_4]$ (◇), $[dEIM][EtSO_4]$ (●), $[BEIM][EtSO_4]$ (□), and $[EOIM][EtSO_4]$ (▽). (b) For $[BMIM][HSO_4]$ (◆), $[HMIM][HSO_4]$ (▼), and $[OMIM][HSO_4]$ (▲).

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M128

CO_2-Switchable Surfaces

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Keywords: Carbon Dioxide, Polymers, Surfaces, Smart Materials, Coatings

Abstract

Industrial inefficiencies, causing wastage of energy and materials, is often the result of failures to resolve *time-separated conflicting requirements*. For example, a drying agent particle needs to strongly absorb water from something that needs to be dried, but needs to easily release the water when the drying agent is being regenerated. Switchable materials can solve such problems. Waste CO_2 is a renewable material that can be used to reversibly trigger changes in the properties of surfaces. There are three approaches that can be used to make surfaces CO_2-responsive.

The first approach is the use of a CO_2-responsive additive in water. Particulates that are suspended in the water can respond to the addition or removal of CO_2 from the system because the particles are affected by the changes in the CO_2-responsive additive [1]. The application that will be highlighted is the creation of artificial latexes from recycled or waste polymer [paper submitted].

The second approach is to use a CO_2-switchable surfactant on the surface of the particles. When the surfactant is switched "on", then interparticle repulsion stabilizes a suspension of the particles in water. Switching off the surfactant breaks the suspension. Careful design of the surfactant is required to ensure that the switching process is efficient in both directions [2]. Potential applications are in emulsion polymerization and in control of latex formulations for paints and coatings.

The third approach is to covalently attach CO_2-responsive groups to surfaces. Applications of include CO_2-switchable drying agents for the removal of water from organic liquids [3] and CO_2-switchable particles for chromatographic separations [unpublished].

In all of these applications, the purpose of using CO_2-switching technology is to reduce energy and materials consumption while enhancing performance and using the greenest materials possible: CO_2 and water.

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M129

Ion-exchange of Cs^+ with Merlinoitezeolite

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Keywords: Ion-exchange, Zeolite, Merlinoite, Cesium

Abstract

In the context of the East Japan Massive Disaster in March 2011, some radioactive materials including Cs, I and Sr were released from Fukushima Daiichi nuclear power plant. Especially, ^{137}Cs is needed to remove as soon as possible because half life of ^{137}Cs is as long as 30 years. Recently, zeolite is used to remove Cs but higher removal performance is required [1].

In this study, a kind of zeolite, Merlinoite, was prepared hydrothermally and used for removal of Cs^+. Merlinoite could be synthesized in 8 h at 250 °C[2].Ion-exchange capacity for Cs^+ was 2.85 meq/L with Merlinoite. When Cs^+ concentration was 0.75 mmol/L, Cs^+ was completely removed within 30 min. With co-exciting cations such as Na^+, K^+, Sr^{2+} and Ca^{2+}, Merlinoite removed Cs^+ in 30 min selectively. Thus, it was revealed that Merlinoite could be promisingas an ion-exchange material for Cs^+.

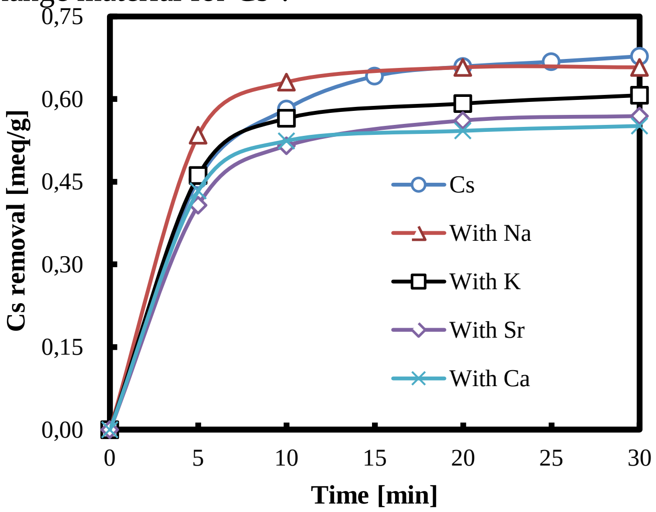

Fig. Influence of co-exisiting cations on Cs removal with Merlinotie

Adsorbent: 0.050 g, Solution: 50 mL, Initial pH: 7.0, Final pH: 7.0-7.3,
Initial conc. : Cs: 0.75 meq/L, Na, K, Ca, Sr : 3.75 meq/L

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M130

Macro- and nanolubrication properties of Ionic liquids as lubricants Confined between Silica Surfaces

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Keywords: Ionic liquid, Lubricant, Tribology, Nanoscale lubrication, Friction coefficient

Abstract

Ionic liquids (ILs) are organic salts consisting of anions and cations that exist as liquids at room temperature. The ILs bear many attractive properties such as negligible volatility, low flammability, and relatively high thermal durability. These properties can be varied in a controlled fashion through systematic changes in the molecular structure of their constituent ions. Recently, some studies have been reported which aim to use the ionic liquids as a new lubricant. However, at present, the details of the lubrication mechanism and tribomaterials using ionic liquids are not reported.

In this study, we chose aliphatic quaternary ammonium type cation [DEME] (*N*,*N*-diethyl-*N*-methyl-*N*-2-methoxyethyl) ionic liquids, namely [DEME][TFSI] and [DEME][BF_4],all of which have a spherical structure. This choice reflected the fact that, we have developed a robust lubrication system using [DEME][TFSI] and ionic liquid polymer brushes [1] but have not reported its lubrication properties when confined in nanometer scale spaces. We examined the nanoscale lubrication properties of these ILs between molecularly smooth silica surfaces using resonance shear measurements (RSM)[2] while controlling the surface separation (*D*) at 0.1 nm resolution. The obtained results were compared with the macroscale properties of ILs between glass surfaces monitored by a tribotester. RSM revealed that an IL layer of ca. 2 nm in thickness was maintained between the silica surfaces under an applied loads (>0.4mN). The relative intensity of the RMS signal for [DEME][TFSI], 0.18, was larger than those for [DEME][BF_4], 0.12, at the higher loads (>0.4 mN). These results indicated that under higher loads (>0.4 mN), [DEME][BF_4] should be a better lubricant than [DEME][TFSI]. On the other hand,the friction coefficients μ_k obtainedfrom the tribotests of [DEME][BF_4] were lowerthan that of [DEME][TFSI]forsliding velocities in the range of 5.0×10^{-4} m $s^{-1}$to 3.0×10^{-2} m s^{-1} under applied loads of 196 mN－980mN.Even though the RSM and tribotest measurement were made under different applied loads, the difference of the friction coefficient between [DEME][TFSI] and [DEME][BF_4] at the boundary lubrication region observed by the tribotest corresponds to their behavior when confined between silica surfaces under the higher load (>0.4 mN) observed by RSM. These results indicate that the nanometer-scale space property observed by RSM can provide important insights for the study ofthe friction coefficients (macro-scale lubrication properties) obtained by tribotests.

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M131

A cost-effective natural product material as a green hydrophilic solid phase extraction sorbent for the selective determination of organic acids in soil

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Keywords: Phenolic acids, Response surface methodology, Soil,Solid phase extraction

Abstract

Natural products have been demonstrated to absorb organic compounds as a novel and green materials. However, there are limited reports about natural products acting as hydrophilic solid phase extraction sorbent for the selective determination of select organic acids. In this study, we aimed to extend the study on natural products as solid phase extraction (SPE) sorbents and present a series of experimental design showing the influence of parameters during the extraction procedure. The chemical structure and surface properties of prepared SPE sorbents was investigated by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The experimental Placket-Burman design was used in the study to screen the important variables that significantly influenced extraction performance, and then selected parameters were statistically optimized by applying a central composite design combined with a response surface methodology. Determination and quantification of phenolic acids residues were carried out using HPLC-UV, and a mass spectrometric detector in the selected ion monitoring mode was also used for confirmation purposes. As a result, phenolic acids provided as a practical example of organic acids in soil was successfully separated by developed natural products based SPE method. The present study suggests that natural products can be used as sustainable, green and safe nanoparticle to be replaced with barely silica based materials for the extraction and separation applications. This work was supported by the Bio-Synergy Research Project (NRF-2012M3A9C4048796) of the Ministry of Science, ICT and Future Planning through the National Research Foundation.

M132

Repairable Woven Carbon Fiber Composites with Full Recyclability Enabled by Malleable Polyimine Networks

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Keywords: Carbon Fiber, Composites, Polyimines, Recyclable, Vitrimers

Abstract

Carbon fiber is a lightweight graphitic material with higher tensile strength than steel and lower density than aluminum [1]. Woven and nonwoven carbon fibers can be combined with polymeric binder materials to form high-performance carbon fiber reinforced composites (CFRCs). With increasing production of CFRCs, the environmental impact of these traditionally nonrecyclable materials and reduction in their material and manufacturing cost are of great concern. Typically epoxy thermosets are used as binders to produce high-performance CFRCs with superior mechanical properties (high strength/stiffness); however, the resulting CFRCs cannot generally be repaired or recycled [2]. We envision that repairability and recyclability of CFRCs could be enabled by introduction of dynamic covalent bonds [3,4] in the binder material. Herein, CFRCs are prepared using catalyst-free malleable polyimine networks as binders. An energy neutral closed-loop recycling process has been developed, enabling recovery of 100% of the imine components and carbon fibers in their original form. Polyimine films made using >21% recycled content exhibit no loss of mechanical performance, therefore indicating all of the thermoset composite material can be recycled and reused for the same purpose.

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M133

A Study on Various Readily-Available Proteins as New Green Scale Inhibitors for Oilfield Scale Control

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Keywords: Proteins, Oilfield scale, Crystal growth, Scale inhibitors, Biodegradation

Abstract

Mineral scales often form in oil wells and pipelines due to inorganic salt supersaturation. Most common scales contain carbonate, sulfate or sulfide salts of divalent metal ions (Ca^{2+}, Sr^{2+}, Ba^{2+} and Fe^{2+}). Phosphonates are very effective scale inhibitors and are widely used in the oil industry, especially in squeeze treatments due to good rock adsorption and ease of detection [1]. Unfortunately, most phosphonate inhibitors are not based on naturally-occurring compounds and show limited biodegradation [1]. Increasing environmental concern and discharge limitations have caused scale inhibitor chemistry to move towards “green scale inhibotors” that readily biodegrade, but are still high-performing and cost-effective. Proteins are known for their specific binding interactions. Proteins can interact with a wide range of substrates and synthetic analogues. In this study, we have evaluated the calcium carbonate and barium sulphate scale inhibition performance of a series of different proteins from sources such as milk, meat, gluten, soya and peas using a classic dynamic tube blocking equipment. The minimum inhibitor concentration (MIC) for protection against scale has been determined and comparison has been made with several commercial scale inhibitors.

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M134
Production of PHA-based microbial bioplastics and pullulan on selected waste materials

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Keywords:polyhydroxyalkanoates, lignocellulose waste, bioplastics, detoxification

Abstract

Polyhydroxyalkanoates (PHAs), have attracted much attention in recent years due to their varied mechanical properties, biocompatibility and biodegradability. The high costsof raw material and relatively low conversion rates are the two main problems in large-scale industrial production of PHAs. With the annual generation of 80 billion tons, lignocellulosic materials have a great potential for the production of a wide variety of industrial and commodity products e.g. biopolymers – PHA-based bioplastics, polysaccharides (pullulan) and others.

In this work PHA-based biopolymers have been produced by utilization of waste substrates by proper microorganisms. For PHA production bacterial strains *Cupriavidus necator, Bacillus megaterium, Bulkholderia cepacia* and *Bulkholderia sacchari* were tested. Lignocellulosic waste materials were represented by waste wood, apple pomace, grape pomace, spent coffee grounds (SCG) and wheat bran. The second group of substrates contained waste frying oil, SCG-oil and cheese whey. Above mentioned wastes, mostly lignocellulosic, were treated by chemical and/or enzymatic hydrolysis to reach higher yield of fermentable saccharides (glucose, xylose). Detoxification methods (active coal, overliming, heating) were applied to hydrolysates to reduce the concentration of potentional inhibitors of growth – polyphenols. Reducing sugars and polyphenols concentrations have been analyzed spectrophotometrically. Glucose, xylose and other sugar yields were measured on HPLC/RI (Rezex-ROA, H+, 8%). GC/FID was used for determination of PHA content in biomass.

Application of chemical hydrolysis to lignocellulosic substrates leads to generate high concentration of reducing sugars. Combination of enzymatic and chemical hydrolysis steps had resulted in increased sugar yield. Polyphenols, as potentional inhibitors of growth were removed in detoxification process, where overliming, heating, activated carbon and extraction by ethanol has been applied on SCG and wooden waste hydrolysates. Application of active coal leads to highest decrease of polyphenolic compounds - up to 90% in case of waste wood.

The highest PHA yields were obtained when SCG hydrolysate was used as sole carbon source (51-56 %). High concentration of PHA has been also reached by utilization of SCG-oil by *C. necator*70 % . High sugar concentration is possible to obtain by hydrolysis of lignocellulosic waste. Application of activated carbon is efficient way for hydrolysates detoxification.

In conclusion we can say that waste substrates can be easily converted to high valuable products as PHA-based bioplastics. This way can lead to substantial decrease of costs of substrates for biotechnological production of polyhydroxyalkanoates and to their broader application.

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M135

Assessment of Polylactide (PLA) as an Environmentally Benign Adsorbent for CO_2 Capture and Storage (CCS)

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Keywords:polylactide, carbon capture and storage, carbon dioxide, gas sorption, renewables

Abstract

Carbon Capture and Storage (CCS) in conjunction with an increasing use of renewables provides a clean pathway to sustainable development and climate change mitigation. [1] In selecting a low temperature CCS adsorbent, parameters such as selectivity, regeneration energy and economicity play a crucial role.[1] Polylactide (PLA) is a renewable resource, obtained from corn and commercially available, representing one of the most promising eco-friendly alternatives to petrobased plastics and is being applied in many fields.[2] Literature data point to PLA as a valid CCS candidate, [3] although no direct gaseous CO_2 adsorption investigation at low temperature or with mild preparation/regenerative energy was reported. Moreover, no study is present on the effect of the sample morphology, important for a viable industrial CCS application.

The aim of these work is exactly a deeper investigation of PLA adsorption properties and its possible realation to structural/morphologial properties and/or synthetis parameters. In particular we focus our research activity on: gaseous CO_2 (up to 1.5 MPa), low operative temperature (RT), mild preparation/ regenerative energy (333 K), morphology (PLA samples in the form of powder, flakes and pellets). PLA samples were characterized by helium picnometry to estimate the skeletal density; by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) to obtain structural and morphological data; by an home-made Sievert-type apparatus [4] to obtain adsorption/desorption data. Regeneration effect was investigated.

Acknowledgments

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M136

OSSO-type Zirconium Complexes in the Ring-Opening Polymerization of Lactide

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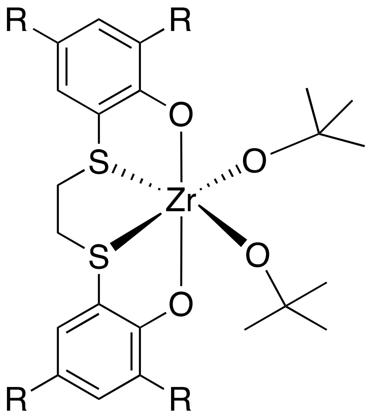
Keywords:polylactide, zirconium, ring-opening polymerization, cyclic esters, OSSO-ligands

Abstract

Aliphatic polyesters, and polylactide (PLA) in particular, are being regarded as valid green alternatives for petrobased plastics. Their biologically and environmentally benign qualities make them suitable for a wide range of practical applications, from packaging to medical and pharmaceutical uses. [1]
The ring-opening polymerization (ROP) of cyclic esters via the coordination-insertion mechanism is the method of election for the control over the microstructure and therefore the production of high molecular weight aliphatic polyesters with narrow polydispersities and well defined end groups.[1]Among the metal complexes investigated as initiators, group 4 metal complexes have shown to be particularly attractive thanks to their low toxicity and good control over polymerization process. However, only a limited number of studies was reported about their use in the ROP of cyclic esters. [2] Notably, OSSO-type zirconium complexes with aryl rings directly attached to the sulfur atom and an ethylene bridge have shown to be promising in ROP, with their catalytic performances affected by the aryl substituents. [3]



Zr-1: R = CH_3
Zr-2: R = Br
Zr-3: R = Cl

We report on the synthesis of zirconium complexes bearing dithiolate OSSO ligands with aryl rings symmetrically substituted on their 3 and 5 positions with methyl, bromide or chloride moieties (Figure). All complexes were characterized by NMR and applied as precatalysts in the ROP of L-lactide. The effect of the substituentswas investigated.

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M137

Combustion Synthesis and Characterization of Fe_3O_4/Ag/C Nanocomposites

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Keywords: Combustion synthesis, Magnetic composites, Iron oxides, Silver, Carbon

Abstract

Fe_3O_4/Ag/C nanocomposites have attracted much interest in many applications due to their valuable properties. These nanocomposites combine the good catalytic and antibacterial activity provided by silver and high adsorption capacity supplied by carbon with the advantage of easy magnetical manipulation given by magnetite. Meanwhile, the carbon presence prevent the oxidation or erosion by acid or base and agglomeration of the composite in aqueous solution [1,2]. Generally, the methods reported for the synthesis of Fe_3O_4/Ag/C nanocomposites require multi-step routes, high temperatures or long reaction times [2]. In this work we report the synthesis of Fe_3O_4/Ag/C nanocomposites by the combustion method. This method is environmentally friendly and has many advantages such as simplicity, short reaction time, low energy consumption [3,4]. The starting raw materials were: iron nitrate nonahydrate ($Fe(NO_3)_3\cdot 9H_2O$, Roth), silver nitrate ($AgNO_3$, Merck) citric acid monohydrate ($C_6H_8O_7\cdot H_2O$, Merck) and granular activated carbon (Utchim).Samples were synthesized under controlled atmosphere, in the absence of air. In this case, the gases resulted from the combustion reaction were bubbled in a large beaker filled with distilled water.Thermal behavior of the powders was studied using a Netzsch STA 449C instrument, in air atmosphere at a flow rate of 20 mL min^{-1}. The TG/DSC curves were recorded in the range of 25-1000°C with a heating rate of 10K min^{-1}, using alumina crucibles. The presence of carbon was confirmed by a large exothermic effect between 400 and 800°C, accompanied by a significant mass loss on the TG curve. The structure and morphology of the Fe_3O_4/Ag/C nanocomposites were investigated by X-ray diffraction (XRD), FTIR and Mössbauer spectroscopy, scanning electron microscopy (SEM)-energy dispersive X-ray (EDX) and N_2 adsorption-desorption technique. Mössbauer analysis confirmed the presence of magnetite in the samples while the presence of silver was confirmed by XRD and EDX analyses. The BET surface area of the nanocomposites varied between 734 m^2/g and 755 m^2/g, which is very close to the BET surface area of the activated carbon used as raw material, 890 m^2/g.

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M138

Environmental Concerns: Need For Green Chemistry Education And Policy Implementation In Nigeria.

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Keywords: Environmental concerns, education, policy, implementation.

Abstract

Globally, the quests for industrialization and technological advancement with their attendant impact on the eco-system have raised environmental concerns [1].Environmental problems are trans-national issues that must be addressed jointly thus implementation of different policies and programme is inevitable to safeguard the eco-system. Though environmental alarm is being sounded in Nigeria but warnings of other crises like political instability, insecurity, low economic productivity, education, religious conflicts and high crime rate seems to drown it. Available natural resources for the ever increasing population can be processed and utilized in such a manner that waste generation will be minimized thereby enhancing its conservation[2]. Human activities greatly influence the environment both positively and negatively. The role of green chemistry education and adequate sensitization at all levels was identified as a veritable tool in the acceptance and application of green chemistry principles and policy to secure the environment. Corruption was pointed out as a key challenging factor to the funding and implementation of environmental regulatory policies and green education programmes. Preventive and remedial approaches to environmental problems are closely interwoven with policies for sustainable development.

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Modification of Silica Coated Magnetic Material with Chitosan Using 3-Glycidoxypropyltrimethoxysilane Linker for Adsorption of $[AuCl_4]^-$

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Keywords: Silica, Magnetic material, Chitosan, Gold

Abstract

The presence of amino groups ($-NH_2$) leads to the application of chitosan for adsorption of metal ions including gold(III) [1]. Immobilization of chitosan on matrix materials and addition of magnetic properties on adsorbent are recently developed to reduce the solubility of chitosan and to separate easily the adsorbent from the solution [2]. In this research, synthesis of chitosan-silica hybrid coated on magnetic material involving a linker of 3-glycidoxypropyltrimethoxysilane (GPTMS) for adsorption of $[AuCl_4]^-$ has been conducted.

Magnetic materials (MM) was separated from iron sand using an external magnet and then treated with 10% HF solution. The targeted material was synthesized via sol-gel process by mixing MM, silica sol of sodium silicate solution, GPTMS and chitosan solution. The mole ratios of chitosan to GPTMS 0:1; 1:0; 1:0.5; and 1:1 were examined. The products were characterized with X-Ray Fluoresence, X-Ray Diffractometer, Fourier Transform Infrared spectrophotometer, Scanning Electron Microscopy and Energy Dispersive X-Ray, Thermogravimetric Analysis, and Vibration Sample Magnetometer. The chemical stability of synthesized materials was studied by determining the amount of Fe dissolved in various acidic solutions. Adsorption of $[AuCl_4]^-$on the adsorbent was carried out in a batch system by variety of pH, concentration and contact time. Concentration of Au(III) not adsorbed was analyzed with Atomic Absorption Spectroscopy.

Results showed that high content of iron in magnetic material from iron sand was found (about 83. 9 %) and treatment with HF 10 % caused silica content in MM to decrease from 3.5 to 1.5 %. Based on the characterization, chitosan has been successful to be hybridized on the silica coated MM with the optimum mole ratio of Chitosan to GPTMS 1:1. Coating on MM decreased magnetization value from 44.8 (for MM) to 19.9 emu g^{-1}. The presence of GPTMS as a linker improved the stability of the material under acidic condition. Adsorption of Au(III) on the adsorbent followed pseudo second-order in term of kinetic model with the rate constant value (k) of 1.99×10^{-3} g mg^{-1} min^{-1}; and fixed to Langmuir model in term of adsorption isotherm with the adsorption capacity of 94.340 mg g^{-1}. Low cost of natural resources used for the synthesis and high capability in adsorbing gold(III), therefore, it is expected that in the future the produced magnetic material may be promoted as a prospective and green adsorbentfor simple separation or recovery of gold(III) from industrial waste water.

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M140

Catalysts based on Nb_2O_5 promoted with CeO_2 for environmental applications.

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Keywords: environmental-catalysis , niobium oxide, cerium oxide, photocatalysts.

Abstract

The aim of this study was preparing catalysts based on hexagonal Nb_2O_5 promoted by CeO_2, to characterize them by different physico-chemical techniques and testing their catalytic properties in the photocatalytic degradation of Methylene Blue (MB, $C_{16}H_{18}N_3SCl$, model molecule of organic compounds) in an aqueous solution under various conditions: UV-radiation (253.7 nm), Visible radiation (white light) and Visible radiation plus H_2O_2. This mixture of these oxides was chosen in order to decrease the band-gap energy of Nb_2O_5, moreover, there are not many works reporting the use of hexagonal-Nb_2O_5 as photocatalyst [1]. For this work $Nb_2O_5$was synthesized by precipitation with NaOH (5 $mol.L^{-1}$) of $NH_4[NbO(C_2O_4)_2.H_2O].xH_2O$. The precipitated was calcined at 500ºC, 5ºC.min^{-1} in air stream [1]. The Nb/Ce mixtures were prepared by impregnation method using the Nb_2O_5 prepared previously, and an aqueous solution of $Ce(NO_3)_2.6H_2O$, calcined at 500 °C. The CeO_2 molar fraction in the mixture was varied as following: 0, 0.3, 1, 2 and 100%. Samples were named as: Nb_2O_5, 0.3CeNb, 1CeNb, 2CeNb and CeO_2.The catalysts were characterized by X-Ray diffraction (XRD), Energy Dispersive X-ray Spectroscopy (EDX), Scanning Electron Microscopy (SEM), Adsorption-Desorption of nitrogen (BET) and UV-Visible Diffuse Reflectance spectroscopy (DRS) and Temperature programed reduction (H_2-TPR). The photocatalytic tests were performed using a MB solution (50mg.L^{-1}) prepared with distilled water and a determined quantity of each photocatalyst (1g.L^{-1}), in a batch reactor (open to atmospheric O_2) of Pyrex glass, at constant temperature (25 °C) and under UV radiation (provided by six UV lamps, 253.7 nm, 15 Watts) or Visible radiation (provided by six Hg lamps, white light, 15 Watts) or Visible radiation plus 0.5 mL H_2O_2 (30% v/v).

The results of characterization indicate that the Nb_2O_5 obtained by the present work is the pure hexagonal-phase; the pure CeO_2 presented peaks related to the fluorite phase (single phase). On the other hand, when CeO_2 was added to Nb_2O_5, two crystalline structures of cerium oxide were found: CeO_2 (a: 5.40370 Å; 65 JCPDS -5923) and Ce_4O_7 (a: 5.5260 Å; JCPDS 65-7999); both of cubic structure. According to DRS spectra, the addition of CeO_2 increased light absorption in the visible-region of hexagonal-Nb_2O_5. The photocatalytic degradation tests MB indicates that the addition of CeO_2 to Nb_2O_5 did not favour the MB degradation in the presence of UV or Visible radiation (probably owing to recombination effect). The addition of CeO_2 was only beneficial for MB degradation under Visible radiation plus 0.5 ml H_2O_2 (30%v/v), at this condition, the progressive increase of CeO_2 concentration in the Nb/Ce mixture increased the MB degradation. This effect may be related to the high mobility of oxygen by CeO_2 and by Ce_4O_7, which could be favouring the generation of hydroxyl radicals in the presence of H_2O_2. Pure CeO_2 did not remove significant quantities of MB.

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Recycled Plastics As Raw Materials for 3D Printed Devices

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Keywords: Recycled Plastic, Sustainability, 3D Printing, Photocatalysis, Pollution

Abstract

Plastic waste generation and management during industrial transformation and at post-consumer stage has been a problem of economic efficiency since the late 1940s [1,2]. More recently, sustainability considerations have gained widespread adoption not only in traditional industrial processes but specifically in 3D Printing (3DP) technologies [3]. Production and distribution considerations of functional 3DP devices as added value recycled products have recently been addressed [4].

In this work, postconsumer recycled poly(ethylene terephthalate) (pcrPET) and industrial scrap polypropylene (srPP) were used as raw materials to produce feedstock filaments to be used in a Fused Filament Fabrication (FFF) 3DP process. Both pcrPET, srPP and their blend (WP ZSK 25 twin screw) were characterized by Fourier transformed infrared spectroscopy (FT-IR), melt flow index (MFI) and differential scanning calorimetry (DSC). The FT-IR spectra of srPP showed bands assigned to polypropylene and polymerized ethylene. Additional absorption bands were observed and assigned to inorganic fillers (carbonates and silicates, 30% w/w, determined by calcination). Morphologies of filaments and 3DP devices were analyzed by polarized light optical microscopy (POM) and scanning electronic microscopy (SEM).

A first feedstock filament was developed with 5% TiO_2 loading (Aeroxide P25) into pcrPET (P25@PET5%) and tested for the removal of Cr(VI) in water in the presence of EDTA. A removal efficiency of 7% and 99% was obtained for the P25@PET5% and free P25 nanoparticles, respectively in 15 min, suggesting low availability of the photocatalyst in the surface of the filament. Subsequently, a TiO_2 loaded srPP probe was developed (Brabender discontinuous mixer) and its photocatalytic activity and surface availability of TiO_2 remains to be tested.

Additionally, a reticulated prism (70% of free space) was designed with Cura software and fabricated in a Chimak3D Leon 200 3D printer by single screw extruded pcrPET filaments produced by Platec S.A. and commercialized by Enye Tech S.A. as BPET. The resulting structure was then used as support for titanium dioxide nanoparticles ($nTiO_2$) and later used in photocatalytic tests. The TiO_2 impregnation was successful and the structure was used in an airtight reactor obtaining 55% of NO removal efficiency under UV light irradiation. A fully 3D printable airtight photocatalytic reactor, combining pcrPET and pcrPET/srPP compound filaments produced by Printalot S.A., has been designed to be fabricated in less than 4 hours.3D printing with recycled materials has been proved to be very promising for the optimization of material costs and manufacturing time.

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M142

Estimation Methods of Biodegradability of Polysaccharide-Based Compositions

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Keywords: Biodegradation, Polysaccharides, Fungus resistance, Scanning electron microscopy (SEM)

Abstract

Binary compositions of natural polysaccharides cellulose, starch, chitin, ethylcellulose, and chitosan with low-density polyethylene (LDPE) as well as their ternary compositions with poly(ethylene oxide) (PEO) of different molecular weight and compositions based on two polysaccharides and LDPE are produced under conditions of shear deformation in the rotor disperser. It is shown that the introduction of both PEO and second polysaccharide leads to increase in biodegradability of the compositions. The biodegradability of compositions is studied by three independent methods: determination of the sample weight loss after holding in soil, investigation of their fungus resistance, and study of the sample morphology before and after holding in soil by scanning electron microscopy (SEM). For the investigation of biodegradability under natural conditions the samples were placed into a container with wet soil meant for plant growing. The containers were kept in a thermostat at room temperature during several months. The rate of biodegradation was controlled by the weight losses of samples measured with certain time intervals. It turned out that the greatest weight loss was for the binary systems of LDPE with starch and chitosan, however it was found that the addition of third component (PEO or second polysaccharide) leads to significant increase in the rate of biodegradation. The tests on fungus resistance were performed according to the techniques based on the exposition of the materials infected with fungus spores under the optimum conditions for their growth with the following estimation of fungus resistance by the degree of fungus growth. It was established that only binary systems based on starch and chitin among blends under investigation contain the significant amount of nutrients for the intensive fungus growth, however the introduction of PEO or second polysaccharide promotes more intensive fungus growth. For example, cellulose–LDPE blend has very high fungus resistance, but the addition of 20% PEO increases significantly the fungus amount and they can be clearly seen by the naked eye. The SEM study of film morphology after holding in soil makes it possible to ascertain the presence of structural defects that form as a result of sample biodegradation and lead to its subsequent fragmentation and destruction up to the formation of holes in polyethylene matrix. This fact testifies that not only the polysaccharide takes part in the biodegradation but also the synthetic polymer does. This result is principal because it provides a direct confirmation of the destruction of the synthetic matrix during biodegradation.

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Self-Aggregation behavior of long-chain Amino Acid Ionic Liquids in aqueous solution.

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Keywords: Amino Acid Ionic Liquids (AAILs), Alanine (Ala), Phenylalanine (Phe), 1-tretradecyl-3-methylimidazoluim amino acid (C_{14}mim.AA).

It has been reported that long-chain Ionic Liquids (ILs), such as 1-alkyl-3-methylimidazolium $[C_n\text{mim}]^+$, can self-assemble in aqueous solutions to form micelles, vesicles, lyotropic liquid crystal, etc. The surface activity of $[C_n\text{mim}]^+$ is superior to that of conventional cationic surfactants and the anion nature and the ring type of cation significantly affect the aggregation behavior.[1]

Among the long-chain ILs most widely studied are $[C_n\text{mim}]^+$ with different anions, such as; $[\text{Br}]^-$, [Cl], $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, etc. Nevertheless, the toxicity of these anions has been questioned in the last years. There are some studies about the toxicity of different fluorine-containing ILs, which emit toxic gases such as HF and POF_3 to the environment.[2] In search of alternatives without environmental commitment, long-chain amino acid ILs (AAILs) have recently been introduced. [3] Among the advantages of using AAILs, is the low cost of the amino acids, the synthesis of them are made from biological reagents, therefore we could obtain a more biocompatible and biodegradable surfactant.

Taking into account the above, we have synthesized 1-tretradecyl-3-methylimidazoluim amino acids (C_{14}mim.AA) where AA are Ala and Phe. In order to characterize these new types of surfactants, we have determined the critical micelle concentration (cmc), by different techniques such as conductivity, fluorescence measurements by pyrene and 9-diethylamino-2-hydroxy-*5H*-benz[a]phenoxazin-5-one (HONR) dye, UV-Vis spectrometry and isothermal titration calorimetric (ITC). Previous results indicate that, at least two different types of micelles are formed, when we use C_{14}mimAla, in aqueous solutions. Firstly, we have observed inflexions points at around 0,2 mM, and about 2,5 mM and the aggregation behavior depend on the amino acid used as anion.

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Electrochemically-induced Phase Transformation of Redox-active Metallomesogens

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Keywords: Metallomesogen, Redox-active ligand, Platinum complex, Electrochemical phase transformation

Abstract

Liquid crystal(LC) with flexible structure has been expected as building block of environmentally-friendly functional materials which could be driven by low energy input. In particular, columnar LCs comprised of disk-shaped molecules have been shown to be particular interest for applications in areas such as photovoltaic solar cells, field effect transistors and semiconductors[1], based on their one-dimensional columnar structures derived from stacking interactions of the central cores. These properties have been mostly focused on using its structural properties (anisotropy, low dimensionality, and long-range ordered columnar structure). These works demonstrated that the nature of the core plays a key role to determine physical structures and properties of the columnar LCs.

Previously, we reported that Pt(II) metallomesogens possessing redox-active catecholato(Cat) or 1,2-benzenedithiolato(Bdt) and 4,4'-di(3-octyltridecyl)-2, 2'-bipyridyl(C8,10bpy), [Pt(Cat)(C8,10bpy)] or [Pt(Bdt)(C8,10bpy)](Figure 1), form a hexagonal columnar orderd LC phase and show the direct electrochemical activity [2]. The combination of flexible liquid crystalline behaviorand redox activity must be attractive, because they have the potential to allow control both their micro-level electronic structures and their macroscopic, physical structures, *via* electron transfer processes. This presentation reports new platinum diimine complexes with alkyl-substituted Cat or Bdt and its electrochemical transformation at ambient temperature.

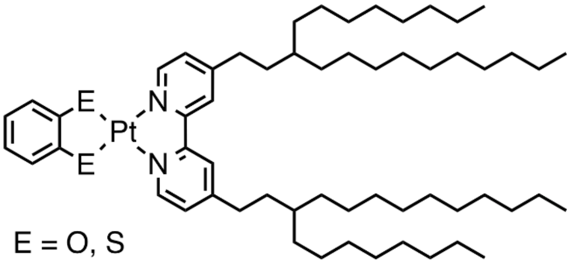

Figure 1. The sturecture of the Pt complex

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M145

Design artificial lignin composites with predictable properties based on peroxidase biocatalysis of the lignin-residues

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Keywords:artificial lignin, biocatalysis, peroxidase, biocomposite

Abstract

Lignin, the second most abundant natural polymer after cellulose in terrestrial sources plays a negative role in pulp and paper industry, where huge amount of lignin is/was produced during the paper manufacturing approach (e.g. over 70 million tons of lignin produced annually in the world). Most of this lignin is burned (95 %) and only few percents are invested in value-added products (e.g. phenolic polymers)[1].

