7th Asia-Oceania Conference on Green and Sustainable Chemistry

19 – 21 November 2018 | Singapore

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Paper No. PS-0007

EXPLORING NEW REACTIONS TOOLS FOR EFFICIENT CONVERSION OF ABUNDANT NATURAL RESOURCES INTO HIGH VALUED PRODUCTS

Chao-Jun Li*

Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, Quebec, H3A0B8, Canada

Chemicals and chemical products are the signatures of our modern society. The efficient making of new molecules is central to any new product in the pharmaceutical, materials science, microelectronics, energy and biotech industries. On the other hand, chemical manufacturing processes and chemical products have also affected us adversely from personal, local, national, and international scales. As a new philosophy over the last two decades, Green Chemistry through the 12 principles of green chemistry has emerged to develop the next generation of chemical science and technologies, as well as chemical products to meet such challenges in a proactive manner both environmentally and economically, ideally from readily available natural resources directly in a benign solvent.

Our abundant natural resources including renewable biomass, nitrogen, CO_2, water, natural products and methane provides the ideal future feedstocks if tools that can transform them into high valued products easily, cleanly and readily. Over the years, we have been exploring such fundamental reaction tools that can potentially simplify the above transformations, decrease overall waste and maximize resource utilization, such as the Grignard-type reactions in water, the aldehyde-alkyne-amine (A^3) coupling reactions, the Cross-Dehydrogenative-Couplings (CDC), the umpolung of carbonyls as alkyl carbanions, the phenol-amine couplings, the photo-nitrogen fixations, and the metal-free light-enabled late-stage functionalization of natural products and pharmaceuticals among others. In this talk, we will give an overview of our research on this subject and then focus on our recent developments.

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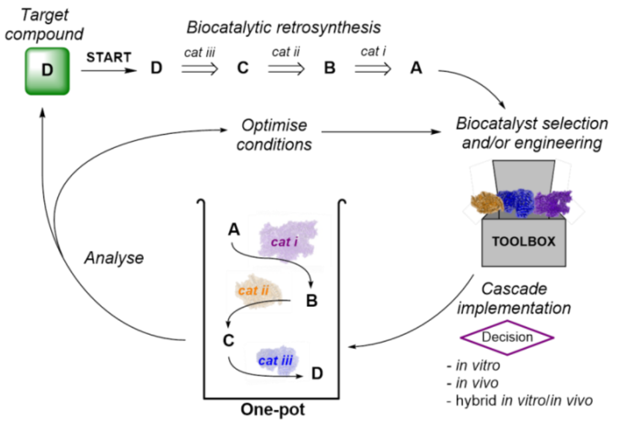
Paper No. PS-0016

DESIGN AND EVOLUTION OF NEW BIOCATALYSTS FOR ORGANIC SYNTHESIS

Nicholas J. Turner

School of Chemistry, University of Manchester, Manchester Institute of Biotechnology, 131
Princess Street, Manchester, M1 7DN, UK.
(nicholas.turner@manchester.ac.uk)



This lecture will describe recent work from our laboratory aimed at developing new biocatalysts for enantioselective organic synthesis, with a particular emphasis on the design of *in vitro* and *in vivo* cascade processes for generating chiral pharmaceutical building blocks. By applying the principles of 'biocatalytic retrosynthesis' we have shown that is now increasingly possible to design new synthetic routes to target molecules in which biocatalysts are used in the key bond forming steps [1].

The integration of several biocatalytic transformations into multi-enzyme cascade systems, both *in vitro* and *in vivo*, will be addressed in the lecture. In this context monoamine oxidase (MAO-N) has been used in combination with other biocatalysts and chemocatalysts in order to complete a cascade of enzymatic reactions [2-4]. Other engineered biocatalysts that can be used in the context of cascade reactions include ω-transaminases [5], ammonia lyases [6], amine dehydrogenases [7], imine reductases [8], and artificial transfer hydrogenases [9]. We shall also present some very recent work regarding the discovery of a new biocatalyst for enantioselective reductive amination and show how these enzymes can be used to carry out redox neutral amination of alcohols via 'hydrogen borrowing' [10].

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Paper No. PS-0059

BEYOND GREEN CHEMISTRY - SUSTAINABLE CHEMISTRY

Klaus Kümmerer

1) Institute of Sustainable and Environmental Chemistry
2) Research and Education, International Sustainable Chemistry Collaborative Center (ISC$_3$)
Leuphana University Lüneburg, Germany

Chemistry as a science as well as an industrial branch is a success story on the one hand. Products of chemical industries including pharmaceuticals are contributing to high living standard and ever-increasing life expectancy. On the other hand environmental pollution and unwanted side effects of chemicals and pharmaceuticals along their lifecycle i.e. from resource extraction, synthesis and manufacturing to usage and end of life are accompanying chemistry since the advent of industrial chemistry. In addition, nowadays we experience a shortage of resources needed for the products as well as production and manufacturing.