In this content, we developed a green method based on the enzymatic process for the polymerization of the lignin residues (monomers/fragments) with controlled architecture in order to generate phenolic polymers (biomaterials) with tunable mechanico-chemical properties.

Lignin monomers (e.g. sinapyl alcohol and coniferyl alcohol) were used as model-monomer for the synthesis of the artificial lignin structure. Peroxidase enzymes (e.g. PADAI[2], 2-1B and R4[3] – mutants of the versatile peroxidase) tested in the proposed system exhibited similar catalytic behavior.

Furthermore, the lignin fragments from the degradation of the natural lignin have been used as substrate, too. Fast kinetic of the biocatalytic process allowed to achieve maximum conversion of the lignin fragments in almost 10 min (*e.g.* 60 % conversion of the lignin fragments). Also, the efficiency of the process can be easily modulated based on the composition of the precursor mixture (*i.e.* content of the mixture in terms of the molecular weight/structure of the lignin fragments).

Detailed study of the process kinetic and also optimization of the experimental parameters (*e.g.* reagents concentration, temperature, buffer pH, enzyme content, etc.) have been performed. Also, the characteristics of the synthetic biopolymer have been investigated and compared to the mother-lignin source. All of these aspects related to the process development and the characteristics of the biopolymeric products will be detailed in the presentation.

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M146

DES assisted synthesis of morphology controlled ZnO nanostructures: Photoluminescence and photocatalytic properties

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Keywords: ZnO nanoparticles, DES, synthesis, hydrothermal, photocatalytic degradation

Abstract: In recent years, considerable interest has been focused on the synthesis of nanomaterials in room temperature ionic liquids, due to their unique properties. ZnO nanostructures synthesized in various ionic liquids with different morphologies and improved properties have been previously explored [1-5]. Deep eutectic solvents have now emerged as an attractive alternate to the conventional ionic liquids showing numerous advantages over the latter due to their ease of preparation in a pure state at low cost, nontoxic nature, more synthetically accessible, biodegradable and can easily be tailored from their inexpensive components to suit certain applications [6].

In continuation to our previous work [7], in the present paper ,the controlled fabrication of flower and cauliflower-like 3D hierarchial ZnO structures, constructed by nanoparticles via simple hydrothermal using deep eutectic solvents (DES) choline chloride/ ethylene glycol and choline chloride/citric acid as efficient templating agents is reported. The characterization of the synthesized samples was done by XRD, TEM, SEM, UV-Vis diffuse reflectance spectroscopy, EDX and photoluminescence (PL) studies. The XRD analysis confirmed the presence of hexagonal wurtzite structure of ZnO and the morphology results demonstrated structure directing effect of deep eutectic solvents. Strong green emission related to oxygen vacancies and defects of the ZnO nanostructures was shown by photoluminescence spectra. The synthesized flower-like ZnO nanostructure showed higher photocatalytic degradation efficiency for methyl orange as compared to commercially available ZnO powders.

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M147

Tunable ZnO spheres *via* a simple starch assisted hydrothermal route

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Keywords: Green chemistry, Carbohydrates, ZnO, Antibacterial activity

Abstract

The developing of some synthetic eco-friendly routes for materials with new properties/performances that minimizes or eliminates the adverse consequences to humans and biosphere represents reasons for the increased interest toward Green Chemistry [1].

The use of carbohydrates (non-toxic compounds, renewable and widely available in great amounts) in the synthesis of various materials oxides synthesis as stabilizers and templates may represent a resourceful green approach of advanced materials *design*/synthesis [2].

The attractive and unique characteristics of ZnO, a bio-safe and bio-compatible semiconductor, together with its huge variety of morphologies, made it a valuable key functional material for applications in different fields [3].

A simple and totally green one-pot hydrothermal route which involve starch biopolymer, followed by an adequate thermal processing, leads to distinct ZnO morphologies - hollow, compartmented, core-shell and full solid ZnO spheres, dispersed or interconnected. The variation of the raw materials concentration dictates the type of ZnO spheres morphology. The carbonaceous precursors were characterized by infrared spectroscopy, thermal analysis and scanning electron microscopy, while the ZnO spheres, obtained after the calcination, were investigated by X-ray diffraction, Raman spectroscopy, scanning electron microscopy, UV-VIS spectroscopy, photoluminescence measurements, antimicrobial, anti-biofilm and flow cytometry tests. The formation mechanism of the ZnO spheres was also proposed. The materials exhibit high antibacterial and anti-biofilm activity against Gram-positive and Gram-negative bacteria, demonstrating great potential for new ZnO anti-biofilm formulations.

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M148

Scale-up of industrial biocatalyst production using sugar beet vinasse as a fermentation feedstock

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Keywords: miniature microbioreactor, scale-up, ω-Transaminase, vinasse, oxygen transfer coefficient (k_La).

The use of renewable resources for bio-production offers routes for the development of green bioprocesses that could serve as interesting alternatives to fossil fuel based processes. This work is concerned with the scale-up of industrial biocatalyst production from sugar beet vinasse with an emphasis on transaminase (TAm); an enzyme useful for chiral amine synthesis. Vinasse is a major by-product of ethanol production from sugar crops. For every litre of ethanol produced, approximately, 9 - 15 litres of vinasse is generated. As the demand for the ethanol is expected to increase in future, large quantities of vinasse will also be produced whereby the disposal has become a major ecological challenge due to its high biological oxygen demand (BOD). Alternatively, there is an increasing trend to reutilise vinasse for bioconversion as it consists of several useful feedstocks such as glycerol. Our preliminary results have shown the feasibility of using vinasse as a fermentation feedstock for TAm production in *E. coli*. Following that, we also have established an optimal production of TAm using dilute vinasse supplemented with yeast extract in 24-well miniature microbioreactor (6.5 mL). Here, we further examined strategies to scale-up the TAm production from the microbioreactor to conventional stirred tank bioreactor (STR, 5 L). Prior to scale-up, several options of sterilisation of vinasse were first evaluated. In this work, the scale-up strategy was based on similar oxygen transfer coefficient (k_La). Our results have shown that the optimised production of TAm from vinasse as achieved in microbioreactor was successfully reproduced at laboratory scale STR. Similar trends of cell growth, glycerol consumption and TAm production were observed in both scales. In general, the results from this study confirmed the promising scale translation of TAm production using sugar beet vinasse from microbioreactor to higher scale under a defined scale-up criterion.

M149

TiO_2-coated magnetic core–shell nanocomposites for enhanced photocatalytic activity

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Keywords : Magnetite nanoparticles, Titanium, Photocatalyst, Organic pollutant

Abstract

The global lack of clean water for human sanitation and other purposes has become an emerging dilemma for human beings. The presence of organic pollutants in wastewater produced by textile industries, leather manufacturing and chemical industries is an alarming matter for a safe environment and human health. For the last decades, conventional methods have been applied for the purification of water but due to industrialization these methods fall short. Advanced oxidation processes and their reliable application in degradation of many contaminants have been reported as a potential method to reduce and/or alleviate this problem. Lately it has been assumed that incorporation of some metal nanoparticles such as magnetitenanoparticles as photocatalyst for Fenton reaction which could improve the degradation efficiency of contaminants. Core/shell nanoparticles, are extensively studied because of their wide applications in the biomedical, drug delivery, electronics fields and water treatment [1].

In this work, a facile, green, and efficient approach for the fabrication of $Fe_3O_4/SiO_2/TiO_2$ photocatalyst has been demonstrated. Magnetically separable $Fe_3O_4@SiO_2@TiO_2$ composite with good core–shell structure were synthesized by the deposition of uniform anatase TiO_2 nanoparticles on $Fe_3O_4@SiO_2$ using tetraethoxysilane (TEOS) as silica source and tetrabutyl titanate (TBOT) as titanium sources. The diameter of SiO2@Fe3O4 core was about 72 nm with thickness of TiO2 of about 12 nm.

The as synthesized catalysts were characterized using HRTEM, HRSEM, X-ray Diffraction; N2 adsorption analysis, Infra-red Spectroscopy and Energy Dispersive Spectroscopy.

The magnetic catalysts was found to be highly efficient in the removal of hazardous dye methylene blue (MB) from aqueous solution. The results showed that the $Fe_3O_4/SiO_2/TiO_2$ superior to that of Degussa P25 titania and uncoated Fe_3O_4/SiO_2 and demonstrated that the rate of photodegradation of MB is was observed within 60 min. The results indicate that the catalytic activity was still present after recycling the photocatalysts three times.

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M150

Adsorption of Cs^+ from aqueous solutions using Na- and H-type titanate nanotube adsorbents

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Keywords: Adsorption, Cesium, Titanate nanotube, Cation-exchange

Abstract

By the disaster of nuclear power plant at Fukushima, Japan, large amounts of radioactive elements such as ^{137}Cs and ^{90}Sr were released and they contaminated soil, forest, and seawater. Especially, ^{137}Cs is known to be a beta-gamma emitter with half-life of about 30 years. High accumulations of this element causes serious environmental and human health problems [1]. Various methods have been used to remove Cs^+ such as precipitation, adsorption, electrodialysis, solvent extraction, etc. Among these methods, Csremoval by adsorption via the cationic exchange is one of the most important methods because this process can achieve high amount of Cs removal and an easy, safe, environmentally friendly and low cost operation. However, the highly effective adsorbents for Cs removal have been continuously studied.In this research, various types of titanate nanotubes (TNT), Na-TNT and H-TNT, were prepared by the hydrothermal treatment using TiO_2-P25 referring to a literature procedure [2]. Characterization by XRD revealed successful synthesis of Na-TNT and H-TNT, having monoclinic layered-structure trititanate. The performance of Na-TNT and H-TNT in Cs removal was investigated and was compared with ZSM-5. Na-TNT showed the highest Cs removal performance with a maximum capacity 1.84 mmol/g, whereas H-TNT exhibited the lowest performance. This suggested that Na-TNT was promising in Cs removal.

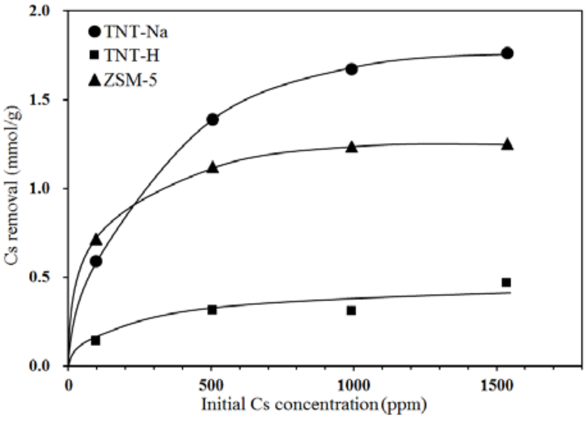

Fig. 1 Effect of initial Cs concentration on Cs removal with Na-TNT, H-TNT, and ZSM-5.

Conditions : initial Cs concentration 100-1500 ppm, 50 ml of Cs solution, pH 5.8, contact time 0.5 h, adsorbent 50 mg

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M151

Green Technique of Coating Propyldiethylenetriamine-silica Hybrid on Magnetite for adsorption of Gold(III)

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Keywords: Magnetite, Silica, Gold, Adsorption, Diethylenetriamine

Abstract

Magnetic material containing active groups has recently gained much attention in applications as an adsorbent of precious metals such as gold from aqueous solution. Zhang et al. reported coating magnetite (Fe_3O_4) with mercapto modified silica through silanization reaction for adsortion of gold(III)[1]. This is not a green process because involving reflux with free water toulena. Additionally, due to strong interaction of mercapto (–SH) groups and gold(III) causes difficulty in removal of gold(III) from the adsorbent. In previous research, a green (sol-gel) process for modification of –SH groups on silica coated Fe_3O_4 has been carried out [2]. Hence, we report the synthesis ofpropyldiethylenetriamine-silica coated magnetite (Fe_3O_4@SiO_2@PDETA) throuh a simple and green technique (sol-gel process) for adsorption of Au(III) from $[AuCl_4]^-$ solution. At low pH ammine groups (–NH) protonated into positive charge ammonium groups may interact electrostatically and reversibly with anion of $[AuCl_4]^-$.

Magnetite was prepared through co-precipitation technique of Fe^{2+}/Fe^{3+} solution with the dispersion agent of citric acid solution and was washed with various solvents. Magnetite was coated through sol-gel process using two different techniques in mixing the precursors and at various mole ratios of sodium silicate (Na_2SiO_3)solution to N-[3-trimethoxysilil)propyl]diethylene-triamine (TMSPDETA). The product was then characterized with infrared spectrophotometer, x-ray diffractometer, scanning electron microscope-energy dispersive x-ray, vibrating sample magnetometer and transmission electron microscope. Adsorption of Au(III) on Fe_3O_4@SiO_2@PDETA was conducted by mixing $HAuCl_4$ solution containing 204 mg/L Au(III) and adsorbent in a batch system at pH 3 for 120 min. The Au(III) containing adsorbent was separated from the solution with an external magnetic field.

Result showed that Fe_3O_4 dispersed with sodium citrate and washed with acetone-water solvent gave smallest aggregate. Route 1, where acidized magnetite was added into a mixture of Na_2SiO_3 solution andTMSPDETA, generated Fe_3O_4@SiO_2@PDETA with higher content of propyldiethylenetriamine groups than Route 2 (Na_2SiO_3 solution andTMSPDETA were added sequentially to acidized magnetite). Coating magnetite with propyldiethylenetriamine-silica made the product to be lower in magnetization but it did not lose the capability to be attracted with an external magnetic field. Fe_3O_4@SiO_2@PDETA synthesized through Route 1 with the mole ratio of Na_2SiO_3 to MSPDETA 1:2 gave highest capability in adsorbing Au(III) (182 mg/g).

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M152

Obtaining biologically active substances by culturing methanotrophic microorganisms using low level of methane in natural gas

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Keywords:«Gaprin», methanotrophic bacteria, biotechnology, biomass.

Abstract

It is well known that one of the perspective directions of the use of natural gas is its biological conversion of the methanotrophic microorganisms. This technology has already been developed and implemented in the last century and it involved the use of natural gas as raw material and obtained microbial biomass contained 70-75 % proteins. In addition to protein, the biomass contained significant number of growth factors, vitamins etc [1]. It should be noted that methanotrophic microorganisms, due to metabolic properties, are capable to assimilate only methane and products of its partial oxidation, while natural gas contains associated gases (such as ethane, propane, etc.). In this case the impurity gases are oxidized by enzymatic system of methanotrophs (methanemonooxygenases), but it is not assimilated and accumulated in the environment and inhibit the growth of target culture of microorganisms. According to that, it was proposed to use a community of microorganisms, which are associated with methanotrophs microorganisms and assimilate the products of oxidation of the impurity gases, thereby removing their inhibitory effect. The composition of this community and the balance between different microorganisms depends on the compound of the gas mixture. In recent years the interest in the use of microbial communities on the basis of methanotrophs for processing methancontainig gases of different composition increased significantly. This approach does not allow obtaining high-protein feed additive, but the resulting biomass is a perspective raw material for highlighting a wide range of valuable biologically active substances. In preliminary studies, when methanotrophic microorganisms were cultured, possibility to grow a biomass with a high content of polysaccharides, particularly exopolysaccharides was obtained. These biopolymers can form gels of different density. Due to this property, exopolysaccharides are used extensively in the food, pharmaceutical, medical, textile and oil industries. Polymer producers are communities that are based on methanotrophic Methylomonas Methylococcus bacteria [2]. Furthermore, in stressful conditions, an increased synthesis of antioxidant pigments was obtained when methanotrophic microorganisms biomass was cultured using low-level of methane gases. These products are actively used in medicine, agriculture, and cosmetics [3].

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M153

In situ loading and release of drugby mesoporous silica SBA-15

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Keywords: Heparin, drug releaser, one-pot synthesis, mesoporous silica, SBA-15

Abstract

Mesoporous silica vessels have been utilized for drug delivery, but the drug loading process is tedious and loading amount is limited. Herein, evaporation-induced self assembly (EISA) is employed to *in situ* load hydrophilic drug heparin and hydrophobic ibuprofen into the micelles/mesoporous silica vessels. Heparin is widely utilized for vein thrombosis and pulmonary embolism, Ibuprofen (IBU) is for anti-inflammatory andanalgesic drug. P123 is elected as structure-directing agent to construct mesoporous vessel and the initiator to control drug release. The stability of the micellar "core" encapsulating drug in vessel will be stabilized by the mesoporous silica "shell", and all drugs can be *in situ* introduced into vessel during synthesis process, avoiding the time for drug-adsorption and the waste of drug in traditional post-loading route.

0.5 g of P123 was dissolved in5 g water and 0.25 g of 2 M hydrochloric acid at 298 K, followed by addition of heparin along with TEOS was added.After treatment at 310 K, monolith sample PH-n formedwhere nmeans the amount of heparin in synthesis. PI-n vesselcontainingIbuprofen was prepared in similar procedure.

PH-n samples showed one XRD peak with 2θ value of around 1^{o} that indexed as the (100) diffraction of SBA-15 mesoporous silica.Proper heparin additive promoted the orderedmesoporous structure, increasingthe amount of micropores from 95 to 128 $m^{2}\cdot g^{-1}$.*In situ* loading heparin in EISA synthesis increased the drug within vessel. PH-250 had the heparin of 167 mg g^{-1}, 4 times higher than that in SBA-15[1].Also, PH-nreleased more heparin than SBA-15 did, along with a higher release/loaded ratio. SBA-15 released 15.5 mg g^{-1} of heparin, 53.4% of that loaded (29 mg g^{-1}). In contrast, PH-125 had the ratio of 62.8% (51.7 to 82.3 mg g^{-1}). PH-250 vessel exhibited the largest heparin content (167 mg g^{-1}) hence it released the largest amount (104 mg g^{-1}).Hemolysis test was conducted to evaluate the blood compatibility of PH-n vessel, and the obtained value was 2.7%, 1.7%, 1.5%, and 0.6% for PH-50, PH100, PH150, and PH-250 composites, respectively. All these values were much lower than the permissible hemolysis level of 5%.

IBU was immobilized into PI-n composite up to 200 mg g^{-1} that was 166% higher than that on SBA-15 (75 mg g^{-1}[2]). PI-300 vessel kept the release of 12 h, longer 5 h than SBA-15 did, and all of the IBU immobilized were released. PI-n had the larger release/loaded ratio (89.9~100%) than that of SBA-15 (66%). *In situ* drug loading saving sample preparation time from about 74 h to 10 h. Utilizing template micelles to adjust the release of drug.The immobilized amount of heparin or IBU in vessel was enhanced to 167 or 200 mg g^{-1}, giving a sustainable release longer than 30 days. The concept of new drug-releaser with "soft core" of micelles and "hard shell" of mesoporous silica will be useful to develop new biomaterials.

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M154

Chemical Composition and Fumigant Toxicity of *Chenopodium ambrosioides* L. Essential Oils against *Callosobruchus maculatus.*

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Keywords: Essential oils, Epazote, bio-pesticide, *Callosobruchus maculates,* chickpea grains.

Abstract

Stored grain pests were currently controlled by chemical pesticides. This control method leads to several problems including pollution of the environment, pest resurgence, lethal effect on non-target organisms, increasing cost of applications and intoxication of consumers. So, to promote environmental sustainability, essential oils of aromatic plants are more considered as good control alternative tools [1-4].
Hence, the objective of the current study was to determine the chemical constituents and bio-pesticide toxicity of the essential oils extracted by hydro-distillation from the aerial parts of *Chenopodium ambrosioides* L. (Mexican tea, Epazote) growing in Algiers regions (Birkhadem and Boumerdès).

The chemical composition of these essential oils was investigated by GC/FID and GC/MS using two capillary columns of different polarities, CP-SIL-5CB and DB-WAX. Mass spectra and retention indices were used to identify a total of 21 compounds. The major constituents were: cis ascaridole (82-74.9%), p-cymene (2.9-8.5%), α-terpinene (0.6-2.4%) and carvacrol (3.9-3.9%), respectively in Birkhadem and Boumerdes oils.
The fumigant toxicity of these essential oils was assessed under laboratory conditions against *Callosobruchus maculates,* an important insect observed in chickpea grains (*Cicer arietinum*).
A little piece of cotton treated with 470µL/L air of test essential oil was placed in the bottom cover of a plastic bottle. Twenty insects per bottle (0 to 24 hours old), were exposed for 4, 6, and 9 hours. All treatments were replicated four times. Probit analysis was conducted to estimate the lethal fumigation times LT_{50} and LT_{90} for each essential oil. The results showed a significant level of toxicity.

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M155

Isolation of flavonoids from *Acacia albida* leaves and evaluation of antihyperglycaemic effects of its extract

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Keywords: *Acacia albida*, flavonoids, anti-diabetic

Abstract

Diabetes mellitus is a chronic disease caused by inherited and/or acquired deficiency in production of insulin by the pancreas, or by the ineffectiveness of the insulin produced. The present study deals with the isolation and identification of the flavonoid constituents from *Acacia albida* leaves and evaluation of antihyperglycaemic effect of an aqueous methanol extract. The aqueous alcoholic extract (MeOH:H_2O, 7:3) of *A. albida* leaves was subjected to extensive repeated column chromatography on polyamide, cellulose and Sephadex LH-20, resulting in isolation of quercetin-3-***O***-β- glucopyranoside, kaempferol 3-***O***- β-glucopyranoside, quercetin-3-***O***-α-L-rhamnopyranoside, kaempferol 3-***O***-α-L-rhamnopyranoside, quercetin-3-***O***--α-L -arabinoside, quercetin and kaempferol. The structures of the isolated compounds were elucidated on the basis of spectral analysis (UV, HRESI-MS and 1D/2D $^{1}H/^{13}C$ NMR spectroscopy). The extract was tested in two dose levels 100 and 200 mg/kg (orally using an intra-gastric) for 4 weeks. At baseline, fasting blood glucose levels of streptozotocin-diabetic rats were elevated to (378.16±25.27 mg/dl) compared to control value. Treatment with the plant extracts significantly reduced blood glucose in a dose dependent manner in treated rats. The *Acacia albida* extract also significantly decreased total cholesterol (120.50±3.26; 102.33±1.56 mg/dl), triglyceride (144.66±2.74; 113.33±3.48 mg/dl) and increased HDL (52.50±1.66; 55.16±2.00 mg/dl) in lower and higher dose compared with streptozotocin-treatment alone. The extract failed to produce hyperglycemic activity in control rats. The chemical constituents of the plant, especially phenolics and other compounds present in the plant may be involved in the observed hypoglycemic effect of the plant extract [1]. The results show that the oral administration of *A. albida* leaf extract on the diabetic state reduced hyperglycemia in this model.

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M156

Fabrication and characterization of p-Si/n-MgZnO heterojunction diode

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Keywords: ZnO, Mg doped, Microwave assisted chemical bath

Abstract

Semiconductor nanorods represent a novel class of materials structure with a number of interesting properties that give them potential applications in optoelectronic devices, including light-emitting diodes (LEDs), photoelectrochemical systems, and solar cells. A chemical bath deposition (CBD) is attracting attention as low-cost film formation processes. In these processes, nucleation and crystal growth on substrate in solution result in the formation of metal−oxide films. We present a fundamental experimental study of a microwave assisted chemical bath deposition (MW-CBD) method for Mg doped ZnO films. The MW-CBD method was used to prepare nanorod Mg doped ZnO (1% and 10%) films onto p-Si substrates. Zinc nitrate hexahydrate and magnesium nitrate were the precursor materials and doping source materials. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) spectroscopy had been used to analyze the morphological properties and structures of this films products, respectively. The current density–voltage characteristics (*I–V*) of the diodes were measured at room temperature. The important junction parameters such as series resistance (R_s), the ideality factor (n) and the barrier height (ϕ_b) were determined by performing different plots from the forward bias *I–V* characteristics. Norde function was compared with the Cheung functions and it is seen that there is a good agreement with both method for the series resisance values.

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M157

Investigation of structural and optical properties of Nickel doped ZnO deposited by MW-CBD method

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Keywords: ZnO, Ni doped, Microwave assisted chemical bath,

Abstract

Transparent conducting oxides having a wide band- gap (>3.0eV) are being used extensively for photovoltaic and optoelectronic devices. The physical characteristics of ZnO can be successfully optimized by doping as well as optimizing the various processing conditions. Among them, doping of ZnO with Ni is interesting as these tend to improve its optical, electrical, morphological and structural properties. In this work, we present the study on the variation on the Nickel content on the crystalline quality and optical properties of ZnO obtained by microwave chemical bath deposition (MW-CBD) on to n-Si substrate. The p-Si substrates were cleaned using the suitable procedure. 0.1 M zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$;ZnNt), nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$;NiNt) and an equal molar concentration of hexamethylenetetramine ($C_6H_{12}N_4$;HMTA) were dissolved in DI water. Doping precursor various amount of NiNt added separetly into the aqueous ZnNt+HMTA solutions. The solution was stirred 2 h at 90 °C. After, solution was irradiated using a temperature-controlled microwave synthesis system at 600 and irradiation times 10 min. The films were washed with DI water to remove the remaining salt. Finally, the films were dried at 60^{o}C for 1 h. Structural characterization of the layers was carried out using X-ray diffraction (XRD). Field emission scanning electron microscope (FESEM) was used to analyze the surface morphology of the ZnO films. The diffuse reflectance spectra of the Ni doped ZnO films were measured and the optical band gap values were determined using Kubelka–Munk theory.

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M158

Plant Oils: Greening Agriculture to Polymer Materials

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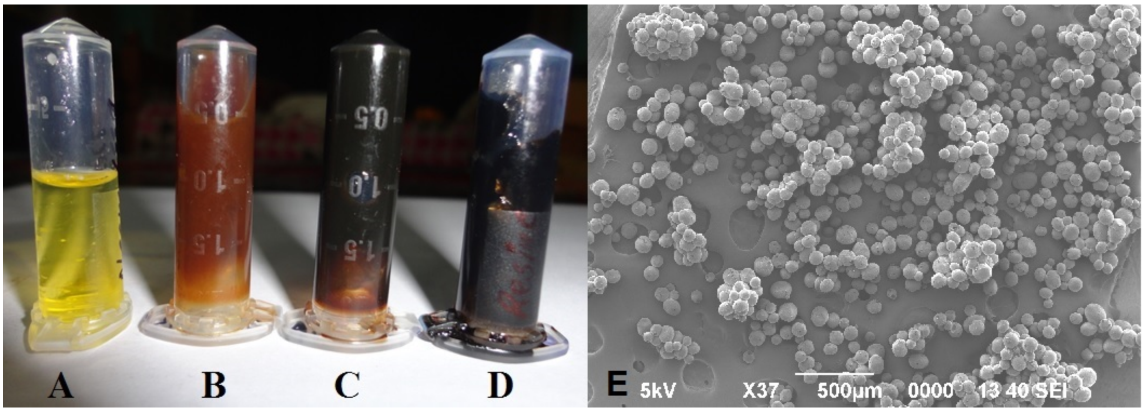
Keywords: Neem seed oil, Encapsulation, Polyelectrolyte complexation, Characterization

Abstract

Azadirachta Indica A. Juss., commonly known as the ‘neem’ is a fast growing tree that belongs to *Meliceae* family. Neem seed oil (NSO), a potent natural pesticide (Fig. A) has been encapsulated and exploited as controlled release pesticide for agricultural applications[1]. Olive oil and curcumin have also been used for encapsulation. Smart spherical carrier particles with varied sizes (nano/micro) and morphology (porous/nonporous) were synthesized by using natural polymers from renewable resource (Fig. E) [2]. Polyelectrolyte complexation behavior of natural polymers such as gelatin and sodium carboxymethyl cellulose/sodium alginate/carrageenan was studied for encapsulation of suitable active agents. The encapsulation efficiency of the active agents was dependent on the amount of crosslinker, oil/drug loading and polymer concentration. The particles were found to be pH responsive. The morphology, particle size and distribution characteristics of these micro/nanocarriers were studied by using SEM, TEM and DLS techniques. All the micro and nanocarrriers were further characterized by FTIR, NMR, XRD, TGA and DSC studies. In another study, alkyd resins (Fig. B, C, D) based on purified NSO were synthesized by two-stage alcoholysis–polyesterification reaction of this oil with phthalic and maleic anhydride. The synthesized alkyd resins were characterized by the FTIR and ^{1}H NMR spectroscopic analysis. Resins were cured by blending with epoxy resin. The coating performance tests revealed that NSO is a good source of renewable raw material having the potential to synthesize plant oil based alkyd resins for the coating industry.



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M159

Microwaves/ball mills-assisted preparation of solid supported Pd-NPs catalyst on cyclodextrin-grafted silica

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Keywords: Microwaves, Planetary Ball Mill, Cyclodextrin, Green catalysis, Silica-supported catalyst

Abstract

The so called *enabling technologies,* create high-energy microenvironments that can be exploited in the field of material functionalization and grafting [1]. With the aim to create new smart materials, reactive cyclodextrins (CD) have been used to graft surfaces under non-conventional techniques [2]. Herein we describe two efficient synthetic protocols to provide a high degree of β-CD grafting onto silica particles, either applying MW irradiation or using a solvent-free planetary ball mill procedure [3].

In the last years the development of highly efficient nanocatalysts and the optimization of metallic nanoparticles (NPs) preparation, has tremendously attracted the scientific community. Palladium-based catalysts remain the most versatile and powerful tool in organic reactions. Silica has found widespread use in the preparation of solid-supported Pd-NPs based on its capacity to host metal nanoparticles (NPs) in the pores, enhancing their stability and reactivity. In this context our new silica derivative was loaded with Palladium to obtain supported Pd nanoparticles [4]. The silica-supported catalyst (Pd/Si-CD) exhibited excellent activity in ligand-free C-C Suzuki and Heck couplings over a large number of aryl iodide and bromides, in which MW irradiation cuts down reaction time. Pd/Si-CD have shown high activity and selectivity in the hydrogenation reaction, and the semihydrogenation of phenyl acetylene was also studied with excellent results.

Acknowledgement

The authors ackowledge the Organic Chemistry Division of the Italian Chemical Society (SCI) for financial support.

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M160

Mustard carbonate analogues: influence of the leaving group on the neighboring effect

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Keywords: Dialkyl Carbonate, Alkylation; Halogen-free, Neighboring effect, Leaving group.

Abstract

The substitution of a chlorine atom with a carbonate moiety in mustard compounds has led to a new class of molecules, namely mustard carbonates that retain the reactivity of the well-know toxic iprites, but are safe for the operator and the environment [1].
Herein we report the influence of the leaving group on the neighboring effect of sulfur half mustard carbonates (HMCs) usually less reactive than nitrogen ones [2]. Several new 2-(methylthio)ethyl alkyl carbonates have been synthesized and their reactivity has been investigated in both autoclave and neat conditions. The results reactions between the HMCs and phenol performed in autoclave (180 °C, no base, in acetonitrile media) showed that the efficiency of the anchimeric effect is directly dependent on the steric hindrance of the HMC leaving group. The least steric hindered 2-(methylthio)ethyl methyl carbonate gave the methyl (2-phenoxyethyl)sulfane in higher yield, whereas the most steric hindered 2-(methylthio)ethyl *t*-butyl carbonate did not reacted at all. The influence of the leaving group on the anchimeric effect has been also investigated in neat conditions at 150 °C in the presence of catalytic amount of K_2CO_3. In this case, due to the absence of the solvent and the presence of the base the reaction is more complicated by transesterification reactions and formation of unwanted products. Interestingly 2-(methylthio)ethyl ethyl carbonate showed to be the most efficient carbonate among the ones studied. This resulted might be ascribed to its ability to free the cyclic intermediate from its *molecular cage* as intimate ion pair more readily than the other HMCs. Finally, several nucleophiles have been then tested in neat reaction conditions using 2-(methylthio)ethyl ethyl carbonate and a catalytic amount of base. In all cases studied it was observed an almost quantitative anchimeric aided alkylation over S_N2 reaction, i.e., formation of ethyl aryl ethers. The best results achieved have led to an enhanced product selectivity, more accessible reaction conditions and a better insight on the reaction mechanism of mustard carbonates.

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M161

ACCUMULATION OF WATER HYACINTH (*Eicornia crassipes*) AT THE MOUTH OF THE CONGO RIVER: "Status report on the availability of basic nutrients in water and ability to generate high value added oligomers"

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Keywords: Proliferation, Eicornia, Congo River, mouth, oligomers.

Abstract

Congo is a long river of 4700 Km with a flow of 41,000 m3/s. It is highly threatened in recent years by the uncontrolled proliferation of *Eicornia crassipes*. This plant has upset the local ecosystem. It is in this context that our study enrolled. For this purpose, water samples were taken at the mouth of the Atlantic Ocean.

The water temperature varies little from one site to another, so no significant difference ($P> 0.05$): minimum 28.4 °C downstream of the mouth of the Congo River and maximum 29.23 °C is observed upstream. This temperature change is probably the metabolic reactions that occur in the streams [4]. The average values of pH on all sites are between 7.6 and 8.4. There is no significant difference between sites ($P> 0.05$). These results corroborate those found on the River Niger [1]. The chemical oxygen demand (COD) is 1 mg/l upstream and 1.66 mg/L, respectively, with no significant difference ($P> 0.05$) between values from one site to another. COD is used to evaluate exactly the amount of biodegradable or non-biodegradable organic matter [2]. The total nitrogen concentration varies from 17.66 mg/l à15,94 mg/l of the upstream to downstream. The highest concentrations of total phosphorus (3.71 mg/l) are recorded on the left bank at the mouth of the river. The authors found that submerged plants absorb phosphorus as well as by the roots by the rods [3].

There is no significant correlation between physicochemical characteristics and density *Eicornia crassipes*. It would be desirable to develop a technology for the integral use of biomass *Eicornia crassipes* to generate high value added oligomers.

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GREEN BIOPROCESSES

B201

The role of Ag^{+}, La^{3+}, and Nb^{5+} in the Cu-Mg-Al amorphous mixed oxides as catalyst for C_4 and C_6 Guerbet alcohols synthesis from hydrous bioethanol

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Keywords: Guerbet alcohols, hydrotalcites, mixed oxides, aldol condensations, catalytic dehydrogenation.

Abstract: The catalytic conversion of bioethanol by aldol reactions in chemicals known as Guerbet alcohols may be achieved by the dehydrogenation and decarbonation processes under self-generated supercritical conditions [1]. The reaction takes place over non noble metal Earth-abundant mixed oxides derived from the calcination (460 °C) of synthetic hydrotalcites (HTCs) ($Mg_6Al_2(CO_3)(OH)_{16}.4H_2O$) modified replacing 10% of Mg^{2+} ions by Cu^{2+}. This process is very promising in being coupled to sugarcane mills, where there is availability of ethanol and energy at low cost. The catalysts were prepared by coprecipitation at pH~10 of suitable amounts of metal nitrates with molar ratio $3M^{2+}/Al^{3+}$ in Na_2CO_3 solution and kept under agitation at 60 ºC for 4 days [2]. The reactivity and selectivity of the oxides with the addition of 1% (w/w) of metal ion of different valences, acidity and ionic radii as Ag^{+}, Nb^{5+} and La^{3+}were assessed. The reactions were carried at 320 °C for 5 h in 10 mL stainless steel reactors containing 100 mg of oxides and 3 mL of hydrous ethanol (96%). In the end, the volume of gas generated, not condensed at 0 °C was measured by the principle of Archimedes and the ethanol conversion was determined by GC-FID. The reaction products were identified and quantified by GC-MS. There is a good correlation between the ethanol conversion and the volume of the gas generated in the process. The reference catalyst containing only CuMgAl gave 32% ethanol conversion into two predominant aliphatic alcohols: n-Butanol (60%) and n-Hexanol (8%). The presence of Nb^{5+} in the catalyst did not cause significant changes in both consumption of ethanol (30%) and selectivity (51% n-Butanol and 11% of n-Hexanol). The highest ethanol conversion (52%) and selectivity ratio (1% n-Butanol and 27% n-Hexanol) was achieved with the addition of the La^{3+} in the catalyst. The addition of Ag^{+} reduced the consumption of ethanol to 23% and selectivity to 45% n-Butanol and 11% n-Hexanol. Dozens of other minority compounds were produced in this process and also suffered variations in their concentrations as a function of the dopant ion. The results indicate that it is possible to modulate the reactivity and selectivity of the mixed metal oxide HTC derivatives in conversion of ethanol to C4 and C6 alcohols. The H_2 andCH_4 produced in the process could be recovered or burned to heat the reactor system, giving more economical feasibility to the process.

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B202

Enzymatic hydrolysis and anaerobic biodegradation of PBAT

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Keywords:*Clostridium hathewayi*, anaerobic digestion, esterase

Abstract

Since a few years biodegradable polyesters have become the focus of research because they combine beneficial material properties with biodegradability in a range of habitats. One example is the aliphatic‒aromatic copolyester PBAT (poly(butyleneadipate-co-butyleneterephthalate) which is a synthetic polyester used, for example, in food packaging or organic waste bags. PBAT is proven to be compostable, which makes it an important raw material for many compostable and biobased plastics. In recent years, alternative biological treatment as anaerobic digestion of organic household wastes has gained importance which is stressing the need to study biodegradability of aliphatic‒aromatic polyesters also under anaerobic digestion since there is considerably less information available on degradation in anaerobic environments. In the microbial degradation of polyesters, hydrolysis by extracellular enzymes is the first step to produce oligomers and monomers, which can be further metabolized in the microbial cell. Thus, enzymatic hydrolysis of PBAT has studied but focus has been on aerobic hydrolases such as the cutinase from *Thermobifida cellulosilytica* or *Humicola insolens*[1] and esterases from *Clostridium botulinu*[2]. Consequently, the potential of anaerobic biogas sludge to hydrolyze PBAT was evaluated in this study. Accumulation of terephthalic acid (Ta) was observed in all anaerobic batches within the first 14 days. Thereafter, a decline of Ta was observed, which occurred presumably due to consumption by the microbial population. In addition, an esterase from a typical anaerobic microorganism namely *Clostridium hathewayi* (Chath_Est1) (anaerobic risk 1 strain) was identified and proved active towards PBAT. Detailed characterization of Chath_Est1 including elucidation of the crystal structure as well as characterization towards PBAT model substrates and PBAT film was performed. The present study gives a hint about how and by which kind of microorganisms these manmade plastics could be biodegraded in anaerobic environments. The knowledge about microorganisms able to hydrolyze polyesters as PBAT could also open the door for new applications, such as the addition of cell or spore suspensions to biogas plants to enhance the anaerobic biodegradation of biodegradable polymers that are, for example, used in food packaging or organic waste bags.

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B203

Enzymatic systems for oxidative cross-linking of coating polyesters

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Keywords: Laccase, Alkyd resins, Mediators, Oxidation, Cross-linking

Abstract

During the past. usage of enzymes in industrial applications has become more and more common. Currently, enzymes are used in different products like detergents, textiles, pulp and paper production and food. Regarding the coating industry, it could be envisaged that in future enzymes will be used as drying agents – so called siccatives – as coating removers or even as acticides. In this work, we investigated the potential use of laccases as siccatives for coatings containing alkyd resins.

Alkyd resins are polyesters containing unsaturated fatty acids that are used as binders in coating formulations. During the hardening process the unsaturated groups get oxidized and consequently cross-linked. Cobalt complexes are the most used conventional siccative systems, but due to the fact that cobalt catalysts are suspected to be carcinogenic, the coating industry has to replace those heavy-metal systems.

We demonstrate an environmentally friendly enzyme based system for the curing of alkyd resins. The potential of a laccase from *Trametes hirsuta* (*Th*L) in combination with different electron mediators was evaluated regarding its capability to crosslink the unsaturated fatty acids and consequently harden the resin. Because water and oxygen are the only product and educt respectivly, laccase presents an environmentally friendly approach to harden alkyd resins.

The oxidation of the alkyd resin using the laccase mediator system was followed by monitoring the oxygen consumption during the crosslinking process with an optical oxygen sensor. Using this method, the measurable decrease in air saturation after the addition of alkyd resin to the preoxidized mediator was correlated to the extent of the oxidation. Additionally, to reveal more mechanistic details on a chemical level of the drying reaction FTIR spectroscopy was used.Finally the drying performance of the laccase mediator system was measured and compared with the cobalt catalyst using the drying time recorder. This method is widely used and accepted in the coating industry to measure the drying performance of new products or formulation additives. The distribution of the enzyme within the alkyd resin film was monitored using the confocal laser scanning microscope (CLSM) after labeling the enzyme with a fluorescent dye.

The different methods prove that this enzymatic system is an alternative to toxic heavy metals that are conventionally used in alkyd resins, which sooner or later become inacceptable in coatings and related products.

B204

Biotransformation of Epiandrosterone by *Aspergillus candidus*

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Keywords: Biotransformation, Epiandrosterone, *Aspergillus candidus*

Abstract

Fungal steroid biotransformations have been widely used for a long time in order to convert and synthesize steroids since they can be carried out by their remarkable regio- and stereoselectivities. A number of efforts are still made to improve the efficiency of fungal steroid biotransformations and to obtain new useful reactions and species [1].

Aspergillus is a very well-known fungal genus in terms of mycotoxins, pathogenicity, fundamental eukaryotic genetics and biotechnological exploration [2]. *Aspergillus* species are ubiquitous fungi found in soil, water, and decaying materials. A few *Aspergillus* species are considered pathogenic to humans and animals [3].

Aspergillus candidus is a moderately xerophilic white mold, a food contaminant in cereals and an opportunistic pathogen for humans [4]. As far as steroid biotransformations by *A. candidus* are concerned, there is only one literature work on steroids such as dehydroepiandrosterone, pregnenolone and progesterone [5].

In this work, epiandrosterone **I** was incubated with *Aspergillus candidus* MRC 200634 for 5 days. Incubation of epiandrosterone **I** with *A. candidus* mainly afforded hydroxylated metabolites, accompanied by some minor metabolites reduced at C-17 or oxidized at C-3.

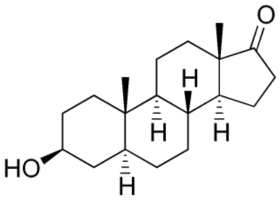

Figure 1. Epiandrosterone (**I**)

The metabolites were separated by column chromatography. Structure determinations of the metabolites were performed by comparing melting points, NMR and IR spectra of starting materials with those of metabolites.

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B205
Termochemical Conversion of Castor Oil for the Production of Aviation Turbine Fuels

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Keywords: Castoroil,aviation jet fuel,hydrodeoxygenation, carbon deposition resistance

Abstract

Castor oil is important multifunctionalnon-edible oil, considered a vital industrial raw material. Still, few studies are available regarding its aviation fuel application[1]due to its highkinematic viscosity and oxygen contentwhich does not meet the appropriate ASTM D7566 standard limits. In this work, high quality and yield bio-aviation fuel can be produced by hydrodeoxygenation (HDO) and hydroisomerization technology over Ni-Mo supported on modified Al_2O_3 and Ni-W/SAPO-11 in a continuous-flow fixed-bedmicroreactor as shown in Fig.1. Carbon deposition and water production is the main reason for the HDO catalyst deactivation because of high oxygen content of castor oil. The results showed that TiO_2 modified Al_2O_3improved the water and carbon deposition resistance as investigated in TGA, BET analysis and catalyst life test, which has important consequences for industrial production. The HDO products (C_{17}–C_{18}) were subsequently converted into C_8–C_{16} using Ni-W/SAPO-11 in extremely mild conditions of 260 ^{o}C, 3 MPa, 1 h^{-1} due to the high acid strength and hydrocracking activity of catalyst as proved in NH_3-TPD analysis and hydroisomerization reaction test. In addition lower reaction temperature and high catalytic activity helps to reduce operating cost.

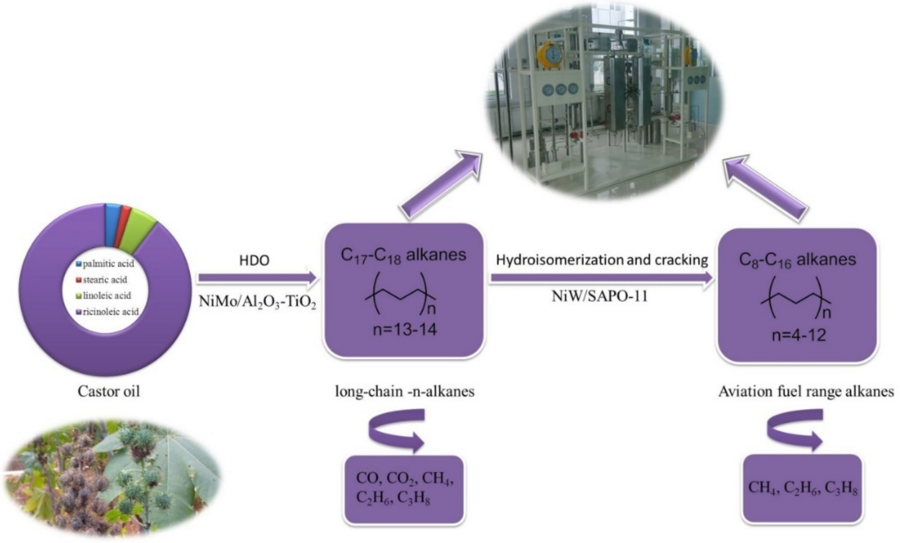

Fig 1. The reaction process for the conversion of castor oil into bio-aviation fuel.

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B206

Use of biorefinery concept to complex processing of waste rapeseed cake fractions for production of high-value added microbial metabolites

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Keywords:rapeseed waste, carotenoids, lipids, bioethanol, biorefinery

Abstract

The biorefinery is a concept capable to produce fuels, solvents, plastics and food for animal stock or even for human beings. In some technologies, these biorefinery products are made from waste biomass. Czech Republic belongs to ten biggest producers of rapeseed worldwide. During manufacturing process of rapeseed oil and production of biodiesel rapeseed cake as a specific kind of waste is formed, which could be a source of cheap and efficient substrate for microbial conversion. This cake is mainly composed of cellulose 17.35 %, hemicelluloses 31.26 %, lignin 1.13% and rest oil 2-9 % (w/w).

Rapeseed oil fraction can be easily extracted and used as substrate for some bacteria. The polysaccharides, cellulose and hemicelluloses are suitable source of sugar monomers, which can be then fermented by yeasts. Final solid rest could be used as an energy source. Valorization of oilseed processing wastes is thwarted due to the presence of several antinutritional factors.

Some microorganisms fulfill all requirements for being utilized as core catalysts in biorefineries, and would be useful in creating new sustainable products. In this work, hydrolyzate of lignocellulose fracion of rapeseed cake was used to produce i) ethanol by *Saccharomyces cerevisiae* CCY 21-4-47 and ii) pigments, sterols and single cell oil by red yeasts *Rhodotorula glutinis* CCY 20-2-26 and *Cystofilobasidium capitatum* CCY 10-1-2. Oil fraction was used for iii) production of PHA bioplastics by *Cupriavidus necato* H16 strain.

Hydrolyses have been carried out by chemical hydrolysis in water bath, chemical hydrolysis enhanced by microwaves and enzymatic hydrolysis. The content of antimuntient compounds (sinapic acid, tannic acid, sinigrin and phytic acid) was determined by HPLC/PDA method, carotenoids and sterols were determined by HPLC/PDA/MS and production of PHA by GC/FID.

After the 48 h fermentation the concetration of the antinutrients has decreased to 2 mg/g of d.w. from the original up to 12 mg/g. The concentration of ethanol stopped at 32 g/L. In red yeasts *R.glutinis* and *C.capitatum* cultivated on lignocellulose fraction in 5-L fermentor the yields of 35-39 g/L of biomass enriched by carotenoids (30-50 mg), ergosterol (60 mg), CoQ (2 mg) and 14-22 % of lipids were obtained. The residual oil fraction from rapeseed cake was further metabolized by *C.necator*. This fermentation resulted in PHB yield of 41.2 g/l after 36 h. The unfermented residue of the rapesees has been enriched by the biomass of yeasts.

In conclusion we can say thet fermenting of the rapeseed residue by yeasts and bacteria is a promissing method for valorization of this waste material. As a result we get high-value added metabolites and enriched biomass for animal feed with lowered antinutrient content.

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B207

Efficient Production of Furfural from Xylose in Water over Phosphate/TiO_2

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Keywords: Biomass conversion, furfural, TiO_2, water-tolerant Lewis acid catalysis

Abstract

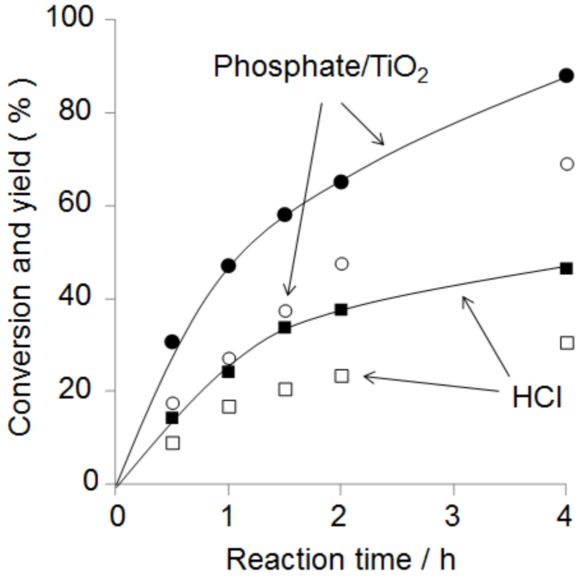

Figure Time courses for xylose conversion (closed square and circle) and furfural yield (closed square and circle) over HCl and phosphate/TiO_2 at 393 K.
Reagents and condition: catalyst, 100 mg, xylose, 50 mg; H_2O, 2.0 mL, Temp., 393 K.

For a sustainable and environmentally benign production of industrially important chemicals, the development of petroleum substitute is strongly demanded. Here, we studied catalytic conversion of xylose into furfural,one of the most important reactions in the refinary of lignocellusic biomass, with varisou solid and liguid catalysts,and found that phosphate/TiO_2 [1-3], a water-tolerant Lewis acid catalyst, is much more effective than other Brønsted and Lewis acid catalysts.

Figure 1 shows time courses for xylose conversion and furfural yield at 393 K. While phosphate/TiO_2 and HCl gave similar furfural selectivities at 30-40% of xylose conversion, reaction rate for furfural formation on Phosphate/TiO_2 was estimated to be 1.01 mmol g-cat^{-1} h^{-1}, which is much larger than that on HCl (0.55 mmol g-cat^{-1} h^{-1}). No apparent decrease in original activity of phosphate/TiO_2 was observed for five consecutive reactions, meaning that Lewis acid sites and phosphate moiety on TiO_2 surface show high stability for the reaction. Phosphate groups on TiO_2 surface greatly supresses side reactions forming water-soluble polymerized species, so-called humin.[2,3] Reactions ofxylose in D_2O suggest that stepwise dehydration of xylose forms furfural containing D atom at C1 and C3 positions over Lewis acid site of TiO_2 catalyst. The step-wise dehydration mechanism enabled large decrease in apparent activation energy (phosphate/TiO_2, 115 KJ mol^{-1}; HCl, 147 KJ mol^{-1}), which resulted in furfural formation in water more efficiently than any other homogeneous Brønsted acid catalysts.

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B208

Biomass Resin Derived from Wool Fiber Waste with Low Thermal Expansionand High Impact Resistance

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Keywords: Woven Wool fabric, Biomass Resin, Reversibility, Low Thermal Expansion, High Impact Resistance

Abstract

Global wool production for clothing is approximately 2.043 million tons per year. In the processes of producing wool from raw wool and manufacturing clothing, a great amount of waste is generated. Furthermore, almost all of a sheep's wool is thrown away as waste when they are consumed as meat. In order to recycle wool waste as a resource, it is necessary to establish effective utilization methods. The purpose of this study is to produce keratin resin by means of heat under pressure; the materials were wool powder, which was made from mechanically crushed wool fiber, and woven wool fabric.

In the case of wool powder, wool fiber was crushed by a planetary ball mill and was screened for uniform fiber with a length of -32μm. Thereafter, this wool powder was pressurized by a hot press at 20 MPa and at a temperature of 150 °C. In the case of woven wool fabric, experiments were carried out wherein the materials were two kinds of woven wool fabric: fabric given scale processing and fabric without scale processing. The scales on the surfaces of wool were degraded with sodium hypochlorite, as the cysteine crosslinking degree of scales was high. The woven wool fabrics were punched in the size of φ55 mm. Ten sheets of fabric were layered in a steel jig and were pressurized at 60 MPa while being heated at 150°C. All resins were evaluated in their characteristics after they were dried at 100 °C under a vacuum for three days.

Resin was obtained from wool powder. It also had a glass-transition temperature of 190.8 °C. The thermal expansion coefficient of the resin was 17×10^{-6}/K: extremely low for resin and could be equal to metals such as copper and aluminum. Their three-point bending test showed that bending strength was 105 MPa and Young's modulus was 5.4 GPa: both higher than PC. The Izod impact value was 14.8 J/m. Additionally, resins were able to be reproduced on the condition that resins were crushed and were heated and pressurized once again.

The experiments using woven wool fabric had different results; no resin was obtained from woven wool fabrics which had not been given scale processing, and on the other hand, woven wool fabrics which had been given scale processing converted completely into resin. Although Young's modulus was 5 GPa, shown by a three-point bending test, it gained 116 MPa in bending strength. The stress-strain curve showed the maximum stress peak of the resin and the maximum stress and deformation peak of wool fabric was identified. As a result, the strain reached 14. Furthermore, the Izod impact value of the resin made from woven wool fabric reached 457 J/m, which exceeded ABS resin. After all of these tests, white fabric clothes emerged on the fracture cross-sections. Reversibility was observed, that resins reversibly turned back into woven wool fabrics when stress was loaded on them. In addition, resins with these white fabric clothes, which were made when the bending tests or impact tests were conducted, were able to reproduce resins on the condition they were heated and pressurized once again.

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Selective Separation of Precious Metals by Keratin ResinMade from Wool Waste

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Keywords: Selective Separation, Wool, Biomass Resin, Precious Metal, Recovery rate

Abstract

There is a trial to recover precious metals only by putting biomass in waste water in order to absorb them. When the eggshell membrane and feathers were immersedin waste water including 200 ppm of Au, Pdand Pt, at a proportion of 0.4 g/L, the recovery ratio of Au, Pd, and Pt were each reported to be 75%, 21%, 10% for the eggshell membrane, and 4%, 13%, and 3% for the feathers[1]. This is attributable to the fact that imidazole radicals of the histidine side chains included in keratin protein not only had an affinity with metal ions but could be reducing agents[2].

A author has found that keratin resins can be easily obtained through resinification of wool powder made from mechanically crushed wool fibers by heating and putting pressure using a hot press. Then we dried the keratin fibers sufficiently and soaked them in room temperature water for one day. As a result, the water absorption ratio which was defined as the proportion in the mass increase of resins before and after soaking was as large as 25%.

This study aims to clarify the selective absorbent characteristics for multiple metal ions : we put keratin resins in a simulated waste water including Au, Hf, Ir, Pd, Pt, Rh, Sb, Sn, and Te.

We crushed Merino wool fibers using a planetary ball mill and collected wool powder with a fiber length of -32 μm in a sieving process. By using a hot press we heated the powder until the temperature reached 150°C under a pressure of 31 MPa. In selective absorbent,we used mixed standard solutions of Au, Hf, Ir, Pd, Pt, Rh, Sb, Sn, and Te (2% HNO_3) along with an Au standard solution ($HAuCl_4$ in 2 M HCl) as simulated waste waters. Then we put keratin resins in the simulated waste waters at a proportion of 10 g/L and stirred them while maintaining for 8～24 hrs. Using the ICP we quantified the concentrations of multiple ions in the simulated waste water. Here, the recovery ratio can be defined as the proportion of metal concentration in waste waters before adding resins and the reduced metal ion concentration before and after adding resins.

First, when we put keratin resins in the simulated waste water including 101 ppm of Au ions, the recovery ratio was 11% after 8 hrs and 100% after 12 hrs. Next, when we put resins in simulated waste waters including 10 ppm of multiple ions, the recovery ratio was 0% without any concentration transition of Hf, Ir, Pt, Rh, Ru, Sb, and Sn regardless of soaking time. On the other hand, the recovery ratio of Au (Pd) increased from 30 (10) to 55 (30) % following the soaking time of four, and 24 hrs. It means that we succeeded to clarify the selective absorbent properties of keratin resins to the metal ions. It is expected that this technology will be put to use not only in the recovery of Au and Pd from the waste waters of metal plating factories but also in selective separation of multiple metals from the alloy catalysts such as Pd-Ru, Pd-Au, Pd-Ru, and Pd-Te.

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B210

Screening for Natural Variation of Cellulase Production in *Neurospora crassa*

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Keywords:anaerobic conditions, Filter Paper Assay (FPA), High Performance Liquid Chromatography (HPLC)

Abstract

Neurospora crassa is an ascomycete filamentous fungus that possesses great potential as an alternative means for the production of biofuels like ethanol. *N. crassa* is an ideal candidate for research due to its rapid growth rate, its full repertoire of enzymes needed for the hydrolysis of biomass, the wealth of knowledge about its genetic makeup, and its genetic malleability. It has the ability to break down complex cellulose into simple sugars (saccarrification) as well as ferment simple sugars to ethanol (fermentation). The present work aims to screen 74 different ecotypes for their response to carboxymethylcellulose (CMC) in solid-state and submerged culture. Enzyme production and secretion was analyzed using plate clearing assays, while the activity of secreted enzyme from submerged cultures was analyzed by the Filter Paper Activity (FPA) Assay [1, 2]. Cellulase secretion was analyzed through Cell Mass Increase (CMI), Area of Cellulase Activity (ACA), Cellulase Production Index (CPI), and most importantly Substrate Utilization Index (SUI) to normalize for differential growth among ecotypes. Significant variation was found in both culture conditions, and ecotypes were identified that performed the best in each. Four ecotypes were identified that performed best in both the FPA and the PCA, and these strains will be investigated further in future experiments.

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B211

Chemical Valorization of Cashew Nut Shell Liquid by Isomerizing Olefin Metathesis

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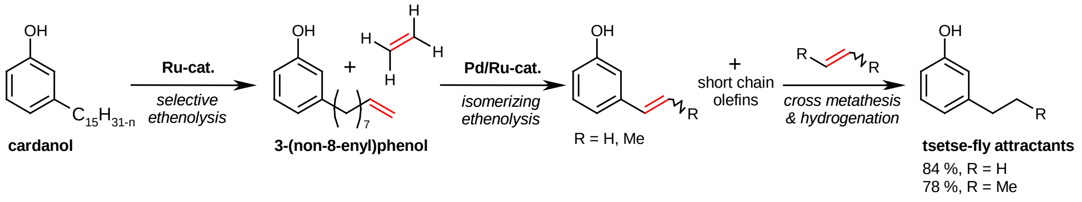
Keywords: Cashew Nut Shell Liquid, Olefin metathesis, Isomerization, Renewables

Abstract

Isomerizing olefin metathesis reactions have recently emerged as a valuable tool for the valorization of renewables.[1]In the presence of a bimetallic catalyst system, consisting of a dimeric palladium isomerization catalyst and state-of-the art ruthenium metathesis catalysts, fatty acids were converted into industrially useful multi-component blends.[2]Furthermore,the isomerizing ethenolysis allowed the conversion of naturally occurring allylarenes (e.g. eugenol, estragol or safrol) into the corresponding styrenes.[3] Cashew nut shell liquid (CNSL) is obtained as a waste by-product of the cashew nut processing (450.000 t/a).[4] Therefore, it is an excellent example of an inedible renewable resource for which no competition occurs between land use for food or raw material production. After distillation at above 140 °C, the liquid consists mainly of cardanol, a mixture of *m*-alkenylphenols.Starting from this technical CNSL, we have developed a concise synthesis of the tsetse-fly attractants 3-ethylphenol and 3-propylphenol with the isomerizing metathesis reaction being the key-step. In order to obtain a homogeneous starting material, the cardanol mixture was first converted into 3-(non-8-enyl)phenol *via* selective ethenolysis and distillation. The olefinic side chain was then shortened by isomerizing ethenolysis. This process was efficiently mediated by the combination of the isomerization catalyst $[\mathrm{Pd}(\mu\text{-Br})^t\mathrm{Bu}_3\mathrm{P}]_2$ and a second-generation Hoveyda-Grubbs metathesis catalyst.An additional non-isomerizing butenolysis or ethenolysis followed by hydrogenation furnished the target molecules in one pot.[5]



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B212

Biorefinery concepts via Achmatowicz rearrangement

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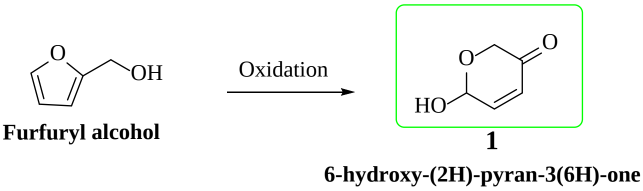
Keywords: Achmatowicz rearrangement, biorefinery, furfuryl alcohol

Abstract

Among other primary biorenewable building blocks, furfural is an important intermediate available from carbohydrates such as xylose and arabinose. Moreover its production from lignocellulosic biomass is one of the few examples of an industrialized biorefinery process.[1] Furfuryl alcohol is a major derivative arising from the hydrogenation of furfural and finds many applications in the production of resins, fragrances and biofuels. A very interesting transformation of furfuryl alcohol was reported in the early 70s by Osman Achmatowicz who demonstrated the formation of 6-hydroxy-(2H)-pyran-3(6H)-one **1** from furfuryl alcohol (Scheme 1). Latter this reaction was named Achmatowicz rearrangement and attracted the scientific interest due to its potential to serve as a key step in the synthesis of many natural products.



Scheme 1. Achmatowicz rearrangement

Trough this investigation we have focused our efforts on the potential of Achmatowicz rearrangement and the derived 6-hydroxy-(2H)-pyran-3(6H)-one **1** to serve as a key biorefinery transformation in the synthesis of novel biorenewable building blocks *via* scalable transition metal catalyzed hydrogenation methodologies. So far we have achieved conversion of furfuryl alcohol to pentane-1,2,5-triol, a promising bioerenewable monomer and biofuel, in up to 90% yield *via* Achmatowicz rearrangement and subsequent Pt catalyzed hydrogenation.

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B213
Homogenous Gold Catalysis: Converting HMF into Phenols

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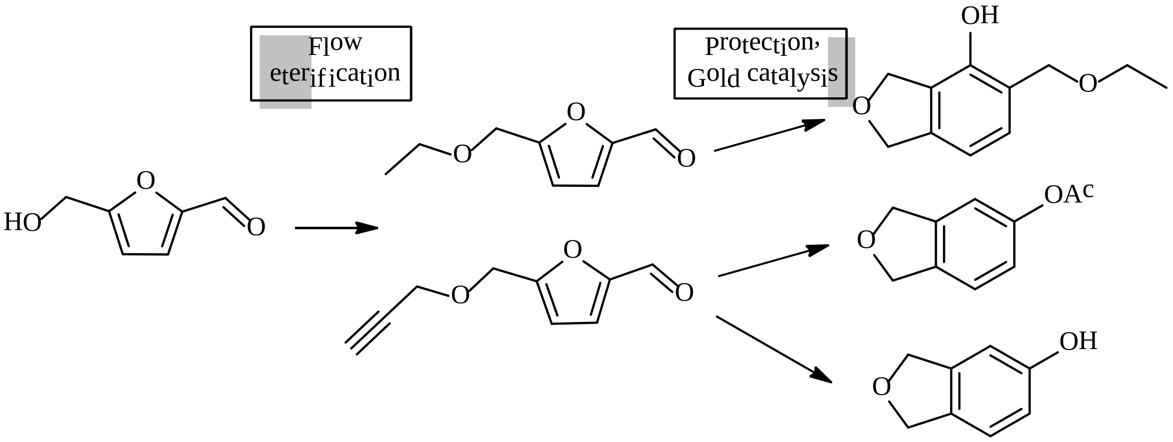
Keywords: Gold catalysis, renewables, homogenous catalysis

Abstract

The Hydroxymethylfurfural (HMF), one of the platform chemicals, offers opportunities as a source of bulk chemicals [1]. Much research is aimed at the generation of fuels from HMF, but possibilities of its transformation to fine chemicals remain largely unexplored. Our research is focussed on the synthesis of aromatic carbocycles from HMF using simple chemicals and catalytic methods. As a start, the method for the formation of HMF ethers from alcohols using solid supported acid as a catalyst under flow conditions was devised.



Scheme 1. Synthesis of phenols from HMF.

Then, the transformation of the easily protected HMF ethers into phenols was explored, according to a methodology previously developed in our group [2]. This reaction is catalysed by cationic Au+ complexes. It proceeds under mild conditions and opens up access to aromatic compounds, which are amongst the most demanded building blocks in organic synthesis. This homogenous gold-catalysed transformation yields different phenols from renewables in good yields

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B214

Fabrication of High StrengthBiomass Resin Using Artifical Spider Silk Powder

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Keywords: Artifical Spider Silk, Fibroin Protein, Biomass Resin, Bending Test, Titanium Tetraisopropoxide

Abstract

Artificial spider silk with strong and heat-resisting properties has been developed and is on the way to mass-production. Artificial spider silk was produced by making a host microorganism which had been transplanted with spiders' genes generate spiders' fibroin protein. An author has found that fibroin resins can be easily obtained through resinification of commercial silk powder comprising the same fibroin proteins or hornet silk powders which had been made by crushing the cocoon thread of vespa simillima larvae by heating at temperatures of 150-180 °C and putting pressure of 30 MPa using a hot press [1].

In this study, we tried to resinify artificial spider silk powders that had been made from freeze dried and crushed artificial spider silk solutions. In addition, we selected a titanalkoxide among other cross-linking agents which was expected to facilitate hardening while connecting the neighboring fibroin proteins by causing them a transesterification reaction with OH radical of the amino acid, and examined its influence on three-point bending strength.

We filled φ20 mm stainless steel jigs with artificial spider silk powders and resinified them using a hot press. The condition of resinification was as follows : we heated the powder until its temperature reached 100-180 °C under an air pressure of 31 MPa and then immediately cooled them. We then dried them for three days at a temperature of 100 °C under a vacuum.

In the case of artificial spider silk powder (grain size : under 53 μm and 30 μm on the average), the temperature at which the whole specimen were resinified evenly was above 140 °C. When fibers were resinified at 140 °C and dried for three days, the apparent density of fibers was 1.3 g/cm³, micro-Vickers hardness was 49, three point bending strength was 98 MPa, and Young's modulus was 6.3 GPa. These values were independent of the resinification temperatures.

Next, in order to examine the influence of moisture in the artificial spider silk powders (grain size: 53-100 μm), we resinified two kinds of powder: a sufficiently dried powder and one which was mixed with 30 wt% water. As a result, the former was not resinified while the latter which had been made by the process of drying for only one day showed three point bending strength (Young's modulus) of 130 MPa(8.4 GPa) and micro-Vickers hardness of 49. Moreover, when we added the titanium tetraisopropoxide ($Ti\text{-}(O\text{-}i\text{-}C_3H_7)_4$, Boiling temperature: 103 °C) by 5wt% to the same powders in the dry air, the three point bending strength (Young's modulus) of the dried fiber was 124 MPa(8.1 GPa)and the micro-Vickers hardness was 49. Consequently, considering that water is the most effective cross-linking agent and titanium tetraisopropoxide easily hydrolyzes, many titanium tetraisopropoxides might hydrolyze with the water included in the artificial spider silk powders before the fibroin protein's bridge formation.

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B215

Sustainable Production of a Dual-Functional Protein based on Biomolecular and Bioprocess Engineering

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Keywords: Selective precipitation; Four-helix bundle; Biomineralization; Silica; Chromatography-free

Abstract

The implementation of efficient processes for the recovery, isolation and purification of biomolecules is a main challenge for the bioengineering field. Most purification methods are heavily reliant on chromatography techniques which are costly, have capacity and diffusional limitations and/or involve the use of heavy metal-ions. Therefore, non-chromatographic methods which enable cost-effective, high-yield and sustainable production of biomolecules without the use of hazardous compounds are highly desired. In this study, we aim to develop a chromatography-free, selective thermochemical precipitation method for the recovery, isolation and purification a dual-functional D4S2 protein from recombinant *Escherichia coli*. The protein was designed at the DNA level by combining a four-helix bundle-based protein [1] with a sequence rich in cationic residues for biomimetic silicification [2], achieving emulsification and biosilicification functionalities, respectively. Additionally, the inclusion of four-helix bundle protein within D4S2 is to gain high protein-stability thermally and chemically. In this purification method, DNA-contaminants were firstly precipitated by using poly(ethyleneimine) (PEI) and then removed. Subsequently, protein-contaminants were selectively precipitated by mixing the protein mixtures with Na_2SO_4 at 90ºC for 5 min. D4S2 protein was then isolated and thus separated from residual PEI by further increasing the concentration of Na_2SO_4. Finally, D4S2-protein precipitate was solubilized which then underwent buffer exchange prior to functionality tests. Compared to the D4S2 yield produced using chromatography methods [3], the final yield of D4S2 in this study can be increased fourfold with a D4S2-protein recovery as high as 80%. The synergistic emulsification and biosilicification functionalities of the bio-produced protein were demonstrated able to catalyze the synthesis of oil-core silica-shell nanocapsules under environmentally-friendly conditions, which confirmed that the conditions applied for the purification of D4S2 has no adverse effects to its functionalities.