That calls for new approaches. One such approach is green chemistry [1], which is gaining momentum all over the world. The 12 principles of green chemistry are giving guidance to greener synthesis of chemicals including designing them less toxic for humans and the environment. The latter is addressed by principle # 10 – design for environmental degradation [2-4]. However, this principle is not only crucial for the design of small molecules but has also to be applied for local, regional and global substance material flows in the context of dissipation of resources, recycling, and a circular economy. However, green chemistry addresses only issues related to chemicals and chemical products themselves [1]. Also there are certain shortcomings of the 12 principles resulting in the fact that green chemistry does not necessarily result in sustainable products or solutions [5]. Have all twelve principles to be fulfilled to call a chemical or a process green or just one? The use of renewable feedstock is recommended, however, these also come at a cost. Even if all twelve principles are fulfilled that does not address the need to reduce substance and materials flows. Neither new business models nor ethical, social and economical issues are addressed. In the extreme even a chemical warfare agent could be synthesised according to the twelve principles, which for sure does not contribute to sustainability.

Sustainable Chemistry in contrast is a more holistic guiding principle [5-7]. It first asks for the function and service needed and then only is thinking about how this can be delivered by chemical products if no non-chemical approach is available. If chemical products are needed these should fulfil the principles of green chemistry. Therefore, sustainable chemistry includes also alternative business and service models as well as social, ethical, and economic issues. It also seeks to avoid entropy transfer from synthesis, manufacturing and application of chemical products to other spheres or to recycling. It strives for long-term sustainable solutions including all stakeholders along the value chain and life cycle of chemical products.

Such a broader approach and guiding principle is needed to successfully enabling chemistry and chemists to meet the Sustainable Development Goals (SDGs) of the United Nations in a truly sustainable manner [5, 8].

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Paper No. PS-0086

SUSTAINABILITY FUELS INNOVATION – AN INDUSTRY PERSPECTIVE

Martin Vollmer
Clariant International Ltd, Hardstrasse 61, 4133 Pratteln, Switzerland

Steadily rising demand and simultaneous decline of resources are creating global challenges in areas such as energy supply, resource efficiency, waste prevention, nutrition and mobility. New and innovative products that address these major challenges of the future are the result of a well-structured innovation process that incorporates sustainability aspects at an early stage, combined with state-of-the-art technology. Moreover, developing customized and holistic solutions requires close collaboration with external partners from various fields.

The conversion of agricultural residues into bio-based products such as biofuels, new environmentally compatible products for printed electronics, or catalysis-based solutions for the treatment of emissions are just a few examples of industrial research linking chemistry, biotechnology, materials science and process technology as enabler for innovation.

Paper No. KS-0008

GOING WITH THE FLOW –
THE USE OF CONTINUOUS PROCESSING FOR ORGANIC SYNTHESIS

C. Oliver Kappe*

Institute of Chemistry, University of Graz, Heinrichstrasse 28, 8010 Graz, Austria,
and Center for Continuous Flow Synthesis and Processing (CC FLOW) at Research Center
Pharmaceutical Engineering GmbH (RCPE), Inffeldgasse 13, 8010 Graz, Austria

Continuous flow processes form the basis of the petrochemical and bulk chemicals industry where strong competition, stringent environmental and safety regulations, and low profit margins drive the need for highly performing, cost effective, safe and atom efficient chemical operations. In contrast to the commodity chemical industry, however, the fine chemical industry primarily relies on its existing infrastructure of multipurpose batch or semi-batch reactors. Fine chemicals, such as drug substances and active pharmaceutical ingredients (APIs), are generally considerably more complex than commodity chemicals and usually require numerous, widely diverse reaction steps for their synthesis. These requirements generally make versatile and reconfigurable multipurpose batch reactors the technology of choice for their preparation. However, the advantages of continuous flow processing are increasingly being appreciated also by the pharmaceutical industry and, thus, a growing number of scientists, from research chemists in academia to process chemists and chemical engineers in pharmaceutical companies, are now starting to employ continuous flow technologies on a more routine basis.[1,2]

In this lecture, contributions from our research group in the field of continuous flow processing will be highlighted. Notably, to make a process greener and more sustainable becomes eminently important when going from lab-scale to production scale. In this presentation, the question to which extent continuous flow processing has an impact as green technology, in particular on the synthesis of active pharmaceutical ingredients (APIs) on manufacturing scale, is discussed. Based on the principles of both green chemistry and green engineering selected continuous processes are evaluated.[1,2]