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B216

Green extraction: comparing the profile of phenolic compounds derived from citrus waste of organic and conventional farming

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Keywords: Orange waste, organic farming, green extraction

Abstract

Organic farming is a production system that contributes to the environmental and animal protection, since it aims at sustaining the health of soils, ecosystems and people in general, by a set of specific agricultural practices [1, 2]. A number of authors have reported that the farming practices affect the composition of fruits [1], and some of them noticed that the absence of pesticides can provide higher levels of antioxidant components [2]. In this context, it is reasonable to conclude that the waste from this type of biomass will also have a different content. This study, therefore, presents the evaluation of citrus waste from both organic and conventional farming processes. Several researches have shown that orange waste as a renewable source can be an interesting opportunity to obtain high-value products, generating profits and increasing the industry's competitiveness [3]. This biomass may contain interesting compounds, such as soluble sugars, cellulose and hemicellulose, pectin, limonene and flavonoids [4, 5]. In this regard, the Brazilian production of this by-product is noteworthy, since the country is one of the larger producers of citrus in the world [4]. Thus, the main purpose of this work is to present an evaluation related to the chemical composition of some types of Brazilian citrus waste, focusing on the secondary metabolites based on a green extraction method. By using ethanol as solvent and ultra-turrax as homogenizer, it was possible to extract a number of phenolic compounds of interest, selected after a phytochemical screening. Many different flavonoids derived from such matrices have been identified. Four flavonoids were used as markers (hesperidin, naringenin, hesperetin and nobiletin) and, through standardized samples, it was possible to identify and quantify some phenolic compounds from organic and conventional citrus waste. It was observed that the presence of the polymethoxylated flavone (PMF) nobiletin was 43% higher in the organic sample when compared to the conventional one. The PMFs are almost exclusively found in the Citrus genus, and they are also known due to their antitumor and antioxidant activities [6], being important compounds to be explored. Furthermore, by comparing the chemical profile of both samples, it was possible to suggest that the organic waste is richer when considering other compounds too. Therefore, this study also shows the potential use of such biomass as a source of high-added value compounds for a number of commercial applications.

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GREEN ENERGY

E301

Sunlight Photodegradation of a Dye Pollutant Over a New Polyoxotungstate- Based Material.

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Keywords: Photocatalysis, Sunlight irradiation, Polyoxotungstate, Dye, Environment.

Abstract

Our work is devoted to the photocatalytic degradationof hazardous organic pollutants from wastewaters, over polyoxometalate (POM)- based materials. Polyoxometalates are considered as green and cheap photocatalysts; so, among the large variety of compounds that have been used in such application [1-3], they constitute an important group.

In the present paper, we report on the photodegradation of Rhodamine B (RhB) in aqueous solutions. RhB is used as a model of organic dye, as it is the most important xanthene dye pollutant from the textile industry.

In a first part of this work, we describe the hydrothermal synthesis of a new macromolecular polyoxotungstate- based material that was further characterized by several physical and photo-electrochemical techniques.

The diffuse reflectance measurements andthe thermal variation of the electrical conductivity show semiconductor properties of the POM - based material, with *n*-type behaviour.

According to the energy scheme, established from the determination of the conduction and valence bands of the compound, both $O_2^{\bullet-}$ and $OH^{\bullet}$radicals are generated upon illumination and may oxidize the organic matter, with a partial mineralization (into $CO_2 + H_2O$).

The photocatalytic experiments for RhB degradation were conducted under natural solar light irradiation, with varying some important factors such as catalyst loading, concentration and pH of dye solution.

The decrease of RhB concentrations, as plotted against the wavelength at different irradiation times, highlighted a good performance of the synthesized material in such application.

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E302

Photocatalytic Properties Of A Copper Hydroxyphosphate Application to Sunlight Photodegradation Of Organic Pollutant

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Abstract

Reactive dyes used in the textile dyeing are azo compounds, characterized by the presence of one or more azo bonds and are among the most notorious widespread environmental pollutants. They are difficult to remove from effluents by the conventional techniques. In this respect, the advanced oxidation processes (AOPs) have been widely used to oxidize these organic compounds into CO_2, H_2O and biodegradable species. Among them, photo-Fenton processes and heterogeneous photocatalysis are very efficient for a wide variety of dyes. In this aim, various solid materials have been used [1-3].The phosphate hydroxide minerals represent an important class of semiconductor materials [4].

As a contribution in this field, the present work reports on the use of a copper phosphate hydroxide material as photocatalyst in wastewater treatment. The material was synthesized by hydrothermal route in the presence of a surfactant as template. Several techniques were used for the physico-chemical characterization of the material: X-ray powder diffraction, scanning electron microscopy with EDS analysis, chemical analysis, X-ray fluorescence, thermal analysis (TG, DTG and DSC), mass spectrometry and UV-visible diffuse reflectance. The photo-electrochemical properties were also investigated. The optical measurements indicated both direct and indirect transitions. The thermal variation of the electrical conductivity shows a semiconductor behavior; the conductivity follows an exponential type law with an activation energy of 20 meV. The conduction band and the valence band of the phosphate material, permit the production of both $O_2^{\bullet -}$ and $OH^{\bullet}$oxidizing radicals. As application, the photo-degradation of Orange G dye pollutant was investigated upon artificial and solar lights.The effect of some physico-chemical parameters such as the amount of catalyst, dye concentration, contact time, stirring and addition of H_2O_2 was optimized. From the results of the study, it was concluded that orange G was removed by a photo-Fenton like process.
Referring to the energetic diagram, a degradation mechanism was proposed.

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E303

Nucleophilic aromatic substitution mechanism of atrazine with biothiols in conventional solvents.

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Keywords: Atrazine; Biothiols; SNAr; Kinetics mechanism

Abstract

Herbicides atrazine (ATZ) derivatives have now a significant contribution to global agricultural productivity. Its effectiveness is as important as its accumulation in wastewater irrigation, ignoring its potential effect on humans**[1]**. Lu et al. studied a mechanism of atrazine sequestration in soil**[2,3]**. We demonstrated that neucleophilic substitution could serve an important pathway causing ATZ sequestration. The carbon bonded to the chlorine in ATZ molecule is partially positively charged due to the strong electronegativity of chlorine and is susceptible to the attack of nucleophiles such as aniline**[3]**. Substantially ATZ transformation was only observed in the presence of those species containing thiol functionality. Thus, we speculated that it was the thiol group in amino acids/peptides acting as the nucleophile. In actuality, there are no reports about the reaction mechanism of this chemical with biothiols in solution, which opens a line of research unexplored.

The aim of this work is the study of the kinetic mechanism of atrazine with a biothiols set, namely, cysteine (CYS), L-cysteine ethyl ester (CEE) and N-acetyl-L-cysteine (NAC) in water and others solvents to establish a medium of detection and cuantification of ATZ. The comparative aspects of the biothiols are expressed in terms of rate constant. The potential energy surface was explored to again useful insight into the reaction mechanism for the title reaction. So, the first task here is in order to obtain the most favorable reaction path, to assess the solvent effects afterwards. The model system used is the reaction of atrazine towards cysteine. For this reaction, two mechanistic scenarios warrant consideration. The first involve the nucleophilic attack from –SH moiety onto the ipso carbon atrazine. However, this nucleophilic attack step was calculated to have a barrier of 37.4 Kcal/mol, which is too high for the reaction to occur. Second scenarios consider a fast pre-equilibrium to give the reactive specie cysteine. Then, this reactive specie can adds to ipso carbon, via transition structure to give the desired reaction product. This process was calculated to have a barrier of 15.9 Kcal/mol. That the activation barrier for this reaction path is consistent with the recorded kinetic data.

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E304

Photochemical Hydrogen Evolution Catalyzed by Iron(II) Complexes with Redox-active Ligands

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Keywords: Hydrogen evolution, non-precious metal complex, iron, redox-active ligand, photochemical process

Abstract

Molecular hydrogen is one of candidates as clean energy carrier.[1] Because of the difficulty in the storage of hydrogen, the development of hydrogen storage materials is desired. Among a several materials, organic compounds, known as “organic hydrides” are fascinating candicate.[1] Recently, quinoline/1,2,3,4-tetrahydroquinoline system has been reported as efficient hydrogen production/storage material that can evolve hydrogen at relatively low temperatures (*ca.* 110-140 °C), under the presence of Ir catalyst.[2]However, even in the excellent example, the operating temperature in the hydrogen-evolution reaction (HER) is still high. Therefore, the creation of a HER that can be driven at moderate temperature with use of nonprecious-metal catalysts is an important issue.

Recently, we reported some of interesting and important reaction of transition metal complexes with redox-active ligands.[3] In particular, the Fe(II) complex with *o*-phenylenediamine (opda), e.g., $[Fe^{II}(opda)_3](ClO_4)_2$, was reported to show the photochemical HER at room temperature.[4]In this reaction, the protons and electrons in opda ligand skeleton were found to be the source of photochemically evolved hydrogen. It was suggested that the oxidized complexes with *semi*-benzoquinoimine (s-bqdi) or *o*-benzoquinodiimine (bqdi) is formed after the HER. We herein report the detailed HER from $[Fe^{II}(opda)_3](ClO_4)_2$ and other related complexes[5] together with mechanistic investigations and photocatalytic HER under the coexisting of electron and proton donor.

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E305

Desigh of viologen derivative for photoinduced formic acid prduction system with biocatalyst and water solube zinc porphyrin

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Keywords:CO_2 reduction, formate dehydrogenase, artificial co-enzyme, zinc porphyrin

Abstract

Formate dehydrogenase (FDH) is one of the attractive biocatalysts for CO_2 fixation and storage.Visible light induced CO_2 to formic acid conversion system consisted of water soluble zinc porphyrin as a photosensitizer, methyviologen (MV^{2+}) as an electron carrier and FDH was reported [1]. In the system, the electron transfer among photosensitizer, electron carrier and FDH is important process. In this study, we attempted to improve the electron transfer efficiency in the photoinduced CO_2 to formic acid conversion system by viologen derivative used as an electron carrier.

The chemical structures of viologen derivatives are shown in Fig.1. Enzyme kinetic analysis, photoreduction viologen derivative with zinc tetraphenylporphyrin tetrasulfonate(ZnTPPS), and photoinduced formic acid production were carried out to investigate the interaction among ZnTPPS, viologen derivative and FDH.

Fig.1 also shows the kinetic parameters, concentration of the reduced form of viologen derivative after 3 h irradiation, and concentration of formic acid production after 3 h irradiation. The result of enzyme kinetic analysis and photoreduction viologen derivative indicate that viologen derivative has the highest affinity with ZnTPPS and FDH by DA^{2+}, cationic viologen derivative. From the reason, photoinduced electron transfer was enhanced and the amount of photoinduced formic acid production was increased by using DA^{2+} as an electron carrier.

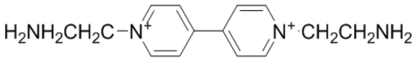
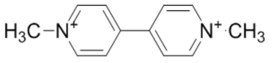
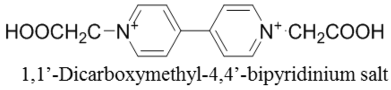
Viologen derivative	Enzyme kinetic analysis k_{cat} / Km / μM^{-1}·min^{-1}	The amount of photoreduced viologen derivative / μM	The amount of photoinduced formic acid production / μM
 1,1'-Diaminoethyl-4,4'-bipyridinium salt : DA^{2+}	0.25	54.7	12.2
 Methyl viologen : MV^{2+}	9.0×10^{-3}	46.2	10.2
 1,1'-Dicarboxymethyl-4,4'-bipyridinium salt : DC^{2+}	9.3×10^{-4}	37.0	8.8

Figure 1. The results of enzyme kinetic analysis, photoreduced viologen derivative with ZnTPPS and photoinduced formic acid production.

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E306
Synthesis and Properties of New Ni(II) Complex with *N*,*N’*-Bis(dialkylphosphino)-*o*-phenylenediamide

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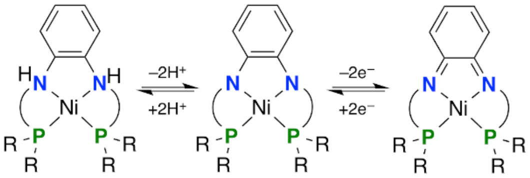
Keywords:*ortho*-Phenylenediamide, Redox-active ligand, Nickel complex, Hydrogen evolution

Abstract

Recently, the development of artificial chemical processes, e.g., water splitting and CO_2 reduction, have attracted considerable attentions so as to deal with the environmental problems.[1] In that context, metal complexes with redox-active ligand, together with their functions, i.e., catalysis, have been extensibly studied so far.[2] In paticular, *ortho*-phenylenediamide (pda^{2-}) is known to possess strong electron-donating property and stabilizes higher valent metal centers.[3] For example, Cu(II) complex with N_1,N_1'-(1,2-phenylene)bis(N_2-methyl-oxalamide) was previously reported to catalyze water oxidation.[4] A number of complexes with tetradentate ligand which has pda^{2-} moiety with additional two N_{amine} or S sites (N_4 or N_2S_2-types) have been reported and are clarified their characteristics, so far.[5] In contrast, little for a complex with tetradentate ligand which has pda^{2-} moiety with additional two P sites (N_2P_2-type) is ever known despite the alkylphosphine ligands are known to stabilize metal centers with low oxidation numbers. In addition, N_2P_2-type ligand is expected to form various electronic states (Scheme 1). Based on these viewpoints, elucidation of the property and reactivity of N_2P_2-type complex should be of great interest.

We report herein the synthesis of Ni(II) complex with N_2P_2-type ligand, [$Ni^{II}(N_2P_2)$], together with its structural and electrochemical properties. In addition, interaction of [$Ni^{II}(N_2P_2)$] with protons and its electrochemistry will also be presented in detail.

Scheme 1. Plausibleelectron and proton transfer property of [$Ni^{II}(N_2P_2)$].



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E307

Flow Metal-Free Aryl-Carbon Bond Formation via Photogenerated Phenyl Cations

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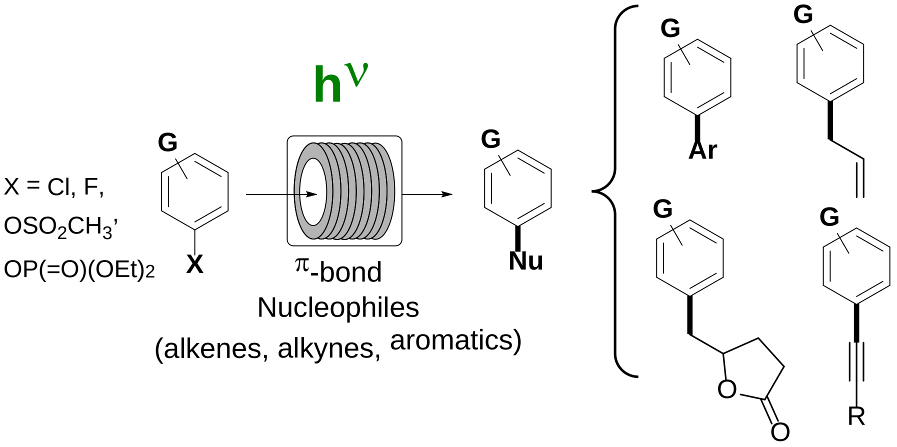
Keywords: Metal Free Conditions, Flow Chemistry, Photochemistry, Arylation.

The use of continuous-flow processes is currently an enabling technology to realize process intensification of organic reactions for the smooth preparation of natural products. Arylations, among others, are a important tool for the construction of different Aryl-Carbon and Aryl-Heteroatom bond under flow conditions. However, most of most of them deal with transition metal-catalyzed cross-coupling processes. [1]

We present herein a convenient photochemical flow procedure for the formation of aryl-carbon bonds under metal-free conditions. The strategy is based on the photogeneration, in polar or protic media, of triplet phenyl cations from substituted electron-rich aryl halides and esters and the reaction of such electrophilic intermediates with π-bond nucleophiles.[2]

A wide range of phenylated products, including biaryls, allylarenes, 2-arylacetals and γ-benzyl-lactones (some examples in Scheme 1), was smoothly synthesized in satisfactory yields, and the adoption of a flow reactor often allowed us to adopt higher concentrations of substrates and shorter irradiation times compared to those usually employed in batch systems.[3]



Scheme 1

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E308

Regioselective Photocatalytic Transfer Hydrogenolysis of Allylic Alcohols without Salt Waste Generation

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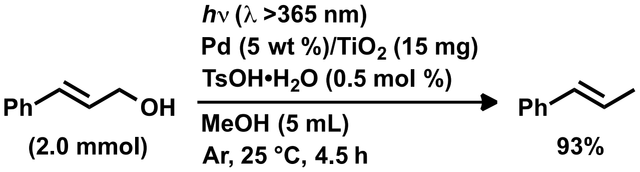
Keywords: Photocatalysis, Hydrogenolysis, Reductive Deoxygenation, Titanium Oxide, Allyl Alcohol

Abstract

Herein we report a regioselective photocatalytic transfer hydrogenolysis (PcTH) [1] of substituted allylic alcohols to olefins promoted by easily preparable titanium oxide-supported palladium catalyst (Pd/TiO_2) without salt waste generation. For example, the PcTH of cinnamyl alcohol was promoted at ambient temperature using methanol as hydrogen source, yielding *trans*-β-methylstyrene in a highly regioselective manner (Scheme). Carbon–carbon double bonds and non-allylic alcohols were well tolerated. Deuterium-labeling experiments showed that a hydrogen atom from methanol was incorporated into the product via S_N2 or S_N2' manner depending on the substrate. By switching photo-reaction to a dark reaction after simply filtrating and extracting the crude reaction mixture, a remaining carbon–carbon double bond was successfully converted to the corresponding epoxide and dibromide. Formal synthesis of (+)-(*S*)-lavandulol from (*R*)-carvone was also achieved in shorter steps using PcTH, by which previous requirements [2] of protection/activation and deprotection steps of hydroxy groups were obviated.



Scheme. PcTH of cinnamyl alcohol.

Acknowledgement

The authors wish to thank Professor A. Kudo (Tokyo University of Science) for fruitful discussion on catalysts.

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E309

Decomposition of Disaccharide by Photocatalysis Toward Production ofDisaccharide Rare Sugars

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Keywords: Photocatalysis, Rare sugars, Maltose, Disaccharide

Abstract

Recently, rare sugars, those amount are very small in nature, have attracted attention because those showed useful bioactivity for human body. To further investigation of the bioactivity using rare sugars, new production method of rare sugars are necessary. We recently reported that lyxose as a rare sugar was obtained by decomposition of galactose by titanium dioxide (TiO_2) photocatalysis under UV light illumination. This result indicates that other type of rare sugars can be produced by the photocatalysis. In this study, we decomposed maltose as a disaccharide with TiO_2 under UV light illumination to produce rare sugars of disaccharide and monosaccharide. In this experimental, we usedPtCl/TiO_2 as a photocatalyst in order to increase the efficiency of decomposition. We evaluated products after the photocatalytic decomposition of maltose by high performance liquid chromatography (HPLC). Fig.1a shows HPLC chromatograph for the products. A peak attributed from maltose was decreased and a new peak was appeared after the photocatalytic decomposition. Fig.1bshows a result of matrix assisted laser desorptionionaization time-of-flight mass spectrometry (MALDI TOF-MS), which indicated that molecular structure of the new product is disaccharide comprising glucose and arabinose (3-O-α-D-Glucopyranocyl-D-Arabinose).

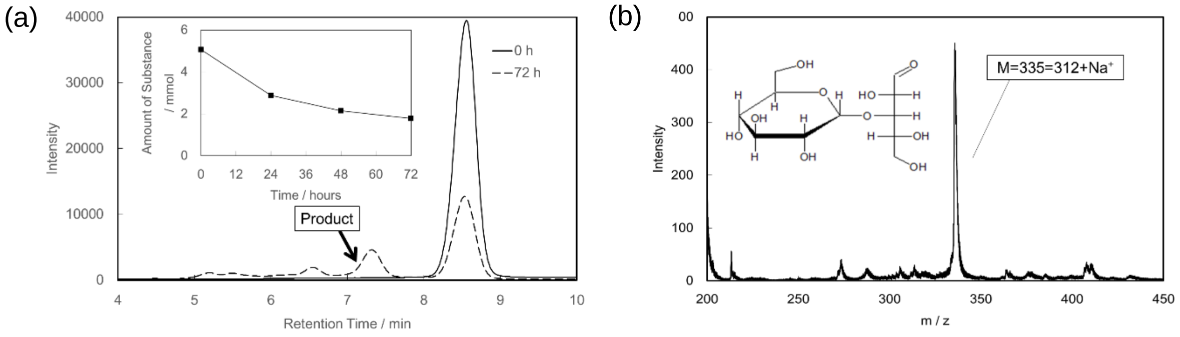

Fig.1 (a) HPLC chromatogram and time course of concentration of maltose during photocatalytic decomposition of maltose with TiO_2 under UV irradiation, (b) a peak of product measured by MALDI-TOF-MS.

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E310

Functionalization of plasmonic Au/TiO_2 photocatalyst with Ag co-catalyst for reduction of nitrobenzene to aniline under irradiation of visible light

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Keywords: photocatalysis, reduction reaction, gold nanoparticles, surface plasmon resonance, visible light

Abstract

Selective reduction of nitro aromatics to amino aromatics without side reactions such as re-oxidation reaction remains a challenging task. Amino aromatics are widely used as intermediates for many fragrances, drugs, and dyes in chemical industries. Catalytic reduction of nitro aromatics with hydrogen (H_2) has been proposed as the most plausible method. These thermo catalytic systems promote selective nitro hydrogenation but require a high temperature and high pressure of reducing reagents such as H_2 and carbon monoxide.

Organic synthesis by using semiconductor photocatalysts such as titanium(IV) oxide (TiO_2) has attracted much attention. However, less attention has been paid to reduction of organic compounds by photogenerated electrons,1) and these photocatalytic reductions by TiO_2 are performed under irradiation of UV light. Therefore, development of visible-light-responding photocatalysts is an important topic for chemical syntheses using solar energy in the future. However, to the best of our knowledge, there are no reports on selective reduction of organic compounds using visible-light-responding photocatalysts.

In this study, we used an Au/TiO_2 sample for photocatalytic reduction of nitrobenzene (NB) in a 2-propanol suspension under irradiation of visible light. Here we report that photocatalytic reduction of NB to aniline (AN) under irradiation of visible light was achieved and that the photocatalytic performances were drastically improved by functionalization of Au/TiO_2 with Ag nanoparticles as a co-catalyst.2)

The photocatalytic activity of Au/TiO_2-Ag for the reduction of NB (initially 75 µmol) was evaluated. Figure shows the time course of photocatalytic reduction of NB in a 2-propanol suspension of Au/TiO_2-Ag under irradiation of visible light from a Xe lamp with a Y-48 cut filter. The amount of NB decreased linearly with photoirradiation, while AN as the reduction product of NB and acetone as the oxidation product of 2-propanol were formed. We noted that the plot of AN always overlapped with the plot of acetone almost completely in Figure (the scale in the right axis for acetone being three-times larger than that in the left axis), indicating that this photocatalytic reaction occurred with maintenance of high stoichiometry.

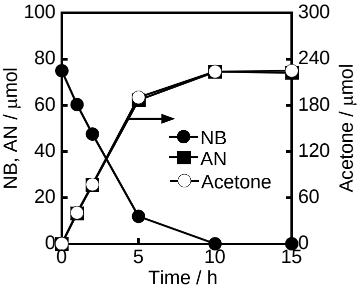

Figure Time courses of the amounts of NB, AN, acetone in 2-propanol suspensions of Au/TiO_2-Ag under irradiation of visible light from a Xe lamp with a Y-48 cut filter.

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E311

Towards New Development in Renewable H_2 Fuel Generation from Water Splitting: Tandem Catalysis and Organic Hydrogen Carriers

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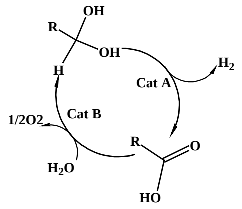
Keywords:water splitting, hydrogen fuel, tandem catalysis, Liquid organic hydrogen carrier

Abstract

The continuity and reconversion of the current energy supply are major challenges increasingly faced by modern civilization. The present massive exploitation of energy resources and the consequent negative impact on the environment is a resulting growing concern. Fossil fuels such as coal, natural gas, and petroleum provide about 90% of the energy used today by developed countries. Renewable and sustainable sources are the only alternative to this rising global problem. Towards this end, the generation of hydrogen fuel from water splitting is an active field of research [1]. However, the separation of the gas mixtures generated by the photocatalytic water splitting is the bottleneck for an efficient industrial hydrogen production plants. The development of a catalytic system that is able to generate pure hydrogen gas from water in industrial scale, provide a solution. However, water splitting also implies oxygen gas evolution in turn requiring a highly expensive and potentially hazardous gas [2]. We have developed and proposed a tandem catalytic cycle based on oxidation and reduction of a carbon carrier, releasing pure H_2 in one step and re-hydrogenation using water (releasing oxygen) in the subsequent step. In this presentation, we will disclose our preliminary results on the utilization of partially oxidized low molecular weight hydrogen carriers in an overall water splitting cycle.



Hydrogen carrier in an overall water splitting cycle

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E312

Photocatalytic Decomposition of Monosaccharide Ketose Toward Production of Rare Sugars

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Keywords: Photocatalysis, Rare sugar, Fructose

Abstract

Rare sugars are defined as quite small amount of monosaccharides and their derivatives being in nature. Recently, some of the rare sugars have effective physiological activities for human. For example, allose, one of the rare sugars, has antioxidative effect and cytostatic activity for cancer cell. Psicosehas sweetness as much as sucrose, but it has lower calory than sucrose, that used for diabetes [1]. Recently, our group successfully obtained lyxose, that a rare sugar, produced by decomposition of galactose with titanium dioxide (TiO_2) under UV irradiation. It is known that TiO_2 photocatalysisshowed high oxidative activitiy for organic compounds under UV irradiation [2]. In this study, we examined the photocatalytic decomposition of fructose as a ketohexose with TiO_2 photocatalyst under UV irradiation and those products were evaluated by HPLC, MS and NMR. From results of HPLC, MS and NMR, new product was identified as D-arabino-1,4-lactone, which should produce from photocatalytic oxidation of fructose.

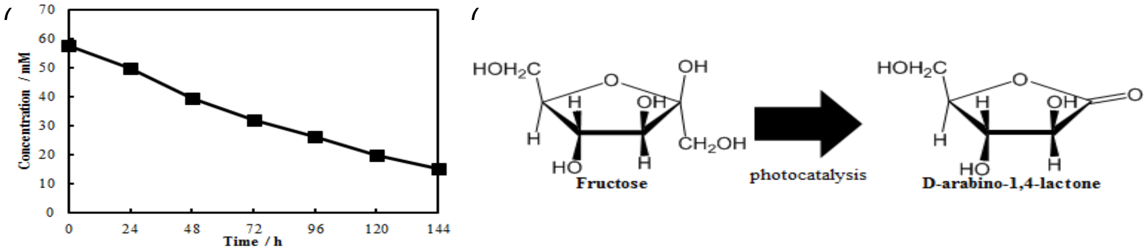

Fig. 1 (a) Time course of concentration of fructose by TiO_2 photocatalysis under UV irradiation, (b) production of D-arabino-1,4-lactone by the photocatalytic decomposition of fructose.

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E313

Inactivation Mechanism of *Escherichia coli* and Qβ Phagewith Visible-Light Responsive Rh-Doped SrTiO$_3$Photocatalyst

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Keywords: Photocatalysis, Phage inactivation, Rh-doped SrTiO$_3$

Abstract

Visible light responsive photocatalysts have been developed for the interior use [1][2]. We recently reported that Rh-doped SrTiO$_3$ (STO:Rh) decompose acetaldehyde as a volatile organic compounds under visible light illumination. In this work, we evaluated antipathogen effect for *E. coli* and Qβ phage using STO:Rh andexamined the inactivation mechanisms.
Survival ratio of *E. coli* was decreased to 0.01% after 24 h in the presence of STO:Rh under visible light illumination, while the survival ratio of Qβ phage was decreased to 0.0001% after 4 h (Fig.1a), which suggested that STO:Rh showed superior inactivation for Qβ phage than *E. coli*. To examine the effect of Rh^{4+} ion in STO:Rh for the superior antiphage effect, we prepared Rh and Sb co-doped STO (STO:Rh/Sb), where Rh ion is trivalent. Survival ratio of *E. coli* was decreased to 0.01% after 24 h in the presence of STO:Rh/Sb under visible light illumination, while the survival ratio of Qβ phage was not significantly decreased after 4 h (Fig.1b). These results suggested that selective antiphage effect can be attributed from the presence of Rh^{4+} ion in STO:Rh.

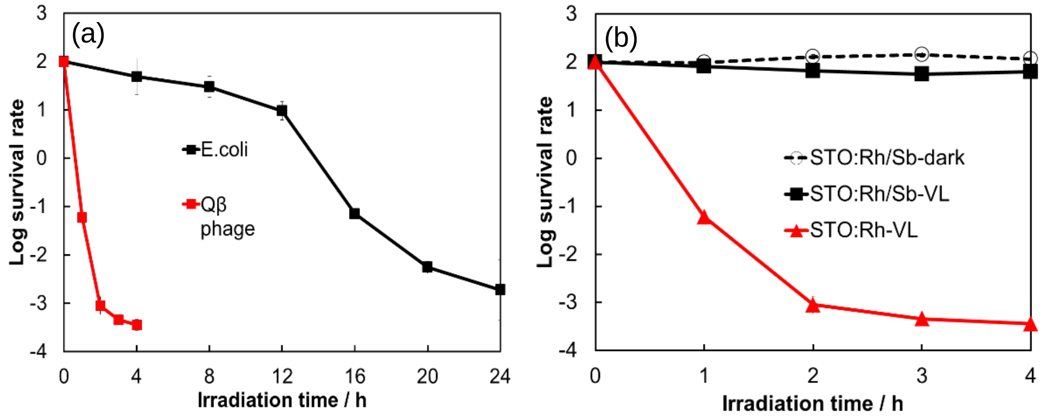

Fig. 1 (a) Inactivation of *E.coli* and Qβ phage with STO:Rh, (b) Inactivation of Qβ phage with STO:Rh and STO:Rh/Sb

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E314

Hyperbranched Polymers with Stable Photocatalytic Activity under Visible Light

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Keywords: Photocatalyst, Polymer, Visible-light, Water -splitting

Abstract

Nowadays, energy and environmental issues caused by fossil fuelhas become an intractable problem all over the world. Semiconductor photocatalysis water splitting under sunlight is a green technology for large-scale application because both water and sunlight are abundant in the nature [1]. Over the past decade, extensive studies have been made to seek innovative photocatalyst working with visible-light irradiation to efficiently utilize the solar light.[2] The explorations have been overwhelmingly dominated by metal-containing inorganic materials.[3]In contrast, there have been few reports on metal-free organic semiconductor photocatalyst that possesses significant advantages including low-cost fabrication, abundant sources and easy processibility.Herein,we report a stable hyperbranched polymer photocatalysts synthesized bya green polymerizationapproach. This method is a solvent-free process withouttoxic substanceproduced and thus well meets the principles of green chemistry.

The synthesis involves an imidization reaction, as shown in Scheme 1, only water is released and a hyperbranched polyimide(PI) network is achieved. The XRD patterns and TEM imageshowthe high crystallinity and dendritic morphologyof PI. The biomimic morphology of the hyperbranched polymer HPI facilitates the fast charge transport from the bulk to surface reaction sites. UV-Vis absorption spectrum indicates that the yellow coloured PI has ability to absorb visible light, suggesting its potential for visible-light-driven photocatalysis.

To evaluate the photocatalytic activity of the PI samples, weexamine the H_2 evolution activity of PI, with methanol as sacrificial reagent and 1wt % Pt as cocatalyst. The light irradiation is carried out under visible light with a cut-off filter of 420 nm. A high photocatalytic activity forhydrogengeneration from water was obtained on PI. The total evolution amount of H_2 after 10 h is 70 µmol, which is prominentfor an organic semiconductor. We also investigate theFTIR andXRDspectrum of PI after the photocatalyticreaction, both indicating no obvious change of the sample during the photocatalytic process which confirms the stability of PI during photocatalysis reaction.Considering the availability of amines and dianhydrides monomers, this work may shed light on preparing polymer photocatalyst with facile green process.

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E315

Stepwise Ligand-based Proton-coupled Redox Reactions of Tris (*ortho*-Phenylenediamineand *ortho*-Benzoquinodiimine) Iron (II) Complexes

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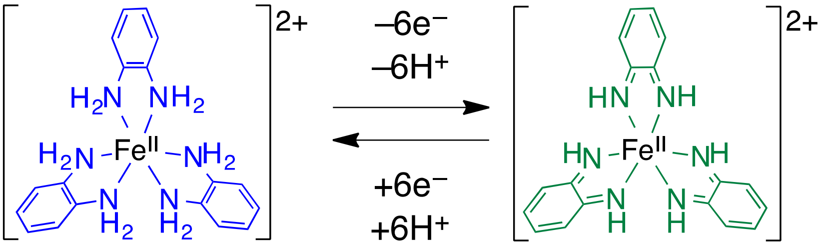
Keywords: Photochemical hydrogen evolution, Ligand-based proton/electron transfer, *o*-Phenylenediamine, *o*-Benzoquinodiimine, Iron complex

Abstract

Molecular hydrogen is one of attractive candidates as an environmentally friendly energy carrier.[1] Since, hydrogen is difficult to store, the development of safe and convenient hydrogen storage materials is strongly desired. Under these circumstances, several organic compounds, known as “organic hydrides”, are fascinating materials.[1]Recently, quinoline/1,2,3,4-tetrahydroquinoline system has been reported as efficient hydrogen production/storage material that can evolve hydrogen at relatively low temperatures (*ca.* 110-140 °C), under the presence of Ir catalyst.[2] However, even in the excellent example, the operating temperature in the hydrogen evolution reaction (HER) is still high. Therefore, the design of the novel HER utilizing nonprecious metals that can be operated under room temperature is of great importance and interest.

Recently, we reported that Fe(II) complex with *o*-phenylenediamine (opda), $[Fe^{II}(opda)_3](ClO_4)_2$, shows photochemical HER at room temperature.[3] In this system, the protons and the electrons in opda act as the source of photochemically evolved hydrogen. This complex also showed ligand-based six-electron and six-proton oxidation to give $[Fe^{II}(bqdi)_3](ClO_4)_2$, (bqdi : *o*-benzoquinodiimine), (Scheme 1).[4]We herein report the detailed experimental results that shows stepwise ligand-based multi-proton and electron transfer of the complexes.

Scheme 1. Proton-coupled redox reaction of $[Fe^{II}(opda)_3]^{2+}/[Fe^{II}(bqdi)_3]^{2+}$



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E316

CO_2 reduction with water over metal oxide photocatalysts: Modification of surface property by loading various cocatalysts

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Keywords: Photocatalysis, CO_2 reduction, Metal oxide catalysts

Abstract

Photocatalytic CO_2 reduction with water into usable chemicals has been considered a promising method toaddress the problems of global warming and energy crisis. Ga_2O_3 is one of the photocatalyststo show the photocatalytic activity for the reduction of $CO_2$with water into CO, H_2 and O_2. In our previous study, the photocatalytic activity forCO production was enhanced bythe loading of Ag as a cocatalyst [1], and we have been studying the role of the Ag co-catalyst in the CO production mechanism. We carried out in-situ FT-IR measurementsof Ag loaded Ga_2O_3 (Ag/Ga_2O_3) photocatalysts at each reactionstep, and proposed the reaction mechanism involving the generationprocess of bidentate formate species as the CO production intermediates [1]. Furthermore, HRTEM and XAFS measurements revealed that around 1 nm sized Ag clustersaccepted more electrons in the d-orbitals as aresult of the strong interaction with the Ga_2O_3 surface and promoted the formation of the reaction intermediates. On the other hand, relatively large Ag particles with an $AgGaO_2$-like interface structure could adsorb CO_2 molecules which were not changed into the reaction intermediates [2,3].

In the present study, we investigated co-loading effects of Ag and NiO (a cocatalyst for water splitting) on the photocatalytic activity for CO_2 reduction with water. A co-loaded photocatalyst prepared by the photodeposition of Ag after the NiO impregnation promoted both CO and H_2 productions compared to the bare Ga_2O_3. On the other hand, the CO and H_2 production rates over the photocatalyst prepared by co-impregnation of Ag and NiO were much lower than those over the bare Ga_2O_3.The photocatalytic activity is likely to correlate with the sizes and chemical states of Ag and/or NiO cocatalysts which depend on the preparing methods of these samples. At the conference, we will also discuss the TEM and XAFS results of these co-loaded photocatalysts.

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Green Industrial Processes and Molecular Innovation

IP401

Efficient Organocatalyzed Chemo/Regioselective Aldol, Aldol Condensation and Morita-Baylis-Hillman (MBH) Reactions of Isophorone

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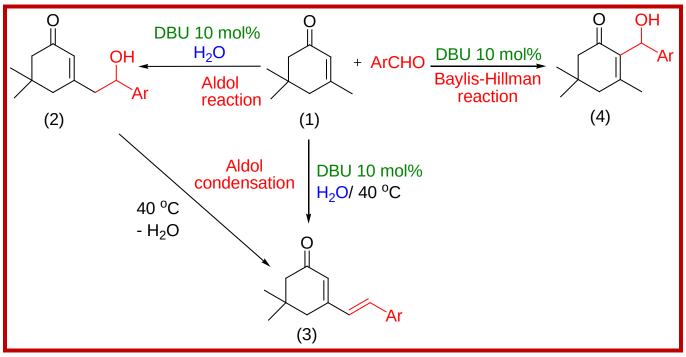
Keywords: Organocatalysis, Aldol reaction, Morita-Baylis-Hillman reaction

Abstract

The directed aldol and Morita-Baylis-Hillman (MBH) reactions are known as two powerful methodologies for new carbon–carbon bonds. Some substantial features of these reactions such as simple starting materials, atom-economy, and possibility of being performed in an aqueous or organocatalytic conditions leading to multi-functionalized molecules are considerable. Particularly, biological and pharmaceutical activities of related adducts have received great attention by synthetic organic chemists in discovery of innovative drugs [1a,b]. However, many of the present methods have drawbacks and disadvantages. So, based on our experience on thiopyran heterocyclic systems [2], we envisaged that isophorone (1) would be an appropriate probe to tackle the Baylis-Hillman and aldol limitations. As a result of our studies, we hereby disclose the potential of an organocatalytic system that can direct the reaction with aldehydes to selectively undergo either BH or aldol reactions. The structure of the products is assigned based on their spectroscopic data and X-ray crystallography analysis. In conclusion, we accomplished green, fast, high yield and chemo/regioselective aldol, aldol condensation and MBH reactions through isophorone and DBU. We also realized that the H_2O has a pivotal role to direct the aldol versus MBH reactions. Furthermore, we showed that the applied organocatalyst can play as a nucleophile or a base upon the reaction condition.Therefore, we properly controlled isophorone active sites via H_2O and DBU.



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IP402

DBU as an Efficient, Environmentally Friendly and InexpensiveCatalyst for Direct Diastroselective Mannich Reactions ofHeterocyclic Ketones

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Keywords: Mannich reaction, Organocatalysis, Heterocyclic ketones

Abstract

The direct catalytic asymmetric Mannich reaction is one of the most efficient methods for the construction of chiral β-amino carbonyl compounds. It is also a very Important C–C bond formation reaction in synthetic organic chemistry due to its atom-economy advantages and its applications in natural products and drugs synthesis. There are several available procedures in the literature for the synthesis of this group of compounds. However, many of the present methods have drawbacks and disadvantages such as long reaction times, harsh reaction conditions, toxicity and difficulty in product isolation [1].

In recent years, we have been trying to conduct synthetic methodologies under environmentally friendly conditions. In this regard, we have reported convenient procedutres for the synthesis of, α,β-unsaturated ketones [2], disulfides [3], and Baylis-Hillman [4] adducts under benign aqueous conditions. In continuation, we would like now to report a very facile stereoselective procedure for the synthesis of β-amino ketones via direct Mannich reactions of cyclic ketones catalyzed by DBU.

As a result of this work, reactions proceed in short time intervals and high yields in favour of *anti* stereoisomer adductswithout using toxic reagents and expensive purification techniques.

The above mentioned direct Mannich reaction proceeds in ethanolic mixture of a ketone and a variety of aldehydes and aniline derivatives in the presence of catalytic quantities of DBU. The structure of the products is assigned based on their spectroscopic data and their stereochemistry is confirmed by X-ray crystallography analysis.

In summary, reactions are rapid and take place under mild conditions and the products are directly obtained from the reaction mixtures by precipitation followed by recrystallization from ethyl acetate. More importantly, only sole formation of the *anti* products is selectively observed in most of the cases.

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IP403

Rapid Analysis of Polycyclic Aromatic Hydrocarbons in Aqueous Solutions by Two-Dimensional HPLC System Using Monolithic Column*

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Keyword: monolithic affinity column, polycylic aromatic hydrocarbon, 2D-HPLC

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds having mutagenic, toxic and carcinogenic effects to human health that formed by incomplete combustion of organic items. Several analytical methods for the separation of PAHs have been reported[1]. Unfortunately, most of them are tedious, time consuming and require labor and considerable amount of high purity of organic compounds. Two dimensional chromatographic separation (2D-HPLC) is considered as an alternative techniques to these shortcoming. The most impressive feature of this study is forming high performance liquid affinity column (HPLAC) with the combination of monolithic affinity columns[2]and HPLC. In the first step, the selective extraction and pre-concentration of desired substance was separated by monolithic affinity columns and then determination of trace amounts of PAHs was carried out by second PAH column. All automation process including of extraction, pre-concentration and determination process performed by "on-line". Herein, monolithic columns were firstly prepared by the in-situ bulk polymerization of N-methacryloyl-L-phenylalanine (MAPA) as a pseudospecific ligand and 2-hydroxyethyl methacrylate (HEMA) conducted in a stainless steel columns. After characterization of the monolithic columns by FTIR, SEM and elemental analysis, they were used for pre-concentration of Benzo[a]pyrene (BaP) through regular one dimensional HPLC system (1D-HPLC). Secondly, most common PAH types found in the hazardous waste sites were investigated with taking into consideration of toxicity and hazardous[2] effects through two dimensional HPLC system (2D-HPLC) for their on-line pre-concentration and determination. As a conclusion, the lower concentration of PAH solutions pre-concentrated by monolith affinity columns were successfully monitored by 2D-HPLC.

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IP404

Electrochemical Study of Methimazole and its Direct Determination in Pharmaceutical Preparations and Human Serum by Square Wave and Differential Pulse Voltammetry

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Keywords: Methimazole, square wave voltammetry, differential pulse voltammetry, serum, validation

Abstract

Two simple and rapid methods were developed for the determination of methimazole[1] in pharmaceutical preparations and human serum by square wave and differential pulse voltammetry. The anodic peak at +0.60 V obtained in a buffer on glassy carbon electrode was used for analysis. The peak current and peak potential depend on pH, scan rate and initial potential. Decrease of the anodic peak with increasing pH, as well as deviations from linear plots of $i\text{p} = f(C)$ and $i\text{p} = f(C)$ and $i\text{p} = kv^{1/2}$ indicate that this peak at higher concentrations is affected by adsorption-desorption phenomena. The linearity was established over the concentration range of 10-80 μg/mLfor both methods in supporting electrolyte and human serum. The repeatability and reproducibility of the methods for all media (such as supporting electrolyte and serum samples) were determined. Precision and accuracy were also checked in all media. The standard addition method was used in human serum. No electroactive interferences from the endogenous substances were found in the serum samples. For the analysis in the presence of biological material standard addition method is preferred. SWV and DPV are effective and rapid electroanalytical techniques with well-established advantages, including good discrimination against background current and low detection limits. And the methods are requiring less than 3 min to run samples. Therefore, the methods can be used effectively without separation for routine analysis of methimazole in pure form, its formulations and human serum samples.

The goal of this work was the development of new voltammetric methods for the direct determination of methimazole in pharmaceutical preparations and spiked human serum samples without any time-consuming extraction or evaporation steps prior to drug assay. For the analysis in the presence of biological material standard addition method is preferred. SWV and DPV are effective and rapid electroanalytical techniques with well-established advantages, including good discrimination against background current and low detection limits[2].And the methods are requiring less than 3 min to run samples. Therefore, the methods can be used effectively without separation for routine analysis of methimazole in pure form, its formulations and human serum samples.

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IP405

Supported and Non-Supported Chiral Ionic Liquids for Asymmetric catalysis

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Keywords: Organocatalysis, Chiral Ionic liquids, Supported Silica Catalysts, Asymmetric Catalysis

Abstract

Nowadays, the discovery of efficient homogeneous and heterogeneous catalytic processes became a relevant research topic in academic and industrial fields. Many publications have reported the advantages to use supported catalysts in order to recycle the catalytic media during several reaction cycles without loss of efficiency [1,2]. The possibility to combine the peculiar properties of chiral ionic liquids as organocatalysts for asymmetric catalytic reaction seems an attractive field [3,4].

Herein, we describe recent studies of the use of supported and non-supported chiral ionic liquids for catalytic approaches:

a) Homogeneous catalysis using non-supported chiral ILs: applications of chiral ILs based on L-proline and cholic acid derivatives as chiral anions for asymmetric aldol, Michael reactions and epoxidation reactions. For some cases, it was possible to obtain the desired pure chiral products in good yields and enantiomeric excesses comparable with the conventional systems. Additionally, for the best homogeneous catalytic processes, the recycling and re-using of the chiral reaction media (ILs or green solvents and chiral catalyst) have been evaluated.

b) Heterogeneous catalysis using supported chiral ILs: the adequate incorporation of chiral ILs already tested as efficient organocatalysts into silica mesoporous supports. All supported chiral ILs have been completely characterized by NMR, FTIR, elemental analysis and microscopic techniques. The most promissory supported chiral ILs will be tested for asymmetric catalytic processes.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support (PEst-C/EQB/LA0006/2013 project) and Solchemar Company.

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IP406

Development and treatment procedures of water contaminated by arsenate using chitosan support derivative

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Keywords: Sequestrating agent, Chitosan, Water treatment, Column sorption, Arsenic

Abstract

More than 200 million persons worldwide are affected by high concentrations of arsenic in water [1]. Arsenic is classified as one of the most toxic element for humans by the World Health Organization (WHO) [2]. With the tightening regulation of drinking water at 10 µg·L-1 by WHO, it is necessary to find efficient sorbent materials for arsenic [1]. In this work, the removal of arsenate from water is presented with modified chitosan using a green methodology. Chitosan is obtained by deacetylation of chitin which is found in shells of crustacean [3]. Kinetic studies have shown a very fast sequestration in less than 10 min. From isotherm models, it was demonstrated that arsenate sorption capacity was 42 mgarsenic·gsupport-1 at pH 7. Results show significant improvement over standard adsorbents according to literature [4]. The adsorption efficiency of the new chitosan support is 99%, even at low concentrations such as 30 µg·L-1. Breakthrough curves obtained from column sorption and desorption with a NaCl solution suggest that this modified chitosan agent is relevant for large scale applications. With this new product, it is possible to treat contaminated water from arsenate at low cost, with good selectivity and few wastes. These results would have important impacts on population from developing countries and contribute to sustainable water treatments. Removal of arsenic in water will have positive effects on the environment and people's health.

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IP407

The use of natural materials (chitosan and humic acid) in the treatment of industrial red mud wastewater

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Keywords: Industrial Wastewater Treatment, Red Mud, Chitosan, Humic Acid

Abstract

The reuse and recirculation of process water in mineral and metallurgical beneficiation plants is mandatory and then of increasingly demanding. Polymers have been used in coagulation and flocculation processes for wastewater treatment and its application is mostly based on the mechanisms of adsorption of soluble material on solid particles, forming metal hydroxide flocs [1][2]. In the case of alumina refineries, which the main residue is the red mud, wastewater flows contain large amounts of very fine particles (d50 = 6.6 μm) and high causticity. The use of flocculant polymers, mostly polyacrylamides, acts in the colloids removal of these effluents [3]. However, alternative and more environmental friendly natural polymers, such as chitosan [4] and humic acid, when used together, may promote greater effectiveness in the treatment of these red mud wastewater. The purpose of this study is to evaluate the use of these natural polymers in the treatment of wastewater containing colloidal material in order to reduce the amount of fine particles to less than 50 NTU, which is the environmentally required standard for water reuse. Based on pH, soluble ions concentration, surface electrical charge and electrolyte addition, operating conditions for destabilization and flocculation of this wastewater were determined. The variables evaluated in the dewatering operations were particle surface charges, dosages of flocculants, stirring speed and time. Particle removal efficiency was calculated based on the turbidity in the wastewater and in the thickener overflow. For red mud wastewater containing 1% (w/v) of particles, the solids removal efficiency by flocculation and sedimentation with a mixture of chitosan/humic acid at pH=12, the solids removal efficiency was 95%. The reduction in color and causticity, besides overflow turbidity values above 50 NTU, indicate the efficiency of these reagents to reach the environmental guidelines for water reuse.

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IP408
Carbon Dioxide Functionalization at CaRLa

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Keywords: Catalysis, carbon dioxide, isocyanate, acrylate

Abstract

CaRLa is a specific model of a public private partnership, in which the two partners, BASF and University of Heidelberg within its broader initiative “Industry on Campus”, work closely together in a joint laboratory. In contrast to classical industry-academia partnerships, the concept of this lab relies on bringing academic and industrial researchers as closely as possible together in one laboratory, fostering technology transfer from basic research to potential industrial applications.

Phosgene-free Synthesis of Isocyanates using CO2 and Organotin(IV) Alkoxides [1]

Polyurethanes are among the most valuable polymers produced by chemical industry. The starting material isocyanate is industrially obtained by reacting primary amines with phosgene, and subsequent degradation of carbamic chlorides, which leads to isocyanates and two eq. of HCl. The synthesis of carbamates also affords a convenient route to iso-cyanates. The reaction between amines and CO_2 leads to a transient carbamic acid which can be trapped *in situ* by an alcohol provided by dialkyltin(IV) alkoxides. The resulting carbamate could ultimately be cleaved into the desired isocyanate and alcohol.

Sodium Acrylate from Ethylene and CO_2 [2,3]

The synthesis of sodium acrylate through catalytic carboxylation of ethylene with CO_2 in the presence of a base is a reaction of high interest. However, the reaction did not yet exist (“dream reaction”) even after ~50 years of academic research. To develop a more efficient and sustainable method to access this valuable acrylate monomer, we optimized the system in a one-step homogeneous nickel or palladium-catalyzed reaction, without the need for stoichiometric amounts of an additional reducing agent. Suitable nontoxic solvents such as anisole instead of the previously reported tetrahydrofuran or chloro-benzene were found to lead to acrylate formation. In combination with appropriate phenolate bases, this could allow a rational process concept for a simple catalyst recycling, product separation, and base regeneration.

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IP409
Catalitic chemical fixation of CO_2 through syntehsis of acrylic monomers

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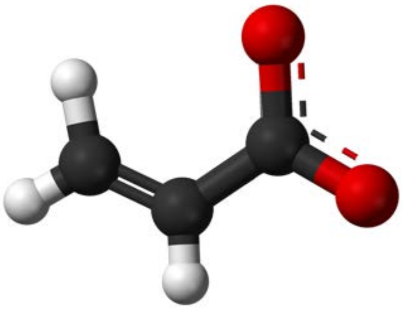
Keywords:CO_2 fixation, acrylic monomers

Abstract

The effects of CO_2 emissions on global climate are well known and studied problems. Many ways of limiting such emissions have been suggested, from the injection in exausted oil fields, to the chemical fixation of carbon dioxide in more stable forms. Among the several routes proposed, the use of carbon dioxide as a raw material in the green synthesis of strategic chemicals has gained a great interest.
From an industrial point of view, an interesting target is represented by the synthesis of acrylates using CO_2 and ethene.



Several transition-metals have been showed catalytic activity in such reaction in particular under controlled basic conditions.
As in the literature it is reported [1] that acrylates can be obtained from CO_2 and ethene by using a Ni(0) phosphine complex, as a catalyst, in the present work we have been studied the catalytic activity of a series of Ni(II) and Pd(II) diphosphine-complexes.
The optimization of the reaction conditions leads to a turnover frequencies (TON) of ca. 300 – 350 h^{-1} [(mol of acrylate)/(mol of catalyst x h)]. A reaction mechanism has been proposed and discussed.

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IP410

Microwave Assisted Extraction Using an Open-end Coaxial Antenna and a Cooling System

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Keywords: Microwave; Coaxial antenna, Polyphenols

Abstract

Microwave (MW) coaxial antennas (CA) have been used so far mainly in cancer treatment because they produce a very intense specific absorption rate (SAR) on a very small volume of irradiated tissue [1]. However, there are some studies related to the use of such antennas to perform chemical reactions or extractions in open vessels, without the existence of a specially designed microwave applicator [2]. Recently, SAIREM Co. introduced in manufacturing an equipment that uses internal transmission line; in other words, an antenna with multiple slots that allows to introduce microwave energy in the system with very good efficiencies [3]. The aim of our installation is to use the microwave assisted extraction (MAE) for some components from plants in a special applicator, built such as to achieve heterogeneous radiation (an intense microwave field around the CA and very weak in the remaining extraction reactor). Due to this type of irradiation and to the continuous heat exchanging towards external wall (which is cooled permanently), an important difference of temperature is emphasized. COMSOL simulation shows that this difference of temperature depends on the microwave power introduced into the system, the heat transfer coefficient and the stirring rate. There are experiments where this difference of temperature was about 30ºC. The innovative experimental installation is based on batch operation into a cylindrical glass cell (CGC) containing vegetable sample (Sea buckthorn - *Hippophaë rhamnoides L.*) for polyphenols extraction with MW-TEM mode in coaxial structure. The 2.45 GHz solid state microwave generator with adjustable output power (0-25W) transfer the MW energy through a cable to an adjustable coaxial antenna (ACA) immersed directly into the CGC. The results obtained using the innovative experimental installation were compared with those obtained by conventional extraction and by a multimode microwave applicator type Biotage. The medium temperature profile was the same for all these experiments. The polyphenolic extracts were analyzed in order to determine the total polyphenolic content, the antioxidant activity and chemical composition. The MAE using ACA and a cooling system proved to be better than conventional extraction or MAE performed in usual MW applicator (Biotage Initiator).

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IP411

Solvent Dependent Kinetics Studies of 4-Chloroquinazoline with Aniline and Hydrazine.

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Keywords: Ionic Liquids, 4-chloroquinazoline

Abstract

Several studies involving 4-chloroquinazoline with two nucleophiles, aniline and hydrazine in a series of solvents were performed in order to compare rate coefficient values mediated by the change of the reaction media on a pseudo-first order regime.

Aniline was shown to have greater rates in water with lower values of pH around the pKa of aniline. This trend implies that the reaction is being favored by acidic media and a high availability of hydrogen bond donor sites in the solvent. A broader study then was made at a fixed concentration of nucleophile and a wide range of pH showing that the highest rates obtained were found around pH=3, achieving a plateau beyond that point. These results suggest that the mechanism involved does not pass through of the Meisenheimer complex (MC) associated to a S_NAr reaction. The results suggest that the reaction mechanism proceeds through another type of intermediate. Computational calculations are being made in order to validate the proposed reaction mechanism.

On the other hand, the same reaction was studied in two types of ionic liquid (IL), the protic IL named propyl ammonium nitrate (PAN). In this solvent similar rate coefficient values with reference to water were obtained and 72,35 times higher than the aprotic IL 1-methyl-3-ethylimidazolium methanosulfonate (EMIMMSO). This fact suggest that the environment promotes that the reaction pathway proceeds through one intermediate or the other.

Studies with hydrazine have shown that in water a more basic reaction environment gives better results respect to aniline. Ionic liquids 1-methyl-3buthylimidazolium dicyanamide (BMIMDCN) and 1-buthyl-1-methylpyrrilidonium dicyanamide (BMPYRDCN) have rate constant around 10 times higher than water, showing a powerful catalytic effect.

IP412
Bioremediation observed by LIFirr: a sustainable alternative

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Keywords: Biorremediation, Petroleum, LIFirr

Abstract

Bioremediation techniques consist of the use of microorganisms (e.g. plants, fungi, bacteria) to neutralize toxic substances, transforming them into less toxic substances or converting them to harmless substances to the environment and human health [1]. In this study, microbial strains were inserted in oil. Microbial activity was observed by laser-induced fluorescence in function of the irradiation time of the sample (LIFirr). This technique (LIFirr) consists of inducing fluorescence of natural chromophores (present in the sample) and of detecting the total fluorescence emitted [2]. The oil from the Bacia do Recôncavo Baiano was used. Its paraffinic percentage was 14.7% w/w, 0.20% v/v emulsified water, sediment below traits density at 15.6 °C 0.8727, API 30.64, pour point of 39 °C and cloud point 49.22 °C. The bacterial strains were selected according to their technological properties related to enhanced oil recovery, biosurfactants production capacity and oil biodegradation potential [3]. The microorganisms were identified by amplification and sequencing of fragments of the 16S rRNA gene (DNA 16 S). Furthermore, the bacteria belong to the genera of *Pseudomonas* and *Bacillus aeroginosas lincheniforms*. The results showed high oil biodegradation potential. It is noteworthy that the oil treated with *Bacillus* bioremediators had the highest LIFirr signals due to its greater efficiency to biodegrade paraffins, generating smaller molecules and, hence, reducing the fluorescence quenching and the non-radioactive decay. The biodegradation of larger paraffins was confirmed by the chromatographic characterization. The samples treated with *Pseudomonas* bioremediators showed surfactant effect that decouples fluorophores, reducing the thermic decay and increasing the fluorescent decay, and decreasing in the LIFirr signal. Bioremediation observed by LIFirr proved to be a sustainable alternative, since it does not generate pollutants into the environment, because it does not require test preparation (chemical reagents), it is fast (due to laser induction) and efficient (due quick response).

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IP413

Production of Xylo-Oligosaccharides Using Hydrothermal Microwave Processing and Antioxidant Activity Thereof

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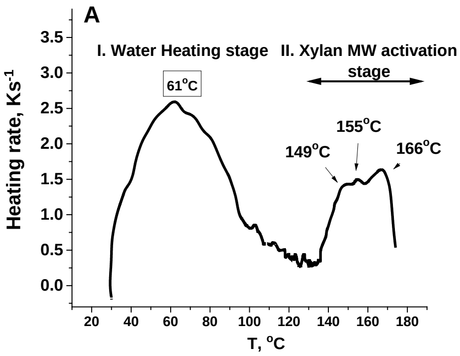
Keywords: Hydrothermal Microwave Processing, Xylan, Antioxidant

Abstract

Xylan hemicellulose is the most abundant type of hemicellulose in nature, present in almost all plants, and making up to 35% of some hardwoods by mass [1]. This abundance makes it a prime target for valorisation in the biorefinery. Xylan consists of a D-xylopyranoside backbone with acetyl, methyl, and ferulic ester appendages, and a degree of polymerization typically between 100 and 200 [2], and so xylan valorisation normally involves a chemical or enzymatic depolymerisation process. The resultant xylo-oligosaccharides have previously been shown to have antioxidant activity [3] [4], and can be further functionalised to produce useful chemicals such as furfural. We investigate here the use of catalyst-free hydrothermal microwave treatment for the depolymerisation of xylan from beechwood. We find that at the optimal holding temperature of 180°C yields of up to 62% water soluble material are obtained, consisting mainly of xylo-oligosaccharides of chain length 1-9. The antioxidant activity of the samples is found to increase with increasing holding temperature up to 200°C, comparing favourably with previous reports. We investigate some possible reasons for this, focussing on aromatic content in the starting material, and production of aromatics due to a caramelization process during microwave processing.



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IP414

Concise Synthesis and Biological Evaluation of C-Glycosyl Flavonoid Analogues Inspired by Natural Product Aspalathin

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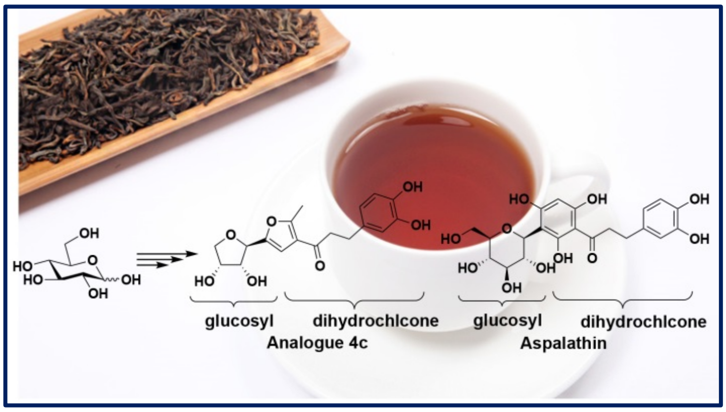
Keywords:C-Glycosyl flavonoid，antioxidant，anticancer

Abstract: Aspalathin, a representive C-Glycosyl flavonoid, was first found in the leaves of *Aspalathus linearis* with excellent bioactivities. Here, we described the synthesis of three kinds of C-Glycosyl flavonoid analogues of aspalathin. For the syntheses of these analogues, the condensation of glucose with acetylacetone in the presence of Lewis acid in ethanol afforded compound **2**, in 87% yield. Next, compound **2** in ethanol refluxed with aromaticaldehydes by using base-catalyst in order to afford (E)-α, β unsaturated ketones i.e. **3a-3c**. Finally, compounds **3a-3c** were subjected to hydrogenolysis in the presence of a catalyst, 10% palladium-carbon, under hydrogen atmosphere in the mixture of dichloromethane and ethanol to afford desired compounds **4a-4c**. The total yield of the three steps is around 44%-52%. Besides, the DPPH radical scavenging method was used to detect their antioxidant activity and the MTT colorimetric assay was employed to test anticancer activity of Hep-G2 liver carcinoma cells and MCF-7 human breast carcinoma cells. The compound **4c** was supposed as the most promising compound with a good antioxidant ability and inhibition of Hep-G2 and MCF-7 cells IC_{50} value at 4.9μM, 19μM respectively.



IP415

Metabolite profiling propolis samples from seven countries by means of a fully green approach – on the track for a truly green propolis

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Keywords:green chromatography, bioethanol, natural products chemistry

Abstract

Propolis' chemical composition is flora-dependent since in different ecosystems the bees will access different plant species for raw materials to produce propolis [1]. From the understanding that specific biological activities can only be expected for specific types of propolis and that these activities might be a result of the synergic effect of several compounds, the need of analytical methods that are able to discern between types of propolis has become clear [1]. High-performance liquid chromatography has been the most popular technique for the assessment of propolis sample type. Ironically, despite the production of quality bee products, as well as bee survival itself depending on the health condition of the environment [2], the potentially harmful methanol and acetonitrile are the organic solvents of choice in reported HPLC methods employed by scientists and traders to monitor the quality of propolis. Although analytical chemistry has been recognized as a target for green principles and the strong evidence that potential drawbacks of the greener ethanol, compared with methanol and acetonitrile, can be circumvented by recent improvements in HPLC related technologies [3], no chromatographic methods guided clearly by Green Analytical Chemistry principles have been reported in the literature to analyse samples of propolis. This work presents an ultra-high performance liquid chromatography method for green propolis identification employing a multiparameter, multi-analyte and solvent and energy-saving experimental design for the method development process itself and the greener ethanol as the organic modifier. This method was able to discern this type of propolis in a set of samples from seven countries as well as to differentiate these samples by fingerprint similarity based on principal component analysis. It also proved to be compatible with the cheap, largely available food grade ethanol 96°GL produced from sugarcane.

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IP416

Resolution of propranolol using supported liquid membranes based on ionic liquids

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Keywords: Propranolol, resolution, ionic liquids

Abstract

Our life depends on the products of the pharmaceutical industry, such as antibiotics for combating diseases and analgesics or anti-inflammatory drugs for pain relief. Many pharmaceutical products are commercialized as racemic mixtures. The pharmaceutical implications of racemic drugs have only extensively been recognized in the last 20 years.[1] On the other hand, the use of membranes has generated an exponentially increasing interest because the classical techniques of separation and purification require large amounts of energy and solvents. The membrane-based techniques are framed on the analysis of the flow of the separating species. This gradient of particles is determined by the difference in chemical potential across the membrane. [2]

In this work we report an investigation of the resolution of racemic propranolol using 3 commercial ionic liquids as a liquid phase in Supported Liquid Membranes (SLM) with the aim to recover the raw material (active enantiomer) from the enantiomer that are inactive for the therapeutic effect present in a drug, increase the yield of the recovery process and the minimization of hazards generated by waste.

A quiral liquid chromatography analytical method was developed and validated to quantify the individual enantiomers of propranolol after applying the different separation processes. The chromatographic separation was done using an Astec cellulose DMP quiral column (15cm x 2,1mm, particule size 5 µm, Supelco Analytical). The deteccion was performed by a diode array UV detector at 290 nm.

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IP417

Mesoporous carbons from carbohydrate biomass and their use for acid-catalyzed reactions of carbohydrate valorization

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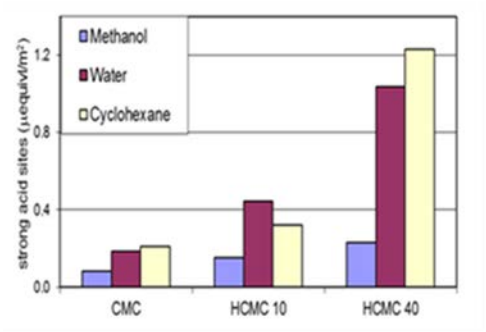
Keywords: Carbons, Heterogeneous catalysts, Carbohydrates, Biomass, Hydrolysis reactions

Abstract

Carbohydrate biomass is considered a renewable source for the obtainment of energy and chemicals. Biomass can also be viewed as an interesting source of functional materials. For use in various applicative fields, as energy-storage systems, catalysts, electrodes and separation processes. The possibility to direct the preparation of carbon materials by addition of metal salts as activation agents to tune their morphological features is very attractive for the possibility to obtain porous carbons.

In this work, starting from a high surface area mesoporous carbon (CMC), obtained from wheat flour as carbon precursor and $ZnCl_2$ to create the mesoporosity [1], others carbon samples have been prepared by HNO_3 acidification operating at 10°C and 40°C (HCMC10 and HCMC40, respectively).



All the samples have been characterized to study their structure, morphology, and surface properties (in particular acidities measured in different liquids [2] to investigate on the *tolerance* of the acid sites of the samples to polar and protic solvents, Figure), and used in reactions of disaccharide hydrolysis (sucrose and cellobiose) to the constitutive monomers in mild conditions of temperature. Sucrose is constituted by glucosidic and fructosidic units linked by α-1,β-2 glycosidic bond, and cellobiose by glucosidic units linked by β-1,4-glycosidic bonds, that are very hard to break.

The *water-tolerant* acid properties of the surface sites of the carbon samples gave them interesting catalytic activity, comparable to the catalytic performances shown by an acid Amberlite catalyst.

Mesoporous CMC has 1460 $m^2 \cdot g^{-1}$ of BET surface area and 2.50 $cm^3 \cdot g^{-1}$ of pore volume with narrow pore dimension around 5 nm. The HCMC10 and HCMC40 samples have also high surface area and high porosity values. XRD showed amorphous structure of the tree carbon samples with presence of graphitic domains, as confirmed by Raman spectra. On CMC, HCMC10, and HCMC40 the reaction of sucrose hydrolysis at 80°C proceeded with high selectivity to glucose and fructose and in the absence of any by-products up to total conversion of sucrose. From the calculated rate constants (k_{obs}, h^{-1}), the catalytic constants were obtained (k_{cat}): CMC ($1.93 \pm 0.14\ 10^{-5} L \cdot h^{-1} \cdot m^{-2}$) ≅ HCMC10 ($1.87 \pm 0.06\ 10^{-5} L \cdot h^{-1} \cdot m^{-2}$) << HCMC40 ($7.12 \pm 0.49\ 10^{-5}\ L \cdot h^{-1} \cdot m^{-2}$). The highest *effective* acid site density of HCMC40 in water justified its enhanced activity.

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IP418

Computational Study of Friedländer condensation catalyzed by hybrid carbon/MgO materials.

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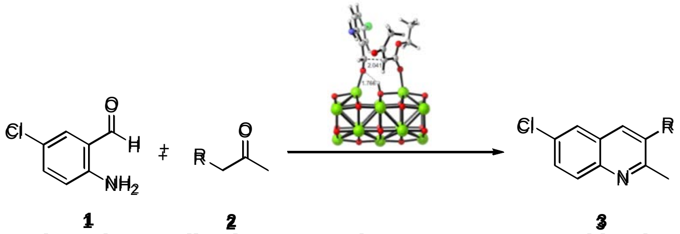
Keywords: Theoretical Calculations, Quinolines, Friedländer Condensation

Abstract

Carbon is old but also a new material. The development of new carbon-based materials able to catalyze interesting chemical processes involving the synthesis of heterocyclic systems still constitutes a challege for the Fine Chemical industry [1].
In other way, Friedländer condensation, proceeding through double condensation between 2-aminoaryl carbonyl components with other carbonyl compounds, with active methylene groups, is considered one of the most cited and useful reactions in organic synthesis [2]. One of our principal researching lines is aimed to the preparation heterocyclic compounds with therapeutical properties, synthetized through Friedlander condensation, by applying catalytic technologies involving porous systems.
In this communication we describe a serie of basic carbons containing supported MgO crystals of different size which efficiently catalyze the reaction between 2-amino-5-clorobenzaldehyde **1** and other carboxylic compounds **2**, under mild and solvent-free conditions (Scheme 1). Only a few studies concerning the reaction mechanism of Friedlander condensation have been reported. In this sense, we have described, for the first time, the reaction mechanism for the synthesis of quinolines **3**, by using computational calculations, in which MgO is the predominant active catalytic specie.



Scheme 1. Quinoline **3** synthesis by Friedländer reaction between 2-amino-5-chlorobenzaldehyde **1** and carbonyl compounds **2**. The optimized transition structure for the C-C bond formation with activing reagents MgO is shown.