Emphasis will be given to highly atom efficient and process intensified chemical transformations useful for the synthesis of APIs or key intermediates that are often too hazardous to be executed in a batch reactor. These involve azide, diazomethane and nitration chemistry, selective precious metal-free olefin and nitro group reductions, oxidation reactions involving pure oxygen, and flow photochemistry applications.[1,2]

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Paper No. KS-0009

BIOSOURCED ANALOGS OF BITUMEN FOR ROAD CONSTRUCTION THROUGH HYDROTHERMAL LIQUEFACTION OF MICROALGAE RESIDUES

Bruno Bujoli* (a), Ilef Borghol (a,b), Mariane Audo (a,b), Clémence Queffélec (a), Olivier Lépine (c), Delphine Kucma (d), Chantal Lorentz (e), Dorothée Laurenti (e), Valérie Montouillout (f), Emmanuel Chailleux (b)

(a) Université de Nantes, CNRS, UMR 6230, CEISAM, UFR Sciences et Techniques, 2, rue de la Houssinière, BP 92208, 44322 NANTES Cedex 3 (France); (b) Ifsttar / Centre de Nantes, Département MAST / Laboratoire Matériaux pour les Infrastructures de Transports, Route de Bouaye CS4, 44344 Bouguenais (France); (c) Alpha Biotech, Le frostidié, 44410 Assérac (France); (d) Génie des Procédés – Environnement – Agroalimentaire (GEPEA), Université de Nantes, Ecole des Mines de Nantes, CNRS, UMR6144, 37 bd de l'Université, BP 406 44602 Saint Nazaire (France) (d) IRCELYON, UMR 5256, CNRS-Université de Lyon 1, 2 av. Albert Einstein, 69626 Villeurbanne Cedex (France) (f)CNRS, UPR 3079, CEMHTI, 1D Avenue de la Recherche Scientifique, 45071 Orléans Cedex 02 (France)

Bitumen is a non-renewable petroleum-derived product mostly used in road construction. Anticipation of the replacement of this material is thus important, in particular prospection of efficient routes to produce bitumen substitutes from renewable biomass sources.

We have reported for the first time that hydrothermal liquefaction (HTL) of microalgae byproducts has high potential for the production of road binders. In the 220-300 °C temperature range, a water-insoluble viscous material was indeed obtained in a ca. 50% yield, which consisted of an oily fatty acid-based fraction mixed with organic and inorganic solids (ca. 20 wt%). The chemical composition of this material was found to completely differ from that of petroleum-based bitumen.

However, when operating HTL around 260°C, in the case of *Scenedesmus sp.* residues, a rheological simple material was obtained which compared well with a bitumen reference, showing similar viscoelastic properties [1]. Interestingly, under the same HTL experimental conditions, in the case of cyanobacteria (i.e. *Spirulina* sp.) residues, the water-insoluble fraction exhibited viscoelastic properties similar to elastomer-containing bitumen [2]. This is the first example of a bio-sourced product showing such properties. At temperatures higher than 260°C, fragmentation of species of high molecular weight occurred, resulting in less viscous materials not suitable as bitumen substitutes.

Finally, the suitability of other types of biomass sources for this application will be discussed in the conclusion.

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Paper No. KS-0010

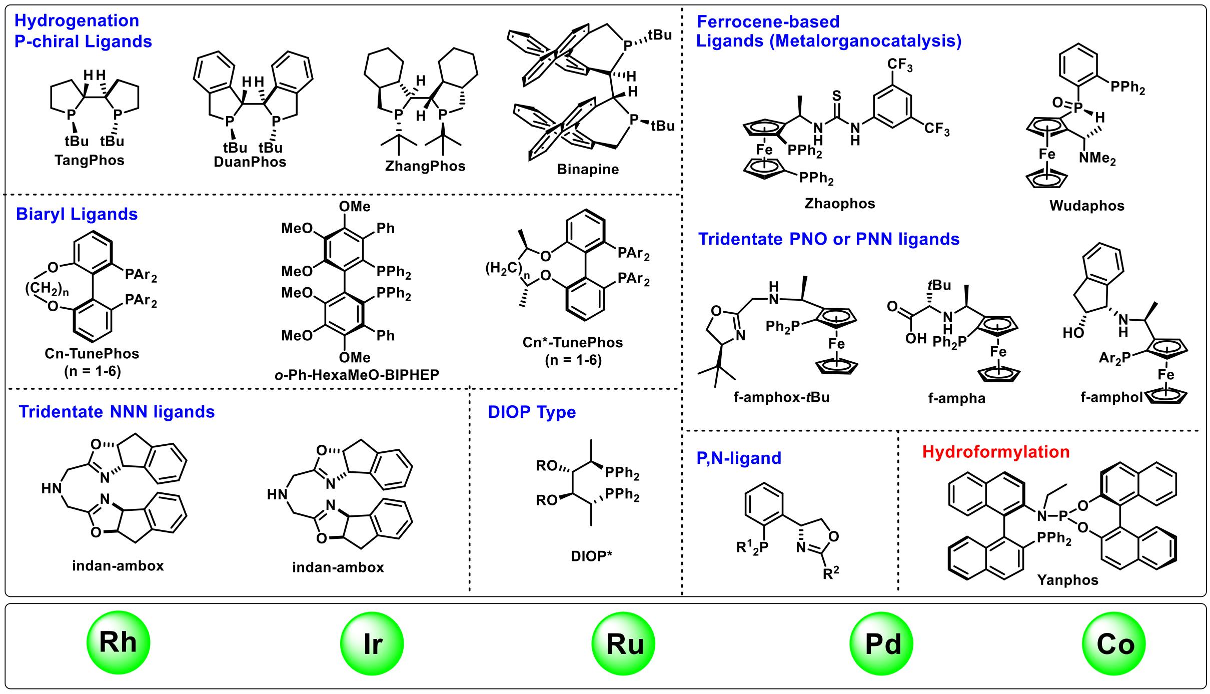
PRACTICAL ASYMMETRIC HYDROGENATION FOR MAKING CHIRAL PHARMECEUTICALS

Xumu Zhang*

Department of Chemistry, Southern University of Science and Technology

Dr. William Knowles, in his 2001 Nobel Lecture, describes his 1960s and 70s work in developing asymmetric hydrogenation catalysts. Now, 45 years later after the first commercial application of asymmetric catalysis, although major advances have been made (e.g.; Professor Noyori's Nobel prize winning work in asymmetric hydrogenation), significant challenges remain. This presentation describes innovation in asymmetric hydrogenation catalysis from both an academic and industrial perspective. Having invented a catalyst that addresses an unmet need in asymmetric hydrogenation, many challenges remain before the catalyst provides an economic return. The knowledge gained and shortcomings recognized during scale-up and commercialization can lead to greatly improved 'next generation' catalysts.

This presentation highlights recent advances in our labs and the commercialization of many chiral phosphine ligands by Chiral Quest, Inc. The broad array of our chiral catalyst toolbox and their numerous applications for a variety of functional group hydrogenations will be reviewed. The emphasis will be on the practical application of asymmetric hydrogenation to make chiral pharmaceutical in ton scale.



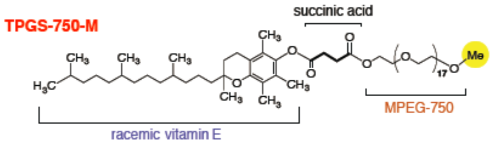
Paper No. KS-0011

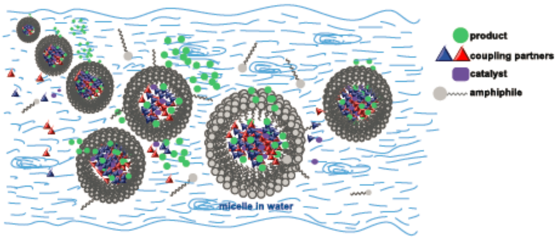
ALTERNATIVE SOLVENTS: FROM A COMPLIANCE-DRIVEN ACTIVITY TO A TRIGGER FOR INNOVATION

Gallou Fabrice*

Chemical & Analytical Development, Novartis Pharma AG, 4056 Basel, Switzerland.
E-mail: fabrice.gallou@novartis.com

During our evaluation of the potential of surfactant technology in collaboration with Professors Lipshutz and Handa,[1,2] we have identified a variety of straightforward and highly advantageous transformations and applied them successfully on-scale.[3] Implementation of the technology typically results into significant benefits across our entire portfolio, not just from an environmental standpoint but also from an economic and productivity perspective. To name a few: Reduction of organic solvent consumption, water use and cycle time, milder reaction conditions, improved yields and selectivities, which all contribute to improved process performance and lower manufacturing costs.[4]





Modern no-ionic surfactants for micellar catalysis in water.