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IP419

Eco-friendly Catalytic Synthesis of 2-amino-4*H*-Chromenes Promoted by Basic Activated Carbon Materials

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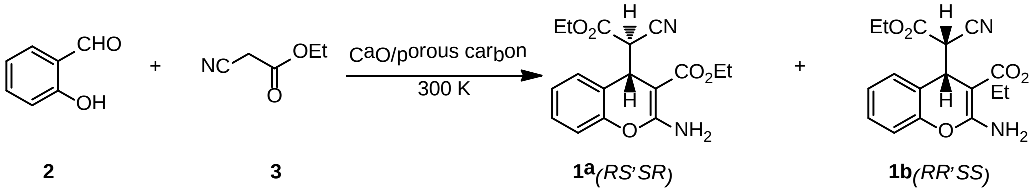
Keywords: Catalysis, basic carbon-materials, chromenes, MCR

Abstract

Nowadays, the development of interesting heterocyclic compounds by using new and efficient synthetic routes is one of the main challenges of the pharmaceutical industry. This industrial sector is also compromised with the environmental protection dedicating substantial efforts on improving the traditional methodologies by implementing others much more efficient and energetically more favorables. Such is the case of using catalytic multicomponent reactions (MCRs) which allow the synthesis of structurally complex molecules in a safer, selective, efficient, faster and economic manner. One of the most important oxygen heterocycles compounds are chromene derivatives, particularly, 2-amino-4*H*-chromenes, because of their therapeutic properties – antimicrobial, antiviral, antiproliferative and antitumoral agents, among others –.

Although several heterogeneous catalysts have been reported for the preparation of 4*H*-chromenes **1**, from 2-hydroxybenzaldehyde (**2**) and ethyl cyanoacetate (**3**), the developed methodologies often required prolonged reaction times, tedious isolation and purification processes, with high polluting environmental damage [1]. Based on that, our work is focused onto the search of new, more active and selective nanocatalyst for an innocuous synthesis of this kind of heterocylces. In this context, we report herein a new methodology for the synthesis of chromenes (**1**) catalyzed by basic metal oxides-supported on carbon materials [2] under solvent-free and mild reaction conditions (**Scheme 1**).



Scheme 1. Synthesis of 2-amino-4*H*-chromenes (**1**) from salicilaldehyde (**2**) and ethyl cyanoacetate (**3**).

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IP420

Catalytic decomposition of hydrogen peroxide by manganese oxides

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Keywords: Catalytice decomposition, hydrogen peroxide, manganese oxide catalyst

Abstract

Hydrogen peroxide is a strong oxidant and its oxidizing properties can destroy a wide range of pathogens. Thus it is used to sterilize biological apparatus at lower temperature.After sterilization, the excess hydrogen peroxide must be decomposed to use it for the next biological operation. To effective and efficient decomposition of hydrogen peroxide, many kinds of heterogeneous catalysts have been investigated [1]. Among heterogeneous catalysts composed of lower-cost transition metal, manganese oxides are expected as highly active catalyst for hydrogen peroxide decomposition [2]. In this study, several types of manganese oxides were prepared and their catalytic activity for hydrogen peroxide decomposition were examined. Especially, the catalytic activity of metal supported bixbyite (Mn_2O_3) was investigated.

In this study, three types of manganese oxides of pyrolusite (MnO_2), cryptomelane (MnO_2) and bixbyite (Mn_2O_3) were prepared. The catalytic activity of the manganese oxides were evaluated in the reaction behavior of hydrogen peroxide decomposition. Bixbyite showed the highest catalytic activity, though the specific surface area was the lowest in these manganese oxides. The bixbyite prepared by co-precipitation method slightly contained cryptomelane phase. Previous studies reported that the multiple valence of Mn oxide showed the higher catalytic activity for the hydrogen peroxide decomposition [3]. Only bixbyite in the products contained both Mn(III) and Mn(IV) ions.

The metal (Zr, Ti, Ce and Ag) supported bixbyites were also prepared by co-precipitation and impregnation method. Zr and/or Ag supported bixbyite showed higher catalytic activity than the other metal suppoted and unsupportedbixbyite. Above these products, Ag supported bixbite prepared by impregnation method showed the highest catalytic activity for hydrogen peroxide decomposition.

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IP421

Nitrene Transfer Catalysis by S-Chelated Metal Complexes

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Keywords: Homogeneous catalysis, Nitrene transfer, Chelating S-ligands, Bio-inspired catalysts

Abstract

Metal-catalyzed nitrene transfer in green catalysis is an important type of reactions in organic transformations[1]. There have been numerous studies on nitrene transfer reactions including alkene aziridination and sulfide sulfimidation catalyzed by transition metal complexes with N- and/or O-chelating ligands using a variety of nitrene sources. We previously performed extensive investigation on metalloporphyrin catalysts for nitrene transfer reactions, including mechanistic studies [2]. In our endeavor to develop new types of biocompatible metal catalysts for nitrene transfer reactions, we found that cuboidal iron-sulfur clusters, which resemble the Fe_4S_4 or MFe_3S_4 active sites in biological systems [3], can catalyze aziridination of alkenes and sulfimidation of sulfides. These metal-sulfur clusters can be considered as metal complexes of inorganic Fe_3S_4 tridentate S-chelating ligands, which inspired our interest in exploring the catalytic behavior of related metal complexes bearing multidentate S-ligands with the metal ion adopting a coordination number and/or configuration similar or identical to that in native metal-sulfur clusters such as those in the active site of aconitase [4]. In this work, we present our findings obtained by examination of the catalytic behavior of the complexes of the first-row transition metal ions with multidentate S-donor chelating ligands includingthe scorpionateS_3 ligands that have been extensively used in coordination chemistry [5] yet unemployed for nitrene transfer catalysis. A series of such metal complexes have been prepared and structurally characterized, some of which, such as Cu(I) complexes with tris(mercaptoimidazoyl)borates, have been found to be highly active catalysts for nitrene transfer reactions, including aziridination of alkenes and sulfimidation of sulfides, affording aziridines and sulfimidesin high-to-excellent yields (up to 99%) with low catalyst loading (1 mol%) at room temperature.

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IP422

Photochemistry; towards more sustainable chemistry

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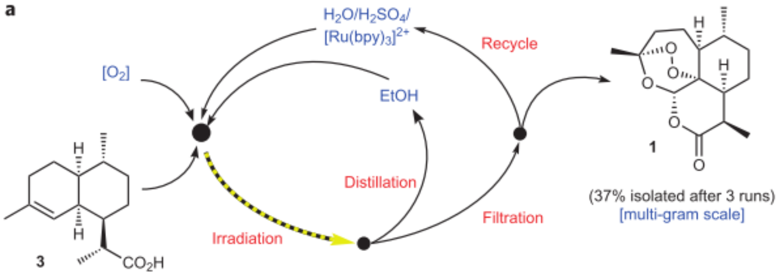
Keywords: Photochemistry, Green Chemistry

Abstract

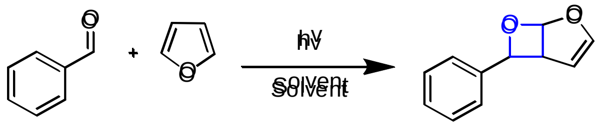
The use of photochemistry for production of chemicals is not new but has recently become highly topical. [1] It has been studied extensively and early work by Ciamician highlighted its application in terms of sustainability more than 100 years ago. [2] Indeed, photochemistry meets many of the criteria of the 12 principles of Green Chemistry. [3, 4]



Scheme 2: Photochemical semi-syntheis of the antimalarial drug Artemisinin.[5]

This poster outlines some recent results from our group at Nottingham using photochemistry. Our efforts have been focused on new reactor designs for UV and visible light photochemistry in flow and their application in synthesis. One reactor recently described [5] uses visible light LEDs around a sapphire tube allowing photochemical reactions to be carried out under high pressure conditions, for example in the reaction of singlet O_2 for the semi-synthesis of artemisinin. [5]

Another reactor utilises excimer light sources, which emit nearly monochromatic UV light at a number of specific wavelengths, either 222 nm, 282 nm or 308 nm. This wavelength specificity should allow chemists to develop more selective reactions, with fewer side-products than broad spectrum light sources. We describe briefly the use of the Paterno-Büchi reaction as a model reaction to benchmark the productivity of different reactors and light sources.



Scheme 2: Paterno- Büchi reaction used to benchmark our new UV flow photoreactors

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IP423

Tools and techniques for green solvent selection

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Key words: Green solvents, Solvent selection guide, Bio-based solvent, Green chemistry metrics

Abstract: due to the legislation and increasing public concern about the environmental issues, developing green solvents has become an important research area. This poster aims to explain the role of several general published solvent selection guides, and how they can be utilised most efficiently to improve the greenness of chemical processes, specifically in laboratory organic synthesis and the pharmaceutical industry.

IP424

Hydrogenation of C8-C9 unsaturated hydrocarbons over the Pd and Pt cataysts supported by porous aromatic frameworks

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Keywords: Catalysis, Olefin hydrogenation, Porous aromatic frameworks

Abstract

Hydrogenation of unsaturated hydrocarbons is one of the most important processes in modern petrochemical industries. Hydrogenation of olefins, dienes and acetylenic hydrocarbons prevents further polymerization and oxidation of these products and permits the stabilization of gasoline pyrolysates [1]. Therefore, the development of new catalysts in purpose to maximize hydrogenation reaction efficiency is attracting increasing interest.

However, the properties of catalysts are strongly depending from the support nature. For example, Ru catalyst supported by graphite possesses remarkably higher activity in hydrogenation of the citral in comparison with Ru supported by KL zeolite [2]. In this regard, the choice of eligible support could improve the catalyst performance. One of the most promising support materials is a new type of organic polymers with regular structure – porous aromatic frameworks. It combines many of the advantages of the conventional inorganic and classical carbon supports, such as high surface area, regular rigid aromatic structure, thermal and chemical stability, relatively facile functionalization.

In current work we present the synthesis of Pd and Pt containing catalysts supported by PAF-30, the porous aromatic framework with diamond-like structure with 4 benzene rings in the edge. The catalysts were active in hydrogenation of different C8-C9 unsaturated compounds in mild conditions.

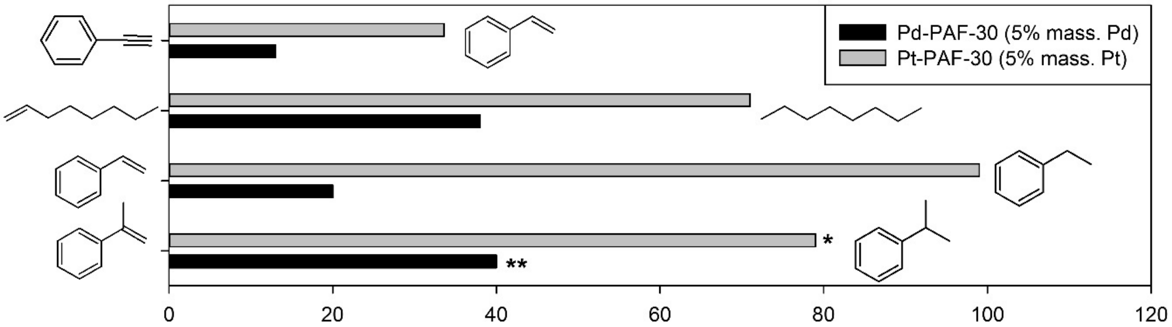

Fig. 1. Hydrogenation of C8-C9 unsaturated compounds over Pd-PAF-30 and Pt-PAF-30. Reaction conditions: m_{cat} = 1 mg; Sub:Me = 27000:1 mol.; 1 MPa H_2; 60^oC; t= 0,5 h. For α-methylstyrene reaction time was 1h for Pt-PAF-30 (*) and 2 h for Pd-PAF-30 (**) catalysts.

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IP425

Two steps synthesis of amphoteric aminoaldehydes, a key intermediate for reduced hydantoins

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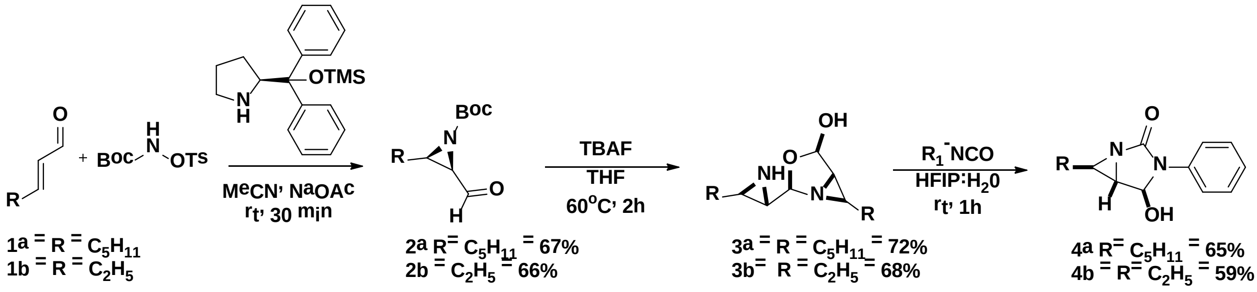
Keywords: Aziridination, amphoteric aminoaldehydes, hydantoin synthesis

Abstract

Amphoteric molecules are of significant interest once the opposing nucleophilic and electrophilic centers allow the formation of multiple bonds, with high chemoselectivity, in a single transformation [1,2]. Despite the overall instability of these compounds and other N-H aziridines, it is known that amphoteric aminoaldehydes exist as stable dimers, with the equilibrium strongly favoring the dimeric species in a variety of solvents. Yudin *et al.* described the synthesis of amphoteric aminoaldehydes in 5 steps with 39% overall yield [1].
In this work, we developed an alternative protocol to synthesize aminoaldehyde dimers in two steps starting with an organocatalyzed aziridination between α,β-unsaturated aldehydes **1** and protected amine to afford a known isolable and stable compound **2** [3]. After Boc-deprotection, dimeric species **3** are immediately formed from monomeric N-H aziridine aldehydes. This second step is under investigation using microwave irradiation, and the enantiomeric excess of compounds **2** have been analyzing. Based on reported applications of aminoaldehydes dimers [4],we also aimed the synthesis of reduced hydantoins **4**, due their presence in natural products and synthetic bioactive compounds.



The authors are grateful to FAPESP, CNPq and CAPES (Brazil) and GSK for financial support and fellowships.

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IP426

Cyclic Carbonates as Alternative and Greener Solvents for both Solution- and Solid-Phase Peptide Synthesis

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Keywords: Cyclic Carbonates, Solid-Phase Peptide Synthesis, Solution-Phase Peptide Synthesis, Green Solvents

Abstract

Therapeutic peptides are recognised as being extremely specific in their binding to *in vivo* targets, resulting in them often being highly potent and very selective, whilst having very few negative side effects. Peptides are therefore expected to play a major role in the future of drug discovery, with approximately 140 peptides drugs currently in clinical trials and over 500 in preclinical trials. Resulting in the peptide medicines market being currently estimated at US$ 14.1 billion, with it predicted to grow to around US$25.4 billion by 2018.[1]

Consequently, there has been a significant interest in the development of peptide synthesis in recent years, resulting in a plethora of coupling agents, racemisation suppressants and solid supports to produce them rapidly and in high purity. However, until very recently very little attention has ever been paid to the solvent, which can account for as much as 80-90 % of the total waste mass generated in a given pharmaceutical/fine chemical process.[2] Peptide synthesis has traditionally been carried out almost exclusively in DMF. However, under REACh DMF and other reprotoxic polar aprotic solvents (NMP & DMA) are likely to face significant restrictions if not an outright ban within the next few years.

Cyclic carbonates have recently been highlighted as highly promising polar aprotic solvents, and potential replacements for those facing issues under REACh.[3][4] In addition to their excellent solvation properties they are stable under ambient conditions, non-corrosive, non-toxic and biodegradable. For the above reasons they present ideal candidates for peptide synthesis. A diverse range of tetrapeptides have been prepared in cyclic carbonates using solution-phase methodology, with couplings and deprotections proceeding in good to excellent yields, with little evidence of epimerisation. The developed methods have then been applied to solid-phase approaches, with cyclic carbonates proving suitable in a study towards the manual and automated synthesis of the natural vasodilator bradykinin, upon 100 % polyethyleneglycol (PEG) based resins.

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IP427
Aromatization of ethylene with zeolite catalysts

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Keywords: ZSM-5, Aromatization, Ethylene, Mechanism

Abstract

Aromatic compounds such as benzene and xylenes have been produced by the reforming or steam cracking of naphtha from oil [1]. As the crude oil resource is limited and oil demand in developing countries has increased, oil price once reached higher than 100 $/bbl. Under these circumstances, technologies have been developed for shale-oil and -gas production and a huge amount of ethane are supplied recently. In USA, almost a half of ethylene has been produced from cracking of ethane and if aromatics could be produced from low-cost ethylene from shale-gas derived ethane, benzene and xylenes would be cost-competitive against those produced by the conventional processes.

In these backgrounds, aromatics synthesis from ethylene was studied in detail. Several kinds of zeolites were tested as catalysts in the fixed-bed flow-type reactor. H-ZSM-5 was the most promising zeolite even though deactivation based on carbon deposition was significant. From time-on-stream behavior for benzene, toluene and xylenes, it was observed that formation of benzene, toluene and xylenes ceased in this order. This suggested another route for the formation of aromatics; namely, xylenes formed first, then toluene formed from xylenes and then benzene formed from toluene [2].

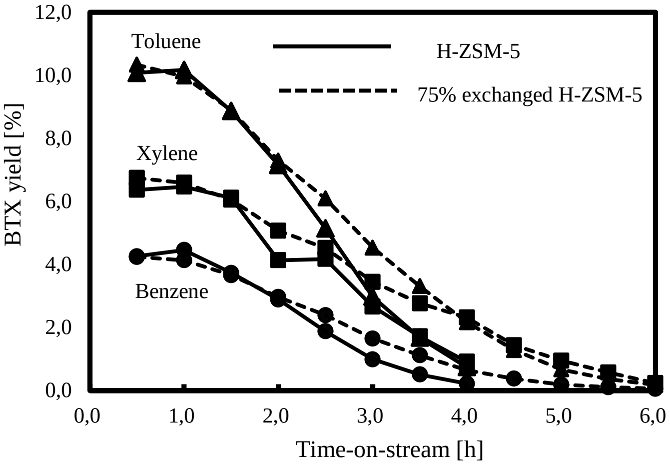

Fig. 1 Time-on-stream behavior ofBTX yield on H-ZSM-5 at 500 ºC
Catalyst: 0.050 g, C_2H_4 = 20 mL/min, N_2 = 30.0 mL/min
$W/F_{Total} = 1.0\times10^{-3}$ min・g-Cat./mL Temp.: 500 ºC

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IP428

Green synthesis of multifunctional Fe-polyphenol catalysts using Spent Tea leaves and Coffee Grounds as Raw Material

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Keywords: Coffee grounds, Green Fenton, Polyphenol, Spent Tea leaves

Abstract

Fenton's chemistry has long been useful in industry because of the power of hydrogen peroxide, in the presence of ferrous iron (Fe^{2+}), to produce a highly reactive free radical species capable of oxidizing aqueous materials. However, its application has been limited due to the rapid oxidation of ferrous iron. The rapid oxidation of ferrous iron limits the production of free radicals necessary for powerful reaction. A novel Fe-polyphenol composite was synthesized using spent tea leaves or coffee grounds as raw material. The new 'green' iron catalysts contained iron in reductive stable status for Fenton's catalysis. The study showed that the developed 'green' iron catalysts can be used as iron fertilizer [1,2] and for the Fenton's and photo-Fenton's processes for degradation of hazardous substances, disinfection of *Escherichia coli* and control of plant diseases [3]. The tea and coffee polyphenols were estimated to be responsible for the reductive stable state of the iron in the developed catalysts due to their reducing power and chelating iron ability [4]. The developed new 'green' iron catalysts are expected to diffuse in wide fields as food, medicine, public health, agriculture, environment or the like.

Effect of the treatments on the degradation of methylene blue. Left: 10mM H_2O_2alone and right: 10mM H_2O_2 and 0.1 mM of Fe as catalyst made using coffee grounds.

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IP429

Magnetite/carbon nanocomposites, application to decontamination of wastewaters

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Keywords: Magnetic nanocomposites, Adsorption, Anionic dyes, Cu(II)

Abstract

Release of industrial effluent, often contaminated with textile dyes and metal ions without proper and prior treatment into the environment is one of the major causes leading to a burden of health care issues in worldwide [1]. The textile dyes possess a high capacity to modify the environment due to their strong color and visual pollution and also affecting photosynthesis processes. Metal ions are reported as pollutants, due to their mobility in natural water ecosystems and due to their toxicity. In this context the availability of clear water for various activities is becoming the most challenging task for researchers and engineers worldwide.Among different methodologiesdeveloped to manage wastewaters, adsorption proved to be a superior technique for dye and metal ions removal from aqueous phase, in terms of cost, availability of a wide range of adsorbents, low harmful secondary products, facile regeneration of the adsorbents and high effectiveness [2,3]. The application of magnetic nanoparticles as adsorbent materials in solving environmental problems has recently received great attention due to their unique physical and chemical properties, which make them superior to traditional adsorbents [4,5]. The present work describes the application of magnetic nanoparticles embedded within a matrix of activated carbon as adsorbent for acid dyes and Cu(II) removal from wastewaters, in selected working conditions.The magnetic nanoparticles embedded within a matrix of activated carbon (MNC)were synthetized by a simple and cost-effective combustion technique [6]. The effects of process variables: solution pH, initial concentration of polutant, adsorbent dose, contact time, temperature was investigated in order to optimize the process.The removal efficiency of pollutants depends on solution pH, and increases with initial concentration of the pollutants, the dose of MNC and the temperature. Pseudo-second order kinetic model was fitted to the kinetic data, and adsorption isotherm analysis was used to elucidate the adsorption mechanism. The experimental results suggest that as-prepared magnetite/carbon nanocomposites has the potential applications in the water purification management.

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IP430
"Green" Oxidation of Pyridine by Nitrous Oxide (I)

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Keywords: Nitrous oxide, coherent synchronized, pyridine, 2,2- and 2,3-dipyridile

Abstract

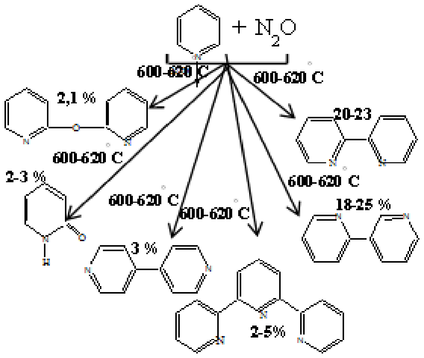
In recent years, nitrous oxide has attracted a great deal of attention from researchers as selective oxidizer for conducting the catalytic oxidation of hydrocarbons.

Experimentally investigated reaction of pyridine oxidation of nitrous oxide in the homogeneous conditions, in the gas phase, without the use of catalysts, at atmospheric pressure.

Installed region of the selective oxidation pyridine of nitrous oxideand was found the optimum conditions for obtaining valuable raw materials, which needed in petrochemical, chemical, pharmacological industries.

For the first time by oxidation of pyridine with nitrous oxide in homogeneous conditions was obtained 2,2- and 2,3-dipyridile on the simplified technology. In the optimal mode yield of 2,2- and 2,3- dipyridile was 23.0 wt.% and 25.4 wt. %, respectively. It is shown that in the system of coherent-synchronized of free-radical reactions of thermal decomposition of nitrous oxide and pyridine oxidation – is carried out reaction dimerization of pyridine.

Thus, conducted the oxidation reaction of pyridine of nitrous oxide demonstrates the use of a new direction in the heterocyclic synthesis such as popular of compounds as the 2,2-, 2,3-, 4,4-dipyridyls, 2,2-oksidipyridyle, 2- pyridone , 2,2:6,2 - terpyridine allows to obtain on their basis the new nitrogen-containing heterocyclic compounds. As a positive factor it should be noted that observed stable formation of 2,2- and 2,3- dipyridile in all experiments. As a positive factor it should be noted that observed stable formation of 2,2- and 2,3- dipyridile in all experiments:



The resulting novel substances are of some certain interest for the synthesis securities of pyridine bases, without the use of catalysts and under atmospheric pressure, as well as getting rid of the disadvantages of the same similarly catalytic reactions, determines the practical importance of this work.

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IP431

Reductive Amination of Aldehydes Catalyzed by Reduced Graphene Oxide Supported Ni_3Pd_7 Alloy Nanoparticles

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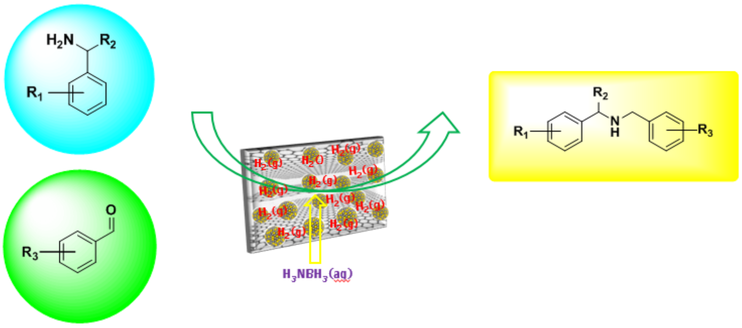
Keywords: Reductive amination, Reusable catalyst, One-pot synthesis, NiPd alloy nanoparticles

Abstract

Due to their basicity, nucleophilicity and biological activity, amines possess special importance in chemical and biological systems. There are numerous natural products including amino acids, nucleic acids, alkaloids and many others that contain the amino motif.[1] Due to their importance, several methods have been developed for the preparation of amines. Among those methods, these include the reduction of nitrogen containing functional groups such as nitro, nitrile, azide, and carboxamide derivatives is of widely used. The alkylation of ammonia is also a general method for the synthesis of primary or secondary amines, however, over-alkylation often occurs as a side reaction. The Curtius or Hofmann rearrangements of carboxylic acid derivatives, and hydro amination of alkenes, alkynes or allenes are also well-known protocols for the construction of various amine derivatives. All of the above mentioned methods have several drawbacks; harsh reaction conditions, commercially unavailable starting materials, by-product formation, low yield and often insufficient selectivity. Therefore, the development of novel and efficient methods for the preparation of amines still present significant challenges in organic synthesis.[2]

In this work, a novel and highly efficient heterogeneous catalytic reductive amination of aldehydes is described. The recently developed reduced graphene supported NiPd alloy nanoparticle (G-NiPd) catalyst using ammonia borane (AB) as a green, stable and safe hydrogen donor in a water/methanol mixture (v/v= 2/3) under ambient conditions. The catalytic system was successfully applied in the reductive amination of various substituted aldehydes with amines and the corresponding products were obtained in (up to) 99% yield in 6 h. The rGO-NiPd catalyst could be recycled up to five times without any significant loss in the product yield.[2]



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IP432

Optimization of Ionic Liquid-Catalyzed Transesterification Reactions of Cellulose

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Keywords: Cellulose, Ionic liquids, Transesterification reaction

Abstract

Cellulose is one of the most abundant natural polymers and sustainable resources. Althoughchemicals utilization of cellulose for a range of applications usually requires solubilizing processes, the cellulose showspoor solubility in both aqueous and organic solvents owing to the strong hydrogen-bond networks within the intra- and inter-molecular structures. This has limited the cellulose applications forthe functional materials. In this context, ionic liquids (ILs) were reported to efficiently dissolve the cellulose under mild conditions. Recently, we reportedona transesterification reaction (TER) of the cellulose with isopropenyl acetate (IPA) in 1-ethyl-3-methylimidazolium acetate (EmimOAc) as the solvent and organocatalyst. In this report, we have found that cellulose acetates with high degree of substitution (DS) values could be produced without additional catalysts and additives. However, the above reaction system suffers froma synthetic drawback of ILs. To be precise, a large excess amount of ILsagainst cellulose was required to dissolve the cellulose for efficient reactions in the system, which has been a synthetic and therefore economical drawback because ILs are fairlyexpensive and viscous.

In order to increase the green nature of the above-mentioned reaction system, IL-catalyzed TERs of the celluloseneed to be optimized. When aiming reaction optimization for IL-based systems, we turned our attention to dimethyl sulfoxide (DMSO) as a co-solvent because DMSO-addition into IL-cellulose solution is well-known not to disturbthe cellulose dissolution process but at the same time to decrease the solution viscosity. Along with a positive effect of DMSO/IL co-solvent system on cellulose dissolution processes, the DMSO-addition was rationalized to increase the TER reactivity based on precise mechanistic understanding of the reaction systems. These rational assumption on the positive effects of DMSO as a co-solvent strongly encouraged us to examine whether or not the DMSO/IL mixed solvent system could lead to a facile optimization of cellulose modification reactions in IL-based solution systems. Herein, we now wish to present an optimization of the TER of the cellulose in EmimOAc/DMSO-mixed solvent, leading to a drastic increase in green nature of the cellulose modification reactions while maintaining high reactivity of the TERs. In the presentation, we will address the optimization of the cellulose modifications with precisely designed experimental and theoritical setups.

Acknowledgment: This research was promoted by COI program “Construction of next-generation infrastructure using innovative materials ~Realization of a safe and secure society that can coexist with the Earth for centuries~” supported by MEXT and JST. This study was also supported in part by an Advanced Low Carbon Technology Research and Development Program (ALCA) of the JST and the Cross-ministerial Strategic Innovation Promotion Program (SIP) from the JST.

IP433

In Silico Opportunities to Design Sustainable and Efficient Ionic Liquids

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Keywords: QSPR, Ionic Liquids, VolSurf Descriptors, Principal Properties.

Abstract

Ionic Liquids (ILs) attracted extraordinary attention due to their versatility in different applications. Their low vapour pressure reduces the air pollution as compared to common volatile organic solvents, but this property is not sufficient to define them as "green" solvents. In fact, release of ILs from industrial processes into wastewaters may lead to pollute aquatic environments due to their high solubility and stability. Sustainability and efficiency of ILs are both fundamental requirements for their industrial applications which boost the knowledge of ILs toxicological and environmental properties to comply with the European Union regulation for the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). Unfortunately "toxicity" and "sustainability" are wide terms being determined on different possible targets. Furthermore, reliable toxicity tests when available in the literature, are reported for a specific class of compounds, other tests for others. In this context a multivariate insight allowed to compact available toxicity data into 104 toxicity scores [1] representative of the most common aquatic living targets. The number of ILs resulting from the combination of cations and anions is estimated to be over a million, hence the ILs experimental space is so huge that it cannot be fully explored and requires a rational selection of highly informative experiments. The development of Quantitative Structure Property Relationships (QSPRs) implies the knowledge of structural descriptors for ILs. Unfortunately, experimentally determined physicochemical properties in the case of ILs are very few, derived by different laboratories and scattered in the literature. To overcome this difficulty, we derived *in silico* cation and anion physicochemical descriptors [2] by using the GRID approach in VolSurf+. The validity of such descriptors was tested in two QSPR models with aquatic toxicity scores [2] and polarity [3], achieving a good correlation and satisfactory predictions. Handling such a high number of descriptors could be very difficult, especially for big ILs data sets. Consequently the descriptors were compacted into the so-called Principal Properties (PPs) [4] highly informative and suitable for multivariate experimental design. PPs can be used as descriptors in QSPR correlations to model both ILs biological activities [4],[5] and physicochemical properties (*e.g.* heat capacity)[6] achieving reliable predictions and allowing an "intelligent" selection of further measurements in order to expand the explored experimental space.

The work presented here moves a step forward for conjugating efficiency and sustainability of ILs, presently a major issue of the scientific community.

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IP 434

Application of flow technology for sustainable metal-catalyzed transformations

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Keywords: Flow chemistry, Heterogeneous catalysis, Waste minimization, Biomass valorization

Abstract

In the modern development of synthetic strategies towards target material, sustainabilitys issues cannot be underestimated. Number of steps, waste and the energy consumption should be minimized, while efficiency and selectivity enhanced.

Our research program aims at the definition of sustainable synthetic processes, by focusing on the implementation of specific tools such as the use of safer reaction media (water, azeotropes, biomass-derived) or *SolFC,* the preparation of novel organic/inorganic supports for heterogeneous catalysis and flow conditions [1]. More speifically adoption of flow technology is proving to be highly effective in accessing novel reactvity while exploting the chemical features of the selected green solvent and of the heterogenous catalytic systems, If properly developed flow protocols can be effective in minimizing waste and simplifying experimental procedures.[2]

In the context of our efforts in the application of our green synthetic approach to several metal-catalyzed reactions, in this communication we intend to present our studies towards the definition of an effective protocol for the hydrogenation and reductive amination of phenolic compounds, commonly regarded as waste of the biomass treatment.[3]

Our approach is based on the use of a heterogeneous palladium catalyst and as hydrogen source we are developing the use of formic acid salt, a bio-based chemical deriving from the production of levulinic acid. Our protocol is developed also to operate in a continuous-flow reactor system.

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IP435
One–pot Synthesis of Imidazoles

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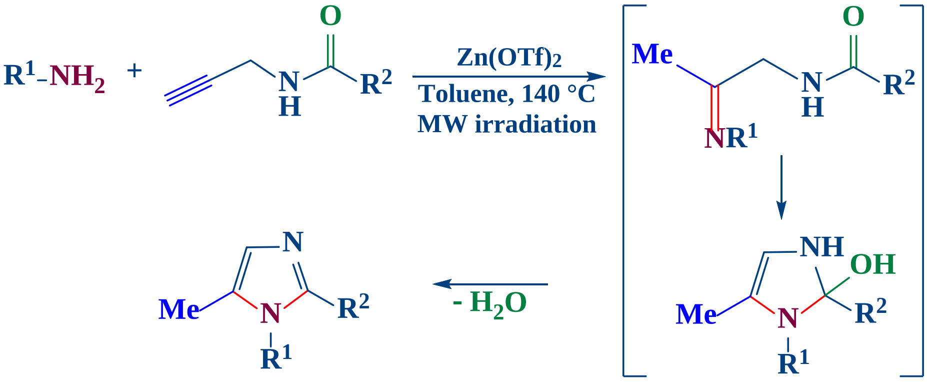
Keywords: Zinc catalysis, Microwave technology, Imidazole, Hydroamination–cyclization, One–pot synthesis

Abstract

Imidazole structure is present in great number of molecules characterized by a variety of biological and pharmacological activities. Natural and synthetic derivatives of substituted imidazoles are useful agents for the treatment of cancer, several CNS disorders, acute and chronic neurodegeneration, diseases associated with ion channels, cardiovascular disorders etc. Imidazoles are also widely used as organocatalysts, ionic liquids and N–heterocyclic carbenes. Because of the importance of this class of compounds their synthesis and functionalization methods have been intensively developed and continue to be a significant subject in organic synthesis. To our delight, our investigations on hydroamination reaction of protected propargylamines with primary amines yielded to the synthesis of novel imidazoles.



We have developed new general synthesis for the Zn–catalyzed synthesis of 2,5(4)–disubstituted and 1,2,5–trisubstituted imidazoles from commercially available amines and acylated propargylamides.[1] Our approach allows for the regiospecific introduction of various substituents into the imidazole ring by simply choosing the proper combination of starting materials. These are the first examples of Zn–catalyzed one–pot synthesis of imidazoles. Advantageously, broad functional group tolerance is observed and target products were obtained in up to 96 % yield as stable solid compounds. Optimization of the reaction conditions and improvements of synthesis performance will be discussed in more details.