These surfactant mediated reactions can be up-scaled in the already existing multi-purpose facilities of pharmaceutical or chemical organizations, using a catalytic amount of a combination of a non-ionic designer surfactant (e.g. TPGS-750-M) in water, and a well-chosen organic co-solvent instead of traditional and undesirable organic solvents. [5]

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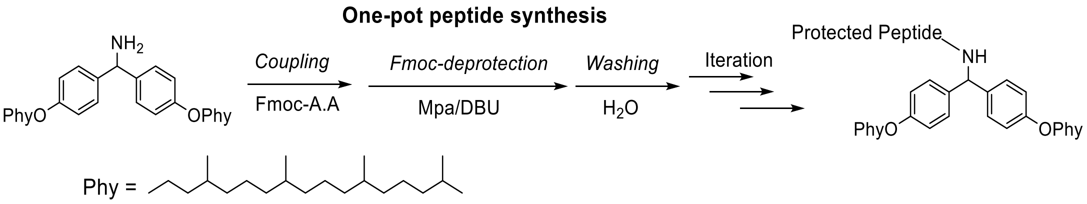
Paper No. KS-0015

AJIPHASE®: HIGHLY EFFICIENT LIQUID-PHASE PEPTIDE AND OLIGONUCLEOTIDE SYNTHETIC METHOD FOR LARGE SCALE MANUFACTURING

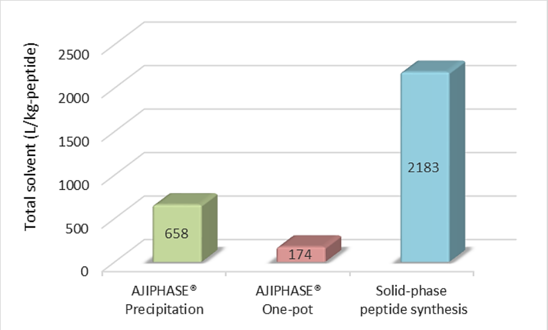
Daisuke Takahashi*, Tatsuji Inomata, Takayoshi Torii, Kunihiro Hirai

Research Institute for Bioscience Products and Fine Chemicals, AJINOMOTO Co., Inc. 1-1
Suzuki-cho Kawasaki, Kanagawa 210-8681, Japan

Recently, the number of peptide and oligonucleotide drugs in development has significantly increased in the world. Most of peptide and oligonucleotide are synthesized by solid-phase approach. However, more practical manufacturing method has been strongly required for the future development and demand. We developed AJIPHASE® as a novel method of liquid phase peptide synthesis (LPPS) by using anchor compounds with long aliphatic chains as a protecting group at the C-terminal. This method retains the advantages of both solid-phase and liquid-phase peptide synthesis. The efficacy of AJIPHASE® has been demonstrated by the successful synthesis of various peptides in high yield and purity even at large scale.



Furthermore we developed an improved AJIPHASE® method using solvent extraction instead of precipitation for isolation. The continuous one-pot synthesis without isolation can be realized in peptide elongation only by solvent extraction using new type of anchor compound having branched chains and using new reagent system. We demonstrated that the synthesis of a 20 mer peptide was successfully achieved by this AJIPHASE® one-pot method. The method can significantly reduce solvent consumption compared with solid-phase synthesis.



Next we have applied the AJIPHASE® technology to the oligonucleotide synthesis. Several liquid phase technologies for the synthesis of oligonucleotides have been reported in the literature, however most of them are suitable only for short nucleotides in small quantities. We have developed a "telescope" elongation system and several reaction manners in the reaction process. The method can synthesize various type oligonucleotides with high purity on a large scale.

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Paper No. KS-0017

DOS ENGINEERING FOR NEW GREEN NANO-MATERIALS

Hiroshi Kitagawa*

Division of Chemistry, Graduate School of Science, Kyoto University
Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, JAPAN
kitagawa@kuchem.kyoto-u.ac.jp

The property of element is correlated directly with its electron configuration. In a solid, the density of states (DOS) at the Fermi level affects the physical and chemical properties. The method of alloying elements has been used to improve the properties of materials for many years. In particular, the solid-solution-type alloy is advantageous because tuning the compositions and/or combinations of the constituent elements can continuously control the properties. However, the majority of bulk alloys are of the phase-separated type under ambient conditions, where constituent elements are immiscible with each other. To overcome the challenge of the bulk-phase metallurgical aspects, we have focused on the nanosize effect and developed methods involving "non-equilibrium synthesis" or "a process of hydrogen absorption/desorption". We propose a new concept of "density-of-states engineering" for the design of materials having the most desirable and suitable properties by means of "inter-element fusion". Novel solid-solution alloys of Pd-Pt, Ag-Rh, and Pd-Ru systems in which the constituent elements are immiscible in the bulk state are presented and discussed [1-3]. Our present work provides a guiding principle for the design of a suitable DOS shape according to the intended physical and/or chemical properties and a method for the development of novel solid-solution alloys [4-6].

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Paper No. KS-0035

HYDROLYSIS OF CELLULOSE BY HETEROGENEOUS CARBON CATALYSTS

Atsushi Fukuoka*

Institute for Catalysis, Hokkaido University, Sapporo 001-0021, Japan

Cellulose is a polymer of glucose linked by β-1,4-glycosidic bonds. Hydrolysis of cellulose gives β-1,4-glucans and glucose (Figure 1), and they are important feedstock to produce chemicals and fuels in biorefinery [1,2]. However, efficient processes for the hydrolysis of cellulose have not yet been established due to the recalcitrance of cellulose. Heterogeneous catalysts are candidates for the hydrolysis of cellulose, as they can be easily removed from liquid hydrolysate after the reaction.

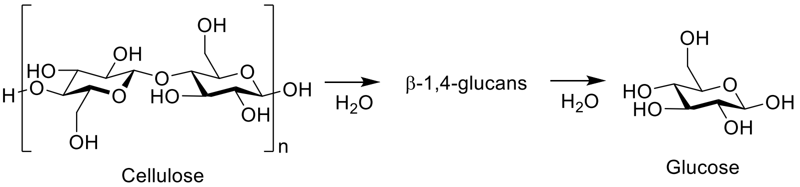

Figure 1. Hydrolysis of cellulose to glucose via oligomers.

We developed weakly acidic carbon catalysts for hydrolysis of cellulose [3-7]. A carbon material bearing weak acid sites hydrolyzed cellulose to soluble sugars after formation of good solid-solid contact by mix-milling. Carbon adsorbs cellulose by CH-π bonding and hydrophobic interactions, and the adsorbed molecules are hydrolyzed by weak acid sites (Figure 2).

Figure 2. Schematic of cellulose hydrolysis on carbon.

A continuous slurry process has been made for hydrolysis of cellulose using the carbon catalyst [8]. Our process utilizes a plug flow slurry reactor and oxygenated carbon catalyst for hydrolysis of cellulose to soluble β-1,4-glucans. Further hydrolysis of β-1,4-glucans to glucose can be achieved by a fixed bed reactor containing Amberlyst-70 or dilute H_3PO_4.

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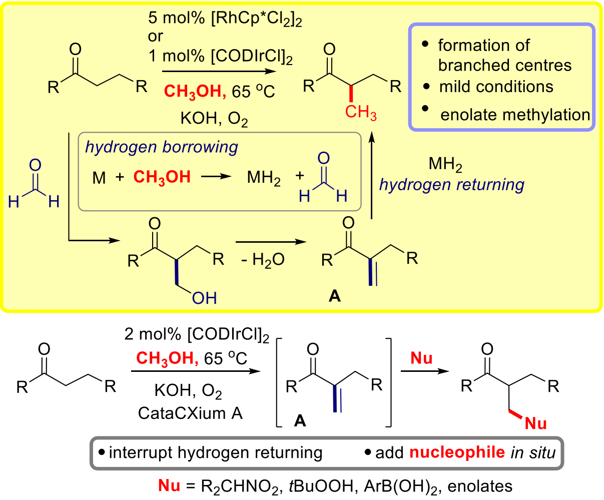
Paper No. KS-0056

METAL CATALYSIS: NEW REACTIONS AND NEW OPPORTUNITIES FOR ORGANIC SYNTHESIS

Timothy J. Donohoe*

Department of Chemistry, University of Oxford, UK

The Donohoe group has recently developed a new catalytic rhodium or iridium-based system capable of engaging methanol in hydrogen borrowing chemistry, and thereby facilitating the methylation of enolates, at relatively low temperatures (65 °C).[1] The use of an oxygen atmosphere is essential in allowing enolate alkylation at these temperatures, and the method is unique at facilitating the production of (branched) doubly alkylated ketones. Moreover, by utilising a bulky phosphine ligand (CataCXium A), the hydrogen returning process can be prevented and the reactive unsaturated ketones (**A**) produced can be intercepted *in-situ* by nucleophiles; oxygen returns the metal hydride to the catalytic cycle.[2] The interrupted hydrogen borrowing sequence prepares a much wider range of functionality than was previously possible.