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IP436

Nucleophilic and electrophilic double aroylation of chalcones with benzils promoted by the dimsyl anion as a route to all carbon tetrasubstituted olefins

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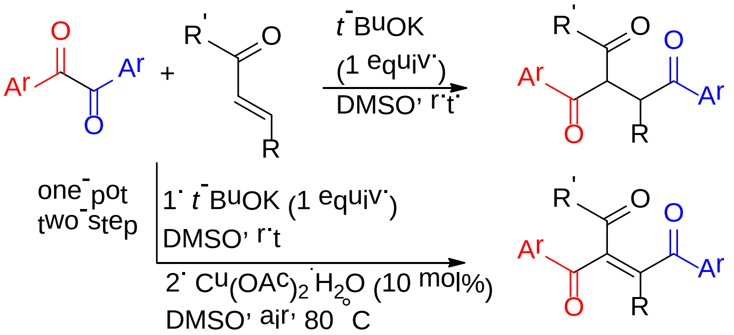
Keywords: Methylsulfinyl carbanion, Umpolung, Double *C*-aroylation.

Abstract

In a previous contribution, we have demonstrated that methylsulfinyl (dimsyl) carbanion, generated by deprotonation of the DMSO solvent, served as surrogate of hazardous cyanide ion promoting the formation of benzoylated benzoins in an atom-economic fashion through sequential nucleophilic *C*- and electrophilic *O*-aroylations [1].
As a logical extension of the study on the benzoin reaction, we reasoned that utility of dimsyl anion catalysis could be further enhanced by conducting a double *C*-aroylation process on activated alkenes, thus providing a novel variant of the parent Stetter reaction (hydroacylation process).
Indeed, Dimsyl anion promoted the polarity reversal of benzils in a Stetter-like reaction with chalcones to give 2-benzoyl-1,4-diones (double aroylation products), which in turn were converted into the corresponding tetrasubstituted olefins via aerobic oxidative dehydrogenation catalyzed by $Cu(OAc)_2$ [2].



Thanks for the support of the Organic Chemistry Division of the Italian Chemical Society (SCI).

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IP437

Synthesis of phthalides from benzoic acids and alkenes by a rhodium-catalyzed tandem reaction

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Keywords:dehydrogenative coupling, C—H activation,tandem, phthalide, rhodium

Abstract

Cross dehydrogenative coupling (CDC) reactions allow to make a C–C bond from two C–H bonds using simple, unfunctionalized reactants with high atom economy [1]. In this work [2] we applied the CDC strategy to the synthesis of phthalides, an important class of natural lactones with a wide range of biological activities [3]. The reaction of benzoic acids and alkenes in the presence of $[(COD)RhCl]_2$, $Cu(OAc)_2 \cdot H_2O$, and dicyclopentadiene (DCPD) affords phthalides in 15–93% yield (Figure 1). A 3-substituted or 3,7-disubstituted product is obtained selectively depending on alkene type. Mechanism likely involves two steps: (a) Heck-type dehydrogenative coupling of benzoic acid and alkene, and (b) intramolecular Michael addition. The reaction is highly atom-economical and uses readily available starting materials.

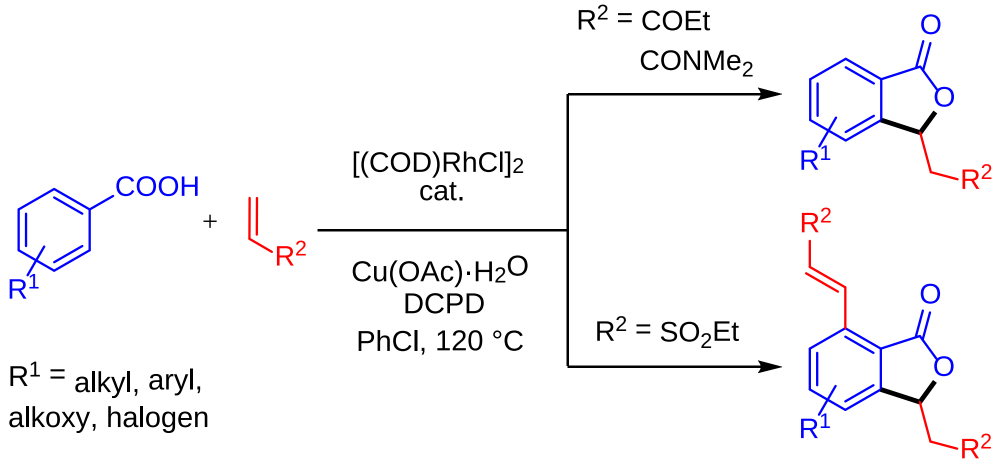

Figure 1

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IP438

Carbon Bonding: Structural Confirmation in Barbituric Acid Derivatives

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Keywords: Carbon bonding, Tetrel bonding, Self-assembly, Barbituric acid, Recognition phenomena

Abstract

The funtional properties of any molecule is a consequence of its structure and how it is recognized by the neighbouring molecules. Attractive intermolecular interactions play a key role in such recognition processes and their understanding is instrumental in the control and tuning of the functional propoerties.

In this communication we will discuss some compounds which, in the solid, show the presence of a "carbon bonding", the attractive interaction beween an electron rich site (*e.g.*, a lone pair possessing atom) and a carbon atom bearing electron withdrawing residue(s) [1]. The interaction is a particularly important subgroup of the wider set of interactions named "tetrel bonds" which consist in any attractive interaction between nucleophiles and an element of the Group 14 [2].The carbon bonding has been rationalized as the result of the attraction between an incoming electron rich group and the positive sigma-hole present at carbon on the extension of the covalent bond with an electron withdrawing residue. It has been shown that the carbon bonding can influence, or even be of considerable importance for, the packing adopted by organic compounds in their crystals, but it has also been observed that hydrogen bonds are engendering the observed short contacts. In fact, hydrogen atoms in organic compounds have a positive electrostatic potential at their surface when germinal to electron withdrawing residues and these hydrogen atoms can function as hydrogen bond donors to nearby electron rich groups. Subtle differences in short contacts directionalities have to be considered if fine and unequivocal distinction between carbon bonding and hydrogen bonding in a crystal is pursued. We reasoned that short and directional contacts between lone pair possessing atoms and perfluorinated carbon atoms might be a particularly convincing evidences of carbon bonding formation as no assistance by potential hydrogen bond donor atoms is possible. We have thus studied the crystal packing of a series of 5,5-didlurobarbituric acid derivatives and other organic compounds bearing perfluorinated groups. Directional O···C contacts have been observed where the oxygen-carbon separation is significantly lower than the sum of carbon and oxygen van der Waals radii. These structures will be discussed as cases of carbon bonding formation.

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IP439

Cross metathesis of guayule (*Parthenium argentatum*) rubber with methyl methacrylate using ruthenium catalysts

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Keywords: Metathesis, guayule, ruthenium catalysts, telechelics, detergents.

Abstract

Olefin metathesis is today used in green chemistry to produce chemical compounds from natural resources. In this regard, end-funcionalized oligomers can be obtained by cross-metathesis degradation of natural rubber [1]–[3]; since Ru-alkylidene catalysts show a high tolerance to a wide variety of functional groups that can be incorporated by the chain transfer agent (CTA) [4]. Also, metathesis is a sustainable route that provides better control on the structure and molecular mass distribution of the products [5].

In this study, we report on the cross-metathesis degradation of the natural rubberfrom guayule (*Parthenium argentatum*) and *Hevea brasiliensis* using second generation Grubbs (G2) and Hoveyda-Grubbs (HG2) catalysts with methyl metacrylate as CTA, in order to produce methyl ester end-functionalized oligomers in a well-controlled manner. Reactions proceeded to give oligoisoprene telechelics with masses in the range of 387 to 488 g/mol determined by MALDI-TOF and also were characterized by FT-IR, NMR (^{1}H, ^{13}C) and SEC. The yields of the oligomers were good and ranged between 90 and 100%. The obtained products can significantly contribute to a sustainable supply for detergents [6-7].

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IP440

Formates as Safe and Green Agent for Catalytic Reduction in the presence of Magnetically Recoverable Pd Catalysts

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Keywords: Magnetically recoverable Pd Catalyst, formates as reducing agent, CO_2hydrogenation.

Abstract

Formates and formic acid, as reducing agent, are well known for long time and their use in several enviroment and with different solvent are yet a hot topic being recently employed also in aquoeus solvent and multiphase systems [1]. On the basis of these studies reduction of CO_2 is an interesting topic, which is directly related, both with CO_2 utilization and with the safe and enviromentally benign reduction of nitrocompounds, usefull for the industrial practice [2].

In this research, we would compare the catalytic properties of several Pd catalysts supported on different materials, in the reduction of nitrocompounds and ketones. In addition we would verify their potential ability in the CO_2 and $NHCO_3$ hydrogenation.

Pd catalyst has been prepared by conventional wet impregnation method followed by a precipiation, a reduction with hydrogen and passivated with water in air. The magnetically recoverable catalyst has been prepared starting from Fe_3O_4 and ZrO_2-Fe_3O_4 as supports prepared following a coprecipitation procedure [4]. Composition of the catalyst has been obtained by dissolution with mineral acid in a microwawe dissolver followed by ICP analysis. Porosity and surface area and has been measured by Nitrogen adsorption. Microstructure and granulometry has been characterized by WAXS, SEM and XPS measurement.

Pd supported on carbon, allumina, magnetite and zirconia-magnetite has been used in the reduction of nitrobenzene and acetophenone by using sodium and potassium formate as reducig agent in the presence and in absence of an acqueous phase. In addition, the same catalysts has been tested in CO_2 and $NaHCO_3$ hydrogenation, for verifying the potentiality in of the CO_2 as hydrogen carrier for hydrogenation processes.

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IP441

Catalytic hydrogenation of CO_2: a step towards liquid fuels

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Keywords: CO_2, RWGS, nickel, catalyst preparation, sputtering deposition

Abstract

The conversion of CO_2 into liquid fuels is considered one of the most promising processes for the valorization of CO_2. The first step can be based on the hydrogenation of CO_2 through reverse water gas shift (RWGS) to form CO and water, then hydrogen can be added to CO to form liquid hydrocarbons by Fischer−Tropsch synthesis (FTS) [1]. If a renewable hydrogen source is used, the entire conversion system could potentially become sustainable.After tremendous research efforts, increasing selectivity and improving catalyst stability remain challenging. The hydrogenation of CO_2 into CO is very sensitive to the metal particle size and support interaction, while large metallic particles or aggregates tend to produce more methane than CO. In this context, we describe a versatile method to prepare nickel nanoparticles (Ni NPs) dispersed on oxide supports via a magnetron sputtering deposition method, which involves ejecting atoms and/or atomic clusters from highly pure targets onto a solid substrate. The sputtering sample holder was especially adapted for the deposition of metal NPs onto powder supports by using a mechanical agitation inside the vacuum chamber [2]. Ni NPs supported on SiO_2 with average particle size of about 2.6 ± 0.5 nm were obtained. The local atomic environment of the Ni NPs catalyst was monitoring using XAFS under in-situ RWGS reaction conditions as functions of temperature. CO is the main product in all temperature range studied; however, the higher the nickel loading the higher the amount of methane produced between 300 – 600 °C. Above 600 °C, CO is produced exclusively with high yields (up to 80% at 800 °C) close to the thermodynamic value.

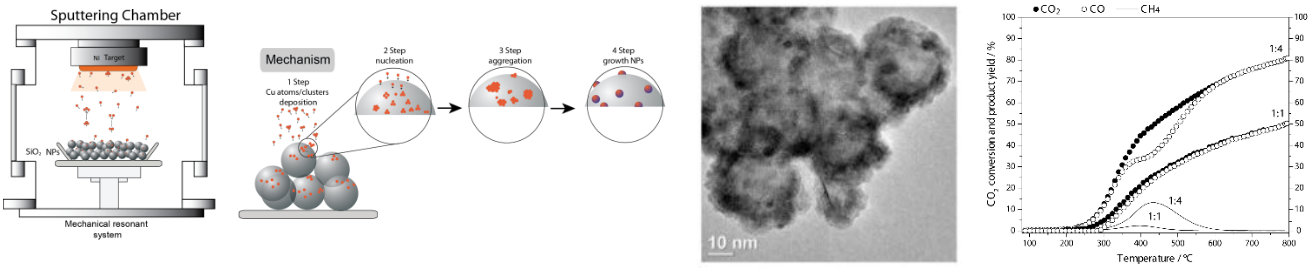

Figure 1. Preparation method, TEM image and RWGS of Ni/SiO_2

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IP442

The influence of multiwalled carbon nanotubes and graphene oxide additives on the catalytic activity of 3d metal catalysts towards 1-phenylethanol oxidation

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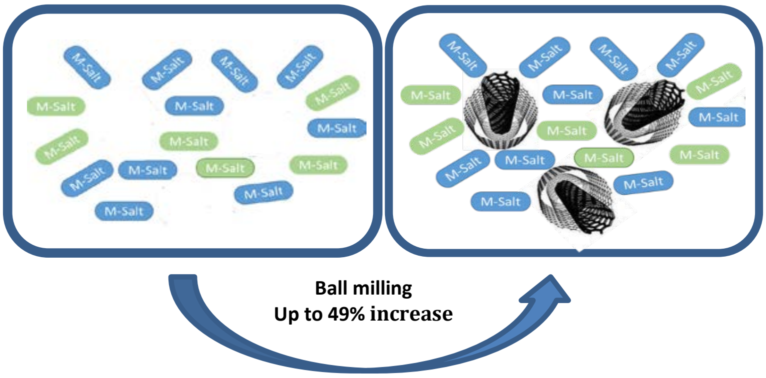
Keywords: Mechanochemistry, Composites, Carbon nanomaterials, Catalysts, Alcohol oxidation

Abstract

3d metal (Cu, Fe, Co, V) containing composite catalysts were prepared by ball milling and tested for the solvent-free microwave-assisted transformation of 1-phenylethanol to acetophenone with *tert*-butyl hydroperoxide (TBHP) as oxidant. The influence of multiwalled carbon nanotubes (CNTs) and graphene oxide (GO) additives on the catalytic activity of the catalysts was studied. CNTs or GO were mixed by ball milling with the metal salts ($CoCl_2$), oxides (CuO, Fe_2O_3, V_2O_5) or binary systems (Fe_2O_3-$CoCl_2$, $CoCl_2$-V_2O_5, CuO-Fe_2O_3). For $CoCl_2$-based catalytic systems, addition of small amounts (0.1-5%) of CNTs or GO leads to significant improvement in catalytic activity, *e.g.* 1% of the CNTs additive allows to rise yields from 28 to 77%, under the same catalytic conditions. The $CoCl_2$-5%CNTs composite is the most active among the studied ones with 85% yield and TON of 43 after 1 h.



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IP443
1,4-hydrosilylation of unsaturated ketones over supported PdAu catalysts

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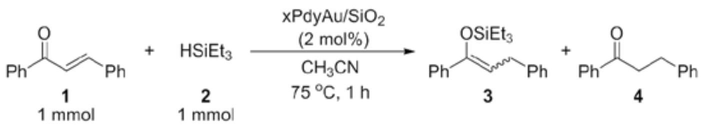
Keywords:hydrosilylation, silyl enol ether, PdAu alloy

Abstract

Silyl enol ethers are the key reagent for Mukaiyama aldol reaction[1], and the development of novel efficient synthetic methods is very important. Transition-metal-catalyzed 1,4-hydrosilylation of *α*,*β*-unsaturated ketones[2] is one of the most useful reactions that enable to synthesize silyl enol ethers in 100 % atom efficiency. However, there are some problems in conventional catalytic systems such as the addition of phosphorous ligands, and a difficulty of recovery and reuse of catalysts. Thus, the development of new environment-friendly catalytic systems is desired. On the other hand, a catalysis alloy nanoparticles attracts much attention due to their unique catalytic functions[3]. In this study, we found that supported PdAu alloy catalysts were effective for selective hydrosilylation of *α*,*β*-unsaturated ketones.

Table 1 Hydrosilylation of *α*, *β*-unsaturated ketone



entry	catalyst	particle diameter^a (nm)	yield (%)^b		
			3	Z/E	4
1	Pd^c	10	0	-	6
2	Au^d	6.6	30	93 : 7	21
3	1Pd1Au	4.3	84	93 : 7	5
4	(1st reuse)	-	87	94 : 6	4
5	(2nd reuse)^c	-	85	94 : 6	4

^{a}Calculated from Pd_1Au_1 (111) phase diffraction by using Scherrer equation. ^{b}GC yields. ^{c}Prepared by impregnation. ^{d}Prepared by deposition-precipitation.

The reaction of *α*,*β*-unsaturated ketones (**1**) and triethylsilane (**2**) with 1Pd1Au/SiO_2 for 1 h in acetonitrile afforded the corresponding silyl enol ether (**3**) in the yield of 84 % with 93:7 *E*/*Z* selectivity (Table 1, entry 3). On the other hand, supported Pd or Au catalysts did not promote the reaction (entry 1, 2). These results clearly show that coexistence of Pd and Au is necessary to promote the reaction. PdAu/$Al_2O_3$and PdAu/TiO_2 catalysts showed a low activity, indicating that the support affects the catalysis of PdAu alloy nanoparticle. PdAu/SiO_2 could be reused for three times without decrease of the activity (entry 4, 5).

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IP444

Green synthesis of hydroxybenzoic acids and its derivaties by carboxylation of phenols with sodiumethylcarbonate

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Keywords: Phenols, sodiumethylcarbonate, carboxylation, hydroxybenzoic acids

Abstract

Products of phenols carboxylation – hydroxybenzoic acids and its derivatives, have wide using as semiproducts for obtaining pesticides, drugs, photostabizers, dyes and polymeric materials. The most widespread industrial process for manucfacturing of hydroxybenzoic acids and its derivatives is the Kolbe-Shmitt carboxylation of alkali metal phenoxides with carbon dioxide. The serious drawbacks of this process is the need preliminary preparation of dry alkali metal phenoxides, which is fraught with great technological difficulties: the removal of water by vacuum distillation and extreme hydroscopycity of dry alkali metal phenoxides. In connection with this, methods for the synthesis of hydroxybenzoic acids without the use of alkali metal phenoxides are of interest. One of these methods is the carboxylation of phenols with alkali metal salts of carbonic acid esters. Alkali metal salts of carbonic acid esters can readily be prepared by the reaction of carbon dioxide with alkali metal alkoxides. We used carboxylation reaction of phenol and m-aminophenol with sodium (potassium) ethyl carbonates for development new efficient methods for preparation of drugs are based on hydroxybenzoic acids (salicylic acid (antiseptic activity, valuable intermediate product for obtaining many other medicines (aspirin, salicylamidum, etc)), p-aminosalicylic acid and sodium salt of p-aminosalicylic acid (antituberculous drugs) and p-hydroxybenzoic acid (bactericide activity; it used to prepare heat-resistant liquid-crystal polyesters)) [1]. The method are based on carboxylation reaction of phenol and m-aminophenol wit sodium (potassium) ethyl carbonates. Chemical synthesis in conditions of microwave irradiation in the present time is dynamical developing method of organic synthesis [2]. Using of microwave irradiation in chemical synthesis connect with its ability hasten many chemical reactions. Wide possibility of using MW-irradiation in chemistry provoke big interest of investigation and applied using microwave irradiation. Optimal conditions of phenol carboxylation in conditions of microwave irradiation has been defined. For determination of influence of nature and position of substitutes in phenyl ring on yields of target products the activity a number of methyl- and haloidsubstituted derivatives of phenol has been defined.

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IP445

Fast Synthesis using Seeding Technique of Novel Zeolite MCM-71 as Green Catalyst for Isomerization and Dewaxing Processes

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Keywords: Zeolite, MCM-71, Medium-Pore Zeolite, Seeding, Fast Synthesis

Abstract

Zeolite MCM-71 (Mobil Composition of Matter Number 71) [1], as medium-pore zeolite, is potential catalyst in isomeriztion and dewaxing processes [2]. Its unique 2-dimensional channel system comprising straight, highly eliptical channels of 10-membered rings (0.43 x 0.65 nm) intersecting with undulating channels of 8-membered rings (0.36 x 0.47 nm) [3]. MCM-71 shows excellent properties of high acid density (946 μmol/g) and high thermal stability (upto 1000 °C) [4]. This makes MCM-71 appropriate acidic catalyst in chemical conversion processes at high temperature. The conventional synthesis of zeolite MCM-71 has been achieved in very long synthesis time, i.e., 20 days [1] in two-step temperature and 14.83 days [4]. Eventhough low cost of raw materials are used and no calcination process is required (its template does not act as void filler), the long synthesis time can uplevel the cost in utility. Therefore finding the suitable technique to shorten the synthesis time is good strategy in industrial point of view. This work contributes the synthesis condition and effect at one-step synthesis temperature of 180 °C by using different amount of its seed (MCM-71) in order to shorten the synthesis time. The reaction with gel composition of 1SiO_2: 0.05Al_2O_3: 0.375K_2O: 0.2triethanolamine: 30H_2O occurs in 120-ml stainless steel autoclave with Teflon-line container under static hydrothermal condition. The result shows zeolite MCM-71 can be synthesized as main phase in one-step temperature of 180 °C for 11 days with minor mordenite impurity. In this synthesis condition at 180 °C, the seed effect at 0.3, 0.6, 0.9 wt.-% can reduce the synthesis time from >11 days to 7 days with comparable crystallinity. Sufficient amount of seed at 0.6 and 0.9 wt.-% can enhance the purity of zeolite MCM-71 by suppressing the mordenite formation. For the best sample of seeding 0.6 wt.-% for 7 days, its composition of 1 SiO_2: 0.064 Al_2O_3: 0.065 K_2O (molar ratio Si/Al = 7.9), specific surface area 355 m^2/g, pore volume 0.15 cm^3/g, and crystal morphology of rectangular shape of large 14 x 14 x 7 μm (in Fig. 1) are obtained.

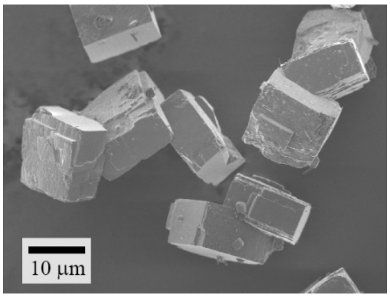

Fig. 1 SEM picture of seed MCM-71

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IP446

Valorisation of renewables by isomerising metathesis

Enhancing biodiesel

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Keywords:renewables, isomerising metathesis, biodiesel

Abstract

Isomerising olefin metathesis has recently emerged as a valuable tool for the valorisation of renewables [1]. In the presence of a bimetallic catalyst system, fatty acid derivatives are converted into industrially useful olefin blends with a tunable chain length distribution (Figure 1) [2]. This orthogonal tandem process is mediated by the combination of a dimeric Pd (I) isomerisation catalyst and state-of-the-art Ru-based metathesis catalysts. Moreover, if ethylene is added as cross-metathesis partner, the resulting olefin blends show a uniform product distribution with a boiling point curve comparable to diesel fuel. This process represents a promising pathway towards replacing petrochemical fuel with biodiesel.

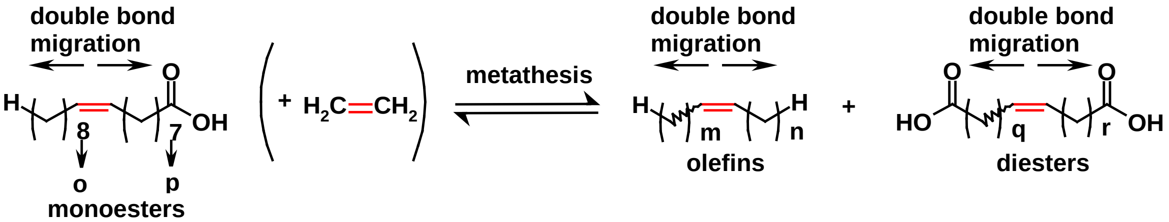

Figure 1 Isomerising metathesis of fatty acid derivatives

A similar synthetic approach was successfully applied in the synthesis of valuable styrenes from naturally occurring allylarenes[3] and in the synthesis of tsetse fly attractants from cashew nut shell liquid (CNSL), a waste by-product of the cashew nut industry [4].
These applications demonstrate the potential that isomerising metathesis has on the incorporation of renewable resources in the chemical value chain.

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IP447
Heavy Metal Removal From Waste Waters By Phosphonate Metal Organic Frameworks

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Keywords:phosphonate metal organic frameworks, adsorption, waste waters

Abstract

The increase interest in the area of phosphonate metal organic framework is exemplified with a variety of applications and a rich chemistry of these compounds. Wastewater pollution caused by heavy metal ions is a major concern due to their toxicity to many life forms. In order to decrease the heavy metals impact upon the environment various technologies of water treatment such as: chemical sedimentation, ion exchange, electrochemical technology, redox process and so on, are studied. The tendency is to find a versatile and economical method of heavy metals removal from waste waters.

Phosphonate metal organic frameworks were obtained in our labs by the reaction of divalent inorganic salts ($CoSO_4{\cdot}7H_2O$, $CuSO_4{\cdot}5H_2O$, $NiSO_4{\cdot}7H_2O$), phosphonic acid (phosphonoacetic, N,N-bis(phosphonomethyl)glycine and unsaturated phosphonic acids) in hydrothermal conditions. The synthesized compounds were characterized by FTIR, X-Ray crystallography and thermogravimetric analysis [1-3].

The adsorption processes represent a very good alternative for heavy metals removal due to low costs and easy of operation. In the present paper the adsorption performance of the mentioned materials in the removal process of heavy metals from aqueous solutions, was studied using the batch method. The adsorption conditions were investigated by varying the initial pH, adsorbent dosage, temperature and contact time for chromium metal ions removal from aqueous solutions [4].

Acknowledgements

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IP448

Application of high-valent titanium (IV) salophen as a reusable and efficient catalyst for methoxymethylation of alcohols and phenols

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Keywords: Titanium Schiff base, Alcohol, Phenol, Formaldehyde dimethyl acetal,

Methoxymethylation

Abstract

The protection of hydroxyl groups is an important reaction especially in the synthesis of fine chemicals and natural products. Several methods such as acetylation, tetrahydropyranylation, methoxymethylation and trimethylsilylation have been reported for protection of hydroxyl groups [1,2]. Schiff base complexes have found many applications in organic chemistry [3]. Recovery ability of catalyst besides reducing the amount of toxic waste is considerable interest in designing of a catalytic synthesis system. Transition metal schiff base complexes, especially heterogenous instances, with simple recovery capability can provide an efficient green catalyst.

In the course of our studies on titanium salophen catalyzed reactions [4-7], we found high-valent [Ti^{IV}(salophen)$(OTf)_2$], as catalyst enables selectively methoxymethylation of alcohols and phenols with formaldehyde dimethyl acetal (FDMA). FDMA is easy handling on the contrary harmful common agent like chloromethyl methyl ether. In this catalytic system, primary, secondary and tertiary alcohols, as well as phenols, were converted to their corresponding methoxymethyl ethers in high yields and short reaction times at room temperature.Investigation of chemoselectivity of this method showed discrimination between the activity of primary alcohols in the presence of secondary and tertiary alcohols and phenols. This heterogenized catalyst was reused several times without loss of its catalytic activity. High yield, less expensive and readily available reagents and easy experimental procedure are the advantages of the present method.

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IP449

Highly Polar Solvent-induced Disproportionation of a Cationic Pt(II)-Diimine Complex Containing an *o*-Semiquinonato

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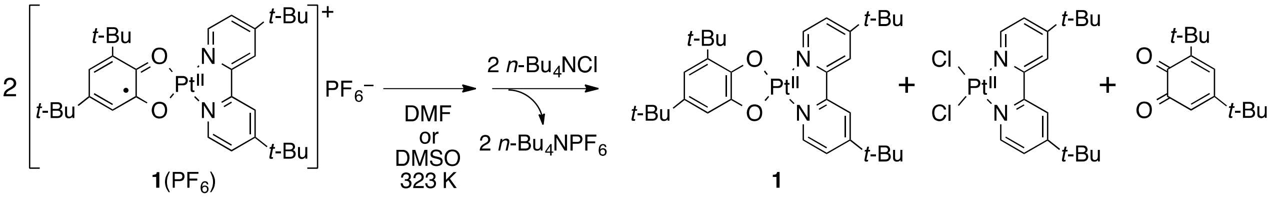
Keywords: Disproportionation, Redox-active ligand, *o*-Semiquinonato, Platinum complex, Polar solvent

Abstract

Electron transfer reaction is the key process both in environmental and artificial chemical systems, e.g., photosynthesis. Platinum diimine complexes with redox-active ligands, such as catecholato or 1,2-benzendithiolato,have been intensively on account of their intriguing physicochemical properties such as solvatochromism, ligand-centered redox activity, and phosphorescence.[1] In contrast to a series of neutral complexes, which have been studied extensively, only little is known about the corresponding oxidized species. Weinstein *et al.* reported that the reaction of [Pt^{II}(3,5-DTBCat)(DTBbpy)] (3,5-DTBCat = 3,5-di-*tert*-butyl catecholato, DTBbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) (**1**) with $FcPF_6$ provided spectroscopic data that suggested the formation of [Pt^{II}(3,5-DTBSQ)(DTBbpy)]$^{+}PF_6^{-}$ (**1**(PF_6)) (3,5-DTBSQ = 3,5-di-*tert*-butyl semiquinonato).[2] However, this oxidized species could not be isolated as a solid, and thus the collection of further spectroscopic information was hampered.

We previously reported the spectroscopic properties of neutral **1** and cationic **1**(PF_6) in variety of solvents.[3] We present herein these spectral properties, togenther with unprecedented solvent polarity-induced characteristic disproportionation reaction of **1**(PF_6) (Scheme 1). The our current efforts directed towards a more detailed understanding of the mechanism will also be presented.

Scheme 1. Disproportionation of **1**(PF_6)in DMSO and DMF.



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IP450

Advantages and disadvantages of membrane contactors with deposited catalytically active layers of heavy metal oxides for wastewater treatment

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Keywords:membrane contactor, metal oxide nanoparticle

Abstract

At the present time in the Russian Federation, there are many different companies, where a small amount of waste water form (in an amount of several tens or hundreds m^3 per month), that are dilute solutions of organic compounds. Ensuring the safe dumping of wastewater requires a technologically simple and relatively cheap method of treatment.

The most perspective way for these enterprises is destructive method, in particular, the catalytic liquid phase oxidation. Using this method for the purification of compounds consisting only of carbon, hydrogen and oxygen, the reaction products are only carbon dioxide and water. Moreover, due to the small amounts of organic compounds, separation of CO_2 is negligible. The introduction of this method is limited to expensive equipment operating at high temperatures and pressures, and catalysts based on metals of the platinum group. An alternative way of carrying out this process is the use of membrane contactors with a catalytically active layers based on transition metal oxides.

There were developed methods of synthesis of aggregatively stable aqueous dispersions of nanoparticles oxygenate copper, cobalt, iron, vanadium and manganese at the Moscow University of Chemical Technology of Russia, department of colloid chemistry. The possibility of using these nanoparticles to prepare oxide layers on the surface of ceramic microfiltration membranes of different geometric shapes. Preliminary experiments showed that the resulting membrane contactors have catalytic activity in the oxidation of phenol under mild conditions.

However, despite the several advantages of this process, the use of heavy metals supported oxide layers may lead to a partial leaching of ions in the water to be purified. This rate must be carefully controlled, as in most of the regions are set very low value norms on the content of heavy metals in the discharged water. For the consumer, the need to monitor the content of heavy metals after such treatment is not obvious, since in relation to the application layer washout very limited. Membrane contactors do not change their appearance and do not reduce the rates of purification.

Studies have shown that despite high catalytic activity of the individual layers of V_2O_5, their use in these processes is undesirable because vanadium transition is observed in water-soluble form in concentrations corresponding to several µg / l. Using individual layers based on CuO is possible only in neutral and slightly alkaline pH range, during the process in weakly acidic media is also observed in the partial transition of copper ion form. Deposited layers based on oxides of cobalt, iron and manganese showed a slightly lower catalytic activity than the oxides of vanadium and copper, but transition metals in water-soluble form was not observed.

Currently the researches is being developed for obtaining the composite layers and enable to provide high catalytic activity of membrane contactors, and to prevent heavy metal ions in the environment.

IP451

Direct metal-free dehydrative cross-coupling of alcohols and alkenes catalysed by molecular iodine under solvent-free reaction conditions

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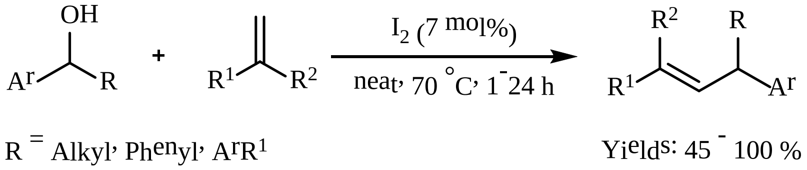
Keywords:solvent-free, iodine, cross-coupling, alkenes, alcohols

Abstract

Direct alkylation resulting in C–C bond formation is a significant method which enables a large variety of chemical transformations and covers a broad spectrum of applications in petrochemical chemistry as well as in synthesis of pharmaceutically active substances. Alcohols are a highly attractive class of alkylating agents since they are inexpensive, they are usually easily derived from natural sources and the only side product resulting from associated coupling reaction is water.[1] On the other hand, the flexibility of the alkene functional group offers a leverage for transformation into various other moieties.[2] In accordance with our continuous interest in greener chemical approaches to transformations of organic compounds, we present a new metal-free method for direct dehydrative cross-coupling of alcohols and alkenes using molecular iodine as a Lewis acid catalyst under solvent-free reaction conditions. The reaction is atom-economical, tolerant to air and allows simple procedure, furnishing coupling products with yields up to 100 %. The method has proved efficient for coupling of secondary benzyl alcohols with phenyl-substituted alkenes.



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IP452

The Solution Characteristics and Metalloenzyme-induced Hydrolysis of Selected Nerve Agent Simulants: QTOF-MS; UV/Vis; FTIR Studies

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Keywords: Metalloenzyme, Substrate, Phosphate monoester, Phosphodiester, Hydrolysis

Abstract

The reported terrorist use of chemical warfare agents (CWAs) such as Sarin, coupled with the global , undetected environmental accumulation of pesticides such as Parathion, demand the development of effective decontamination and bioremediation systems for these toxic chemicals. Organophosphorus (OP) nerve agents remain a threat to human health since they affect the nervous system by the irreversible phosphorylation and inactivation of the enzyme acetylcholinesterase (AChE) [1,2]. Thus some metalloenzymes such as the Organophosphate degrading Agent (OpdA) and Organophosphorus hydrolase (OPH) have gained considerable research interest by virtue of their biological roles and their use in bioremediation, coupled with their capability to hydrolyze highly toxic OP nerve agents [3,4].