The application of an iridium-catalyzed hydrogen borrowing process to enable the formation of α-branched ketones with *higher* alcohols was introduced in late 2015. In order to facilitate this reaction, which normally fails because of facile retro-aldol processes, *ortho*-di-substituted phenyl ketones (Ph*) were introduced as crucial structural motifs for C–C bond formation because the twisted nature of the aryl amide significantly reduces steric hindrance around the carbonyl alpha position.[3] Having optimized the catalysis step, the *ortho*-di-substituted phenyl products could be easily manipulated by a retro-Friedel–Crafts acylation reaction to produce many synthetically useful carboxylic acid derivatives and greatly expand the scope of the methodology.[4]

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Paper No. KS-0057

SUSTAINABLE SYNTHESIS OF N-MOTIFS

Jonathan Sperry*
Centre for Green Chemical Science, 23 Symonds Street, University of Auckland, Auckland,
New Zealand

The incorporation of biomass-derived platform chemicals into synthesis processes will have implications for the sustainable production of value-added products relevant to the fine and specialty chemical industries.[1] However, much of the research in this area involves platforms derived from cellulose and lignin, terrestrial biopolymers that comprise only C, H, and O atoms and hence cannot be used to access compounds containing nitrogen (N), an atom widespread throughout society-enhancing chemicals (pharmaceuticals, agrochemicals, dyes, etc.).[1] Ongoing efforts towards the sustainable synthesis of N-heterocycles will be discussed,[2] including our research with the chitin-derived building block 3-acetamido-5-acetylfuran (3A5AF),[3,4] a unique biomass degradation product that retains the biologically fixed nitrogen present in chitin.[5-7] The substitution pattern in 3A5AF enables us to access valuable molecules that are inaccessible or protracted using current methods. Some promising results regarding the solid-state synthesis of N-heterocycles will also be presented.

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Paper No. KS-0066

FERMENTATION OF INDUSTRIAL OFF-GASES FOR FUEL AND CHEMICALS PRODUCTION

Christophe Mihalcea*

LanzaTech Inc., 8045 Lamon Ave, Suite 400, Skokie, IL 60077, USA
Phone office +1 847-324-2555; Phone mobile +1 312-973-9187

Efficient, reliable and cost-effective transportation solutions lie at the heart of the modern global economy. Power can be carbon free and come from solar, wind or hydro sources, but we require carbon for liquid fuels and chemicals, as certain sectors like commercial aviation, are far away from electrification. Today, we face a challenge and responsibility to drastically reduce greenhouse gas emissions in the transport and chemicals supply chain.

Recycling carbon rich gases through gas fermentation has been demonstrated as a novel biological pathway for low carbon fuel and chemical production, while adding value to industrial waste streams. This approach embodies the circular economy as it takes waste streams to make new products with reduced environmental impact.

LanzaTech's disruptive technology uses ancient biology to recycle off-gases from many process and metals industries, including the refining sector, adding value through high volume, sustainable, production of fuels and chemicals. Exceptional feedstock flexibility and metabolic diversity make LanzaTech's gas fermenting process unique.

LanzaTech's process has been demonstrated since 2008, with over 40,000 hours of operation using off-gases from steel mills and over 15,000 hours using syngases from gasified Municipal Solid Waste (MSW). The first commercial scale unit has recently been commissioned in China.

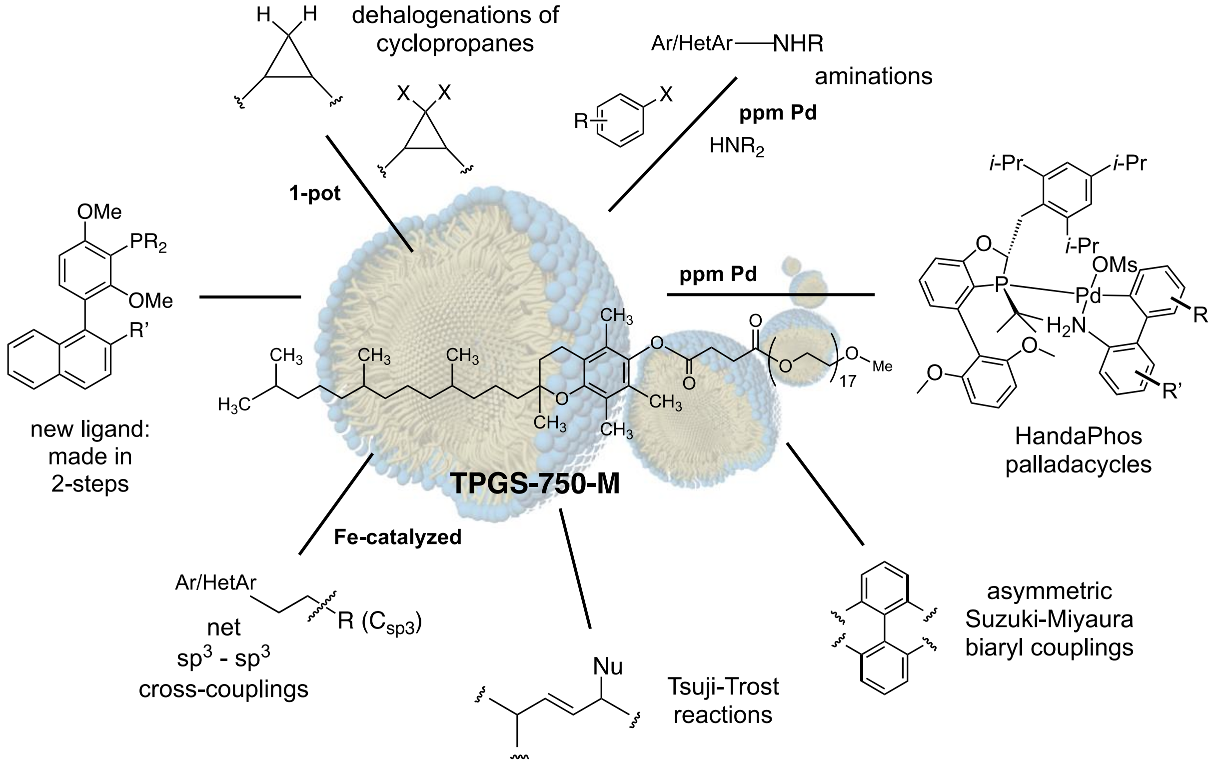
This talk will address the science and chemistry of Gas Fermentation, LanzaTech's demonstration and commercial scale experience and the application of this evolving technology to address the global demand for sustainably produced fuels and chemicals.