The present study seeks to investigate the hydrolytic properties of Co(III) enzyme models of the type: $[Co(L)_2(OH)(H_2O)]^{2+}$, (L = bidentate amine ligand), under physiological pH conditions. The nerve agent simulants, phenyl phosphate (PP), 4-nitrophenyl phosphate (NPP) and bis-(4-nitrophenyl) phosphate (BNPP) have been chosen as model substrates to probe their structural characteristics, reactivity, chromatographic and spectroscopic properties. The approach involves separately evaluating the fragmentation patterns of both the enzymes and substrates in solution followed by monitoring the hydrolysis process using a combination of chromatography (LC-QTOF-MS), and spectroscopic techniques (UV-Vis; MS/MS; FTIR). Preliminary studies reveal that in neutral aqueous solution, the phosphate monoesters (PP and NPP) fragment to give the metaphosphate intermediate ($^-O – PO_2$) and the corresponding phenolate conjugate. (RO^-). This observation suggests that metaphosphate exists in solution as an intermediate which is subsequently attacked by the nucleophile in the transition state, a clear evidence of a dissociative pathway in the monoester hydrolysis process. By contrast, the phosphodiester, BNPP appears to prefer the solvent-assisted, addition – elimination process that proceeds through the initial hydrolysis of one nitrophenolate moiety.

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IP453
Photocatalytic Selective Oxidation of DDT to Dicofol

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Keywords: DDT, Dicofol, photocatalysis, dioxo- Mo(VI)-complex/TiO_2

Abstract

The selective oxidation of halogenated hydrocarbons is of interest in various areas, such as chemical industry, green chemistry, and organic syntheses. Particularly, DDT (dichlorodiphenyl trichloro ethane), used as pesticide, is a persistent pollutant and rests one of the main dangers to human health and to the environment. Being chemically stable in ordinary conditions, until about 468K, its oxidation or oxidative degradation, especially, in large amounts or in industrial scale, is problematic in certain aspects. In the chemical industry the oxidation of DDT, directed to the production of dicofol, is performed as a multistep process, including: elimination of HCl from DDT, giving DDE (1,1-bis(4-chlorophenyl)-2,2-dichloroethene); chlorination of DDE to tetramer (dichlorodiphenyltetrachloroethane);hydrolysis of tetramer to dicofol, using para-toluene sulfuric acid. The aim of this work is to evaluate the feasibility of a direct oxidation of DDT with dioxygen, cheapest oxidant agent, under “mild” conditions, by the application of
using as a heterogeneous photocatalyst, the fully characterized metal organic complex dioxo-Mo(VI)-dichloro[4,4′-dicarboxylato-2,2′-bipyridine], anchored on the surface of a TiO_2 by chemical bonds, at room temperature, in acetonitrile medium. The oxidation of DDT was carried out as a two stage cyclic process, involving: (i) the direct interaction of Mo-complex/TiO_2 with DDT under UV-irradiation (λ= 253.7nm) and (ii) regeneration of the photocatalyst with molecular oxygen in the dark conditions. These two stages of the process were separated temporarily. It has been shown that the dioxo-Mo complex, anchored on the TiO_2, plays the role of photocatalyst in selective oxidation of DDT to dicofol (2,2,2-trichloro-1,1-bis-(4-chlorophenyl)ethanol) in chosen “mild” conditions. About 36% of the initial DDT was oxidized to dicofol by the yield 21% during in 5 consecutive experimental cycles (32 h). It has been shown that the formation of products (other than dicofol) is intermediated mainly by the oxidative and partially reductive decomposition of dicofol. They are dechlorinated (28-30%) and non-dechlorinated or partially dechlorinated organic compounds (34-36%), as well as the products of the complete degradation into CO_2, H_2O and HCl (15-17%). On the basis of kinetic data and analysis of products it has been proposed the probable mechanism of the photocatalyzed oxidation of DDT in the mentioned conditions. The scheme of the reaction mechanism includes the primary reaction of the oxo-atom transfer of the Mo-complex to tertiary carbon-atom of DDT by the formation of dicofol. About twofold increase of the turnover number of the reaction (Δ[DDT]/[anchored complex]) in second and further catalytic cycles evidences that the re-oxidation with molecular oxygen of Mo(IV) metal centers, formed in the first stage of catalytic cycle, to Mo(VI) may occur by the formation of intermediate Mo(VI)-oxo-peroxo moieties of the anchored complex.

IP454

Gas Chromatographic Analysis of Natural Substances Using a New Liquid Crystal as Stationary Phase.

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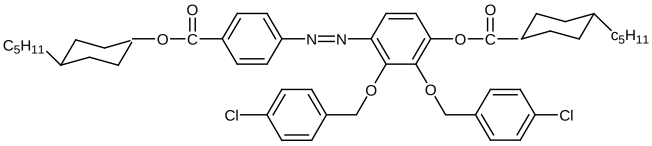
Keywords: Gas Chromatography, liquid crystal, volatile compounds.

Abstract

Application of a nematic liquid crystal used as stationary phase in capillary gas chromatography is investigated using some volatile natural products. The structure of the mesogenic compound is shown in the figure.



Azobenzene liquid crystal

The liquid crystal synthesis method uses simple reactions such as esterification, alkylation, diazotation. The thermal properties were established with scanning calorimetry (DSC). The chromatographic separations abilities of stationary phase were studied by capillary fused silica column. Headspace microextraction (HS-SPME) was used for determination of natural substances in water samples.

The SPME extraction of volatile compounds from water was done using a 100 μm PDMS fiber.

Interesting analytical performances were obtained in different fields: isomeric separation of aromatics, volatile aroma compounds, and cis/trans isomers.

The pairs of geometric isomers, α- and β-cedrene, estragol/anethol, thymol-carvacrol, are separated with good resolution by the liquid crystal in the nematic phase.

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IP455

Application of Substituted Liquid Crystal as Stationary Phase for Determination of Phenolic Compounds in Waste Water Using solid Phase Extraction.

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Keywords: Gas Chromatography, liquid crystal, Salicylidene imine, phenolic compounds.

Abstract

A nematic new liquid crystal stationary phase for the determination of some derivatives phenol in water using solid phase extraction (SPE) is used. Two techniques were used for isolation of phenols in waste water: classic liquid-liquid extraction (LLE) and extraction from solid phase (SPE). In the classic extraction the phenols from an alkaline milieu into chloroform was found sufficient. Solid-phase extraction and liquid-liquid extraction were used as preconcentration step for determination of phenol in water.
In SPE, the C_{18} cartridges were used. Chromatographic analysis is achieved on salicylidene imine liquid crystal stationary phase: 4-(4'-alkoxybenzoyloxy)-benzoyloxy salicylidene imine N-(propyl).

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IP456

Comparison of Soxhlet Extraction, Microwave-assisted Extraction and Ultrasonic Extraction for the Determination of PCBs Congeners in Spiked Soils by Transformer Oil (Askarel)

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Keywords: Soxhlet extraction, Microwave-assisted extraction, Ultrasonic extraction, Polychlorinated biphenyls, Soil.

Abstract

In this work, we compare the extraction effectiveness of three extraction methods commonly applied for the determination of polychlorinated biphenyls (PCBs) in spiked soil by transformer oil (Askarel oil). The techniques included are Soxhlet extraction (SE), Ultrasonic extraction (UE), and microwave-assisted extraction (MAE) , also comparison of organic extracting solvents were examined in this study. For none of these techniques were the extraction conditions optimized, but the choice of extraction parameters were based on the experience from pervious successful investigation published by a number of research groups worldwide.
This study focused on the variation in the extraction quantities for each PCB congeners (29 PCB) with different extraction methods. The results of chromatography analysis showed highest recovery was found by using (n-hexane-acetone, v/v) as solvent extraction compared to other solvents. However, a comparison between microwave-assisted extraction (MAE), Ultrasonic extraction (UE and Soxhlet extraction (SE), methods has been made. It evidenced that MAE is suitable alternative to SE for the analysis of PCBs in soils, but UE did not give a good recovery in the present work

IP457

Cu-Catalyzed one-step synthesis of acrylates from ethylene and CO_2

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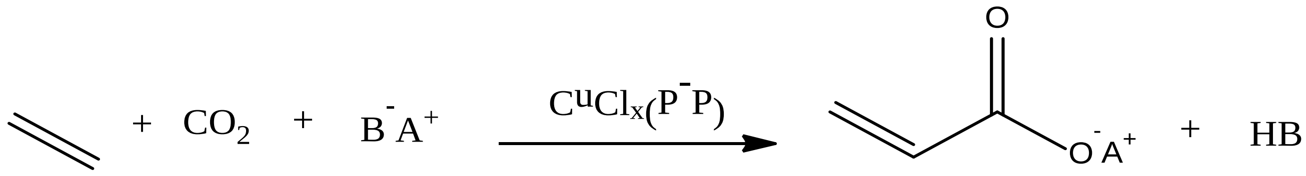
Keywords: CO_2, Cu-Catalyzed, acrylates

Abstract

The use of carbon dioxide as a building block for the synthesis of a wide array of molecules is a very promising field of research[1]. Acrylates are a widely used starting material in the synthesis of ions-exchange resins, fibers, varnishes and super-adsorbent polimers (SAP). The direct synthesis of acylates from ethilene and CO_2 in presence of alkaline phenoxides has been developed in literature[2] by using a diphosfine Ni(0) complex as a catalyst, which leads to a TON (turover frequency) of ca. 100 h^{-1}.



In the present work we have studied the catalytic activity of several Cu(I)-based complexes in the synthesis of acrylates from carbon dioxide and ethene.
The new catalysts proposed showed interesting catalytic activity also at room temperature.
An optimization of the reaction conditions has been carried out and proposed.

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2nd Generation PLA; L-lactide directly from aequeous lactic acid

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Introduction

The reduction of carbon dioxide emission and the substitution of crude oil e.g. in the polymer production are significant and of great challenges in the 21st century. One of these topics is in the field of biodegradable polymers starting from renewable resources by using the carbon framework of nature. The aliphatic polyester polylactic acid (PLA) has become the most promising biodegradable polymer in recent years. PLA is well known for biomedical applications over years [1] and there is a highly increasing demand for its use as a thermoplastic polymer [1-4]. PLA is a practical alternative to the commonly used plastics based on petrochemicals such as polyterephthalate. Moreover, the biocompatibility by its degradation into CO2 and water, the highly versatile properties and the low toxicity to humans are even of more advantageous.

A 2nd generation PLA process was developed by direct synthesis of L-lactide (L-LD) from aqueous commercially available 90 % lactic acid (LA) to avoid the commercially used prepolymerisation and depolymerisation as shown in figure 1.

Materials and Methods

Experiments were conducted in a continuous plug flow fixed bed reactor under gas phase conditions. In the presence of various zeolites [5] the influence of pressure, temperature, residence time and water content of the starting material was investigated. The catalysts were characterized by inductively coupled plasma atomic emission spectroscopy (ICP AES), X-ray powder diffraction (XRD), nitrogen adsorption isotherms (BET), temperature programmed desorption of ammonia (NH_3 TPD) and pyridine Fourier transformed infrared spectroscopy (Py FTIR).

Results and Discussion

The activities of three H ZSM 5 zeolites were strongly connected to their module. The conversion decreases with an increasing SiO_2/Al_2O_3 ratio due to the less acidic centers from 54,0 % (M 25) over 52.3 % (M 300) to 33,7 % (M 1000). The highest selectivity achieved over these pentasil zeolites was 71,7 % using the H-ZSM-5 with a modul of 300. The H ZSM-5 with the lower ratio of 25 has a too many acidic sites with strong (500 °C NH3 desorption) acidic centers as well as a high number of Brønsted acid sites. These properties lead to low selectivity due to cracking reactions. The formation of acrylic acid, acetone, acetaldehyde, formaldehyde and carbon dioxide could be observed in minor amounts.

The cheap amorphous γ-Al_2O_3 with its simple structure was chosen for the parameter optimization. Figure 2 shows conversion and selectivity under subatmospheric pressure of the γ-Al2O3 catalysis over the temperature. The conversion rises from 8.5 % (90 °C) to 27.1 % (270 °C) because of the accelerated kinetic. In addition the selectivity increases from 1.4 % at 90 °C to 98.9 % at 240 °C. The results prove the expected correlation between the catalyst acidity and the LA conversion. Moreover, the acidity and the temperature have an impact on the LD selectivity.

The aqueous 90% LA consists of different amounts of monomer (L_1A) and oligomers such as linear dimer lactoyllactic acid (L_2A) which is assumed to be the starting material of LD. Changing the starting material (90 % LA) to highly concentrated oligomer rich 97 % LA with a minor amount of water leads to a slightly selectivity decrease but increased the conversion from 15 to 53.6 %.

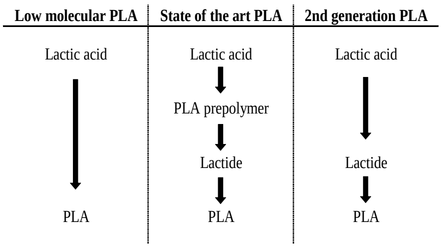

Figure 1. PLA Production routes

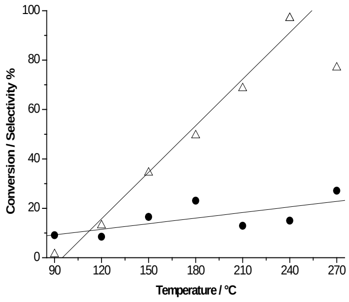

Figure 2. Conversion / selectivity in dependence of temperature over

γ-Al_2O_3 at 20 mbar

Conclusion

In this study a new pathway for 2nd generation PLA, a very valuable polymer based on the renewable feedstock lactic acid, was found. Thereby, L-lactide was produced directly from commercially available aqueous LA. By this new procedure the prepolymerisation and depolymerisation steps in presence of the homogeneous catalysts H_2SO_4 and Zn compounds could be replaced by a single heterogeneously catalysed step. It is not only a shorter and less investment intensive process procedure but also an environmentally benign route because the disadvantageous of homogenous catalysis (e,g. salt formation and its disposal) can be avoided by the application of a heterogeneous catalyst.

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Acknowledgement

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GREEN POLICY, SUSTAINABILITY AND SAFETY

P501

Preconcentration and determination of levoglucosan in ambient air

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Keywords:levoglucosan, atmospheric aerosol, ACTJU, LC-MS

Abstract

Monosaccharide anhydrides are widely abundant water soluble organic compounds (WSOC) in fine fraction of atmospheric aerosol. The most abundant species from them is levoglucosan, a product of cellulose combustion. Mannosan and galactosan, the isomers of levoglucosan formed during combustion of hemicellulose, are present in aerosol in minor amount. The levoglucosan is frequently used as specific molecular marker of biomass burning. The determination include mostly the collection of aerosols on filters, extraction and GC-MS determination after derivatization step. The main aim of this work was a development of the analytical method for levoglucosan determination including direct collection of aerosol into water phase, preconcentration, and determination by LC-MS.

The collection of levoglucosan was performed by an improved version of the Aerosol Counter-flow Two Jets Unit (ACTJU) aerosol collector [1]. A combination of the original version of ACTJU collectorwith water-based condensation growth tube (GT) located upstream of the ACTJU collector enabled quantitative sampling of aerosol particles at the size of a few nm in diameter [2]. Thus, the levoglucosan was continuously collected into water samples using the GT/ACTJU. A time resolution of the sampling was changed according to concentrations in the atmosphere. Water samples with low concentrations of the levoglucosan were preconcentrated and dissolved into a small volume of acetonitrile/water mixture for subsequent analysis.

Before LC-MS analysis, an optimization of separation and detection by LC-MS was carried out. The separation of levoglucosan, mannosan and galactosan was performed with a polymeric amino column Prevail Carbohydrate ES. To enhance ionization efficiency, and therefore the detection limits of target compounds, post-column additions of various aqueous solutions were compared. The best results were obtained for LiCl post-column addition.

Acknowledgement

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P502

Green and Sustainable Chemistry at Nottingham

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Keywords: Green Chemistry.

Abstract

The University of Nottingham is home to the Centre for Sustainable Chemistry which aims to change the way we think about chemistry by putting sustainability at the heart of research. Through this project the School of Chemistry is focusing on major challenges which affect us all – healthcare, energy and sustainability. [1]

One of the most exciting developments is the recent completion of the GSK Carbon Neutral Laboratories for Sustainable Chemistry (CNL). [2] The CNL, part funded by a very generous gift from GSK, will serve as a hub to catalyse new collaborations with industry. The CNL is unique in the UK, particularly for its design which should prove completely carbon-neutral over a period of 25 years. It is constructed of wood and is largely self-sufficient in electrical energy *via* solar panels and bio-derived fuels. A particular innovation is the lab instrumentation which is all designed to have low power consumption. Research at the CNL will aim for the highest "clean and green" standards to minimise environmental impact and ensure that the new chemistry developed is sustainable and efficient in terms of energy and resources.

The CNL is also home to the Centre of Doctoral Training (CDT) in Sustainable Chemistry. [3] Developed in collaboration with Industry and as a partnership of several disciplines including chemistry, engineering, biosciences and business, the Centre aims to train students in the development of sustainable processes and compounds for the chemistry-using industries. The defining principle that has driven the co-creation of the CDT training programme is a shared vision and commitment to foster a new generation of champions for sustainable chemistry – these individuals will be equipped with the skills and experience to lead chemistry-using industries towards a more sustainable future. The CDT already has more than 40 students. Recruiting is about to start for the 2017 cohort. Full details can be found at http://suschem-nottingham-cdt.ac.uk/

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P503

Extraction of Essential Oil from Ginger Using Microwave Hydro-diffusion and Gravity Method – Energy Considerations

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Keywords: Microwave; Essential oils; Ginger; Specific energy consumption

Abstract

Microwave hydro-diffusion and gravity (MWHG) is a recently developed technique for the extraction of essential oils (EOs) from vegetable materials. In literature, there are a few number of papers describing such a process [1-3]. However, this work present an innovative equipment for the MWHG extraction of EO from ginger with the following characteristics: continuous setting of microwave power depending on the desired operating temperature or desired specific absorption rate; a stirring system that allows an uniform microwave irradiation; extractions performed at normal or low pressure; the possibility of introducing saturated steam in the system or an inert gas.Also, in this study are established energetic characteristics of the process that haven't been presented before in the literature.

The experiments were carried out using as feedstock shredded ginger rhizomes or pressed pulp obtained from mechanical pressing of ginger rhizomes. The microwave hydro-distillation (MWHD) was used as reference method for comparing the amount of EO resulted after the extraction by MWHG.

According to the literature [4], was observed a significant decrease of the absorbed microwave power when the mass sample is reduced below 200 g.

The influence of two parameters was followed: the microwave power and the addition of saturated steam in the system.

The total efficiency of the EO obtained from pressed pulp ginger and separation efficiency of the EO in distillate were calculated.

The analyzed data reveal that the experiments performed at variable SAR with limited values leads to good enough results in terms of the efficiency of EO extraction. In addition, for the best extraction conditions, the energy consumption is approximatively 3 fold lower than the classical extraction by MWHD or than the experiments performed by MWHG at constant power.

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Detoxification of crude *Jatropha curcas* seed oil by Removal of Phorbol Esters using Modified Nanosilica from Purified Rice (*Oryza sativa)* Hull Ash

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Keywords: detoxification, *Jatropha* curcas, modified nanosilica, phorbol esters, rice hull ash

Abstract

Crude *Jatropha curcas* seed oil, which is regarded as an alternative biodiesel source [2], was found to contain about 6 % phorbol esters that were extracted using methanol. Further cytotoxicity studies revealed that these phorbol esters were mainly responsible for the toxicity of the oil. Seed oil detoxification was accomplished by adsorption on nanosilica modified with phorbol esters or their oxime derivatives to further increase the ability of the adsorbent to remove these toxic components. The oxime derivative was prepared from derivatization of phorbol ester-rich methanol extract with hydroxylamine hydrochloride.

Nanosilica was prepared from purified rice hull ash using a sol-gel method and subsequent calcination at 600-650 °C. Further modification using organic templates was carried out using different mass ratios of nanosilica mixtures prepared using 1 % and 10 % stock template solutions consisting of 10 g silica per 8 g NaOH and 80 g distilled H_2O. Atomic force microscopy images of modified nanosilica products showed an agglomeration of amorphous, porous materials with an estimated mean size of 46-47 nm.

Removal of phorbol esters through adsorption on modified nanosilica was performed based on the following parameters: 8 % (w/v) amount of adsorbent, 60 minutes adsorption time, 300 rpm stirring rate and room temperature which resulted in a maximum removal up to 90 % of toxic phorbol esters from *Jatropha* seed oil. This adsorption method using modified nanosilica was determined to be an effective alternative method compared to 70 % phorbol ester removal by solvent extraction [4].

Brine shrimp cytotoxicity assay showed that untreated *Jatropha curcas* seed oil was highly toxic based on LC_{50} value of 0.30 µg/mL. Treatment with 10:3.3 (w/w) modified nanosilica:crude phorbol ester yielded the least toxic oil sample with LC_{50} value of 124.40 µg/mL. Tukey's test showed that the differences in adsorption treatments using unmodified nanosilica and modified nanosilica products were found to be highly significant. Therefore, 10:3.3 (w/w) modified nanosilica:crude phorbol ester product was considered the most suitable adsorbent for the removal of phorbol esters from crude *Jatropha curcas* seed oil.

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Green chemistry principles for optimum technology of biological conversion of vegetable

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Keywords:oilseeds; deproteinized sunflower meal; microbial conversion; efficiency assessment; green chemistry

Abstract

Nowadays the development of low-waste and resource-saving technologies of food products based on renewable raw materials and waste products of their processing enriched with protein is one of the priority tasks to be solved in the framework of sustainable development of modern society. The method of assessing the effectiveness of waste pretreatment of deproteinized sunflower meal (DSFM), one of oil and fat industry waste products is proposed for its microbial conversion into vegetable carbohydrate and protein concentratesaccording to the principles of green chemistry. The methodology proposed includes an assessment of three factors: amount of wastes per unit of the desired product; the amount of hazardous substances used in the pretreatment process, and process efficiency.

1) Waste generation. E-factor = waste weight/desired product weight [1]

2) The amount of hazardous substances that are used in the synthesis. H-factor = hazardous substanse total weight/desired product weight

3) Energy efficiency. ProcessEnergy consumption is proposed to assess through the *Q-factor* (J/kg) using the ratio: Q-factor = hazardous substanse total weight/desired product weight

The methodology testing was based on the experimental data obtained by chemical hydrolysis of DSFM, and also two-stage pretreatment process of DSFM comprising the steps of chemical and enzymatic hydrolysis.

The recommendations for selection of optimal DSFM pretreatment conditions based on the calculated assessments of the process efficiency are submitted. To the desired output in assessing the process for compliance with the requirements of green chemistry took into account such parameters as:

The worst waste index ($E\text{-}factor_{max}$), the hazardous substance index ($H\text{-}factor_{max}$) and/or maximum energy consumption (Q-factor_{max}) of the process were taken as 100% each. Process Efficiency, *EF* (%) is defined as:

$$EF = \frac{\mathrm{E} - \mathrm{factor}\ (or\ \mathrm{H} - factor\ \mathrm{or}\ \mathrm{Q} - factor)}{\mathrm{E} - \mathrm{factor}_{max}(or\ \mathrm{H} - factor_{max}\ \mathrm{or}\ \mathrm{Q} - factor_{max})} \times 100\%$$

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Development of the Methodology for the Evaluation of the Chemicals Footprint. Russian Example

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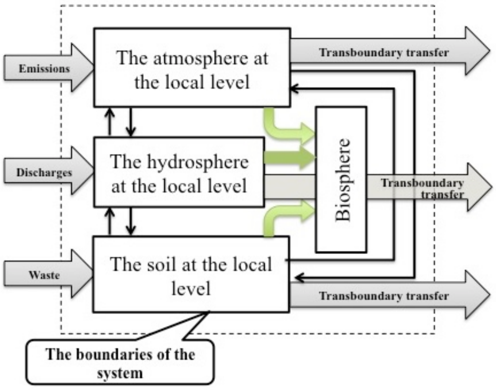
Keywords:environment, chemicals footprint, planetary boundaries, modeling

Abstract

Rockström et al. [1] who introduced the concept of “planetary boundaries” that set a “safe functional space for the humankind” did not define a quantitative indicator for the “chemical pollution” planetary boundary. One of the implementations of approach for the definition of this indicator is based on the evaluation of the chemicals footprint [2], which is defined as a quantitative measure describing the ecological space required for the dilution of the chemical contamination caused by human activity to a level below the defined threshold.



Common model of chemicals fate in environment.

Various mathematical models are used to obtain reasonable forecasts of chemicals effects on the environment. One of them is the USEtox model. The technique of assessing the “sustainability” of chemical compounds in various environmentshas been developed based on it [3]. The matrix algebra based approach is used as a tool for the modeling and evaluation of chemicals fate in the environment. This technique has been tested using the data for the federal districts of Russia. Calculations were performed for the three-component system, including the atmosphere, soil, and freshwater. Reference data, as well as the results of experimental observations for priority pollutants have been used to evaluate physical and chemical parameters of the model.

Comparison of the results of calculations with the observed data show a sufficiently high correlation. The result confirms the effectiveness of the developed method, which might be considered as an effective tool for the chemical footprint evaluation. Also the possibility of the combination of the-above mentioned approach and the methodology of calculating the concentrations of harmful substances in the air (OND-86), adopted in Russia, is considered in this presentation. The algorithm that incorporates the parameters of hygienic regulation of the environmental media (used in Russia) has been applied for the assessment of the impact of chemicals on the environment.

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P508
How to improve student's motivation to learn?

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Keywords: Emotional intelligence, educational technologies,technological education

Abstract

Technical education in contrast to humanitarian is formalized andaimed to solve technical problems that imply a definite solution algorithm and have the expected result. In the modern world chemical technologies are developed and are changed, are becoming more flexible. There are also required specialists who are ready to find a creative approach to solve problems. At the same time traditional educational technologiesmay not be successful for the modern generation of students.

J. Mayer model may be useful to improve the efficiency of thought and action[1]. According to this model the teachers have to cause emotions that contribute to the solution of problems. Teachers and students should communicate in the same "language". At present teachers have to be leaders with high emotional intelligence. On the one hand they should be able to operate the educational process, on the other hand they should be able to use emotional factors as motivators of learning.

It was accomplished an following experiment during the lesson of physical chemistry. It was proposed to students to select the traditionaltest answers or to participate in quiz as a game. About 65% of students were ready to participate in the game in the first lesson, about 95% - in the second one. At the mean time the motivation for study has grown.

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Atom-economic approach for vinylation of indoles and phenols using calcium carbide as acetylene surrogate

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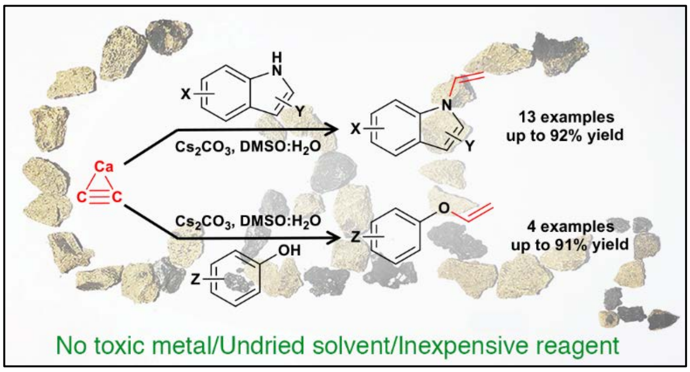
Keywords:calcium carbide, vinylation, vinyl indole, vinyl ether

Abstract

An efficient *N*-vinylation of indoles and *O*-vinylation of phenols to give *N*-vinyl indoles and phenyl vinyl ethers is reported. The vinylated products can be produced in satisfactory to excellent yields (65-92%) upon treatment of indoles or phenols with calcium carbide in wet solvents in a standard laboratory setup. Key features of this reaction include the use of calcium carbide as a safe and inexpensive slow released acetylene source for *N*- and *O*-vinylation under simple reaction conditions without the need for metal catalyst or halogenated substrates.



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Nanostructured biodefensive based on the encapsulation of *Licaria puchury-major* essential oil

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Keywords:*Licaria puchury-major*, Essential oil, Encapsulation, Biodefensive

Abstract

Three most common pests in tropical and subtropical countries are currently causing severe damages [1-3]. For this reason, essential oil extracted from the seeds of *Licaria puchury-major* ("puxuri")was encapsulated in biodegradable polymeric nanoparticles and tested against *Aedes aegypti* larvae, *Tetranychus urticae* Koch. mites and *Cerataphis lataniae* aphisunder laboratory conditions. Twenty compounds were identified by GC/FIDand GC/MS, representing 98,4% of the total oil. The major compounds were safrole (38,8%), eucalyptol (21,7%) and limonene (8.3%). A new rote for the synthesis of biodegradable polymeric nanoparticles was developed and allowed the oil encapsulation. Bioassays were conducted to test the larvicidal activity against *A. aegypti*. A significant larvicidal potential for 24 h of exposure was observed with lethal dosage LC_{50} of 98.9 ppm. Acaricidal and insecticidal activities were evaluated against the adults of *T. urticae* and *C. lataniae*. Volatile phase effects of different concentrations of the essential oil indicated complete mortality of mites and aphis above 250 ppm. The mean lethal concentrations (LC_{50}) of mites and aphis for 24 h of exposure were 30.8 and 13.5 ppm, respectively. The essential oil showed no inhibition against acetylcholinesterase (AChE) in the same tested concentrations for bioassays. Our results may be explained, beside the controlled release mechanism of nanoencapsulated systems, by the larger amounts of safrole and eucalyptol in the essential oil, which present important antioxidant properties [4]. Bioactivities of *L. puchury-major* essential oil have not been reported in scientific literature. These results suggest that essential oil of puxuri could be an important candidate for the development of new encapsulated green material since the nanoparticles are biodegradable, the seeds are abundant in the Amazon region and the yield of essential oil obtained by hydodistillation is substantial.

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Green Chemistry Education for Chemistry Undergraduate Students in Mexico using Online Educational Resources

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Keywords: Green Chemistry Education, Online Resources, Sustainability, Safer Planet

Abstract

As strange as it may sound, not many chemistry students in Mexico are really interested in the sustainability of their world. On the other hand, growing public concern over global warming and greenhouse gases, should make students want to understand how human actions affect the health of our planet, but is not of their interest at the level one can expect.

Of course, some students are deeply concerned about pollution, practice recycling and want to contribuye to achieve a better world, a safer planet. But they are, unfortunately, just a few.

With the use of Online Educational resources for Green Chemistry Education, already available, as part of a Green Chemistry Workshop we hope to show them, that they have a unique opportunity to start at the ground floor of the exciting and expanding field of green chemistry and at the same time doing something meaningful for the future generations.

The Tools used are supposed to be for anyone trying to teach or learn more about green chemistry (online guides, reading materials, databases, alternative chemicals and processes to use in the lab., methodologies, etc.) and also as main activity of the Green Chemistry Workshop GCHW some lectures from specialists wil be delivered. These activities will give some extra credits to our students. In the Poster we will present the first results of the Project.

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Undergrad and graduate teaching of Green Chemistry at McGill University

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Keywords: Teaching, peer review, student journal, workshop

Abstract

The concepts and ideas of green and sustainable chemistry were embraced at McGill University over 20 years ago. A senior undergraduate course entitled Green Chemistry (CHEM 462) was then created and has been offered since. This course teaches principles of green chemistry, and covers recent research advances in the topic. In the recent years, we have experimented teaching practices including peer evaluation among the class, debating and the creation, edition and publication by the students of an online journal, the "McGill Green Chemistry Journal". The learning outcomes included decision making, communication, data mining and sorting, and critical thinking. The quality of the material produced by the students, their involvement in the class and their evalution of the course were all excellent. Besides undergraduate teaching, McGill currently hosts a centre dedicated to graduate training in green chemistry, funded through the CREATE program of the Natural Science ad Engineering Research Council of Canada (NSERC). This multidisciplinary center gathers research groups from chemistry, engineering and the school of management. The centre organizes training sessions in technical and soft skills, offers internships and international research exchange opportunuties and provides funding for stipends. Among our activities, we have created a workshop and case competition in sustainable innovation, with the support of the Marcel Desautels Institute for Integrated Management and the Trottier Institute for Sustainability in Engineering and Design. This event brings together students from all the different areas of the CREATE center and runs over 2 days. After keynote lectures, given by prestigious entrepreneurs, professors and industry leaders, we introduce the students to important concepts of green chemistry, engineering and management. The second day, students work in teams to study an innovation case and present a full business plan to a panel of experts. Evaluation of this event by students reveal that they find stimulating and enriching to work with students with a different background and learn a lot on innovation, business and green chemistry.

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	Wednesday* September 07			
9.00	PL4 - Dr. Martin Kayser *Toniolo Theatre*			
9.45	K12 L. Giannini *Toniolo Theatre*	K13 M. Philippe *Small Conference room*	K14 C.J. Mota *Conference room*	K15 T. Zhang *Auditorium*
10.15	M15 I. D.V. Ingram	P1 P. Anastas	IP10 K. Schroeder	E1 Y. Amao
10.35	M16 I.A. Shuklov	P2 P.M. Jacob	IP11 B. Jhumur	E2 H. Shi
10.55	Coffee Break			
11.25	M17 C. Brett	P3 M.C. Cann	IP12 C. Zhang	E3 V. Kalousek
11.45	M18 H.Kagawa	P4 C. Blum	IP13 J. Gagnon	E4 S. Protti
12.05	M19 A. Jardine	P5 Š. Možina	IP14 K. Nakajima	E5 Y.N. Zhang
12.25	M20 W. Liu	P6 J.G. Stevens	IP15 D. Gomes Rodriguez	E6 Y.J.O. Asencios
12.45	M21 Y. Sasanuma		IP16 K. Takahashi	E7 T. Yoshida
14.15	Social Event – Boat Lunch			

* Wednesday morning: open round table – Industries *Small room Toniolo Theatre*

	Thursday September 08			
9.00	PL5 – Prof. Willfried Braje *Auditorium*			
9.45	K16 G. Reginato *Auditorium*	K17 V. Zuin *Library*	K18 L. Vaccaro *Conference room*	K19 I. Evstigneeva *Small Conference room*
10.15	E8 L.C. Branco	Ed1 L. Mammino	IP17 G. U. Obuzor	IP241 N. Quici
10.35	E9 C. Drago	Ed2 S. Tantayanon	IP18 L. Rossi	IP25 J.C. Rodriguez-Reyes
10.55	Coffee Break			
11.25	E10 V. Kotia	Ed3 T. A. Logothetis	IP19 N.V. Plechkova	IP26 S.R. Wan Alvi
11.45	E11 I. Thapa	Ed4 H. Pérez Delfín	IP20 P. Filippousi	IP27 A. Hubina
12.05	E12 W. Wannapakdee		IP21 B. Nisanci	IP28 A. Aldoshin
12.25	E13 B. Iliev		IP22 A.O. Terent'ev	IP29 X. Peng
12.45	E14 S. N. Chavan		IP23 H. Konnerth	
13.05	Lunch			
14.30	PL6 - Prof. Fernando Galembeck *Auditorium*			
15.15	Ali Maleki – Winner of the 2016 IUPAC-CHEMRAWN VII Prize for Green Chemistry *Auditorium*			
15.45	Coffee Break			
16.15 - 17.30	Closing Ceremony - Posters Prizes *Auditorium*			

PL	Plenary Lecture	K	Keynote speaker
M	Green Materials	B	Green Bioprocess
IP	Green Industrial Processes	P	Policy
E	Green Energy	Ed	Education
OP	OPCW Session	R	Restoration Cultural Heritage

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