Paper No. KS-0067

NEW ADVANCES IN SUSTAINABLE SYNTHETIC CHEMISTRY

Bruce H. Lipshutz*
Department of Chemistry & Biochemistry
University of California, Santa Barbara, CA 93106 USA

New technologies that address several important problems from both the synthetic and environmental perspectives will be presented, as illustrated below. Each is enabled using nanoparticles that serve as the reaction "vessel" in water, derived from a tailor-made surfactant. Reactions take place under mild conditions, typically between rt and 45 °C. For transition metal catalyzed processes, especially those involving precious and endangered metals such as Pd, catalysts that function at the ppm level of the metal have been developed and will be presented.



all reactions in water between rt and 45 °C

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Recent reviews: Lipshutz, B. H.; Ghorai, S.; Cortes-Clerget *Chem. Eur. J.* 2018, *24*, in press (DOI: 10.1002/chem.201705499; *The Hydrophobic Effect Applied to Organic Synthesis: Recent Synthetic Chemistry "in Water"*); Lipshutz, B. H. *J. Org. Chem*. 2017, *82*, 2806 (Perspective: *When Does Organic Chemistry Follow Nature's Lead and Make the Switch?*); Lipshutz, B. H. *Johnson Matthey Technol. Rev.* 2017, *61*, 196 (invited: *The "Nano-to-Nano Effect…"*); Lipshutz, B. H.; Gallou, F.; Handa, S. *ACS Sustainable Chem. Eng.* 2016, *4*, 5838 (invited: *Evolution of Solvents in Organic Chemistry*).

Paper No. KS-0081

TOWARDS A CIRCULAR ECONOMY USING GREEN CHEMISTRY

James H. Clark
Green Chemistry Centre of Excellence, University of York,
James.clark@york.ac.uk
(www.york.ac.uk/chemistry/research/green)

Increasing demand for consumer goods from an increasing world population is placing enormous strain on the resources needed by the worlds manufacturing industries. Traditional mineral-derived resources have often been from non-renewable sources located in relatively accessible regions but these are finite, their exploitation non-sustainable and in some cases they are becoming scarce. At the same time, the wastes generated in manufacturing and in use of the articles of today's society have been allowed to accumulate in rapidly filling landfill sites or disposed of in other environmentally harmful ways leading to serious pollution problems in the atmosphere, land and seas. Waste valorization is becoming more popular but it is mostly small scale and with low efficiency. The most chemically interesting of the large volume wastes is bio-wastes including forestry and agricultural by-products, and industrial wastes including from paper and pulp and food companies. Current bio-waste valorization is largely limited to anaerobic digestion which has a very low conversion efficiency. However, these renewable resources can form the basis of future bio-refineries that can make a very wide array of chemical, material and energy products. To fully exploit the concept and make it widely useful while maintaining environmental advantage, we need to use *Green Chemistry* to ensure that future processes in, and products from bio-refineries are genuinely green and sustainable.

Energy efficient green chemical technologies that can convert a wide variety of waste streams into valuable chemicals include low-temperature microwave processing and benign solvent extraction. These can lead to bio-based platform molecules which in turn can be used to make new green bio-based products including solvents and polymers. The integration of thermo-chemical and bio-chemical technologies will also become increasingly important as we seek to increase the efficiency of biomass conversion and develop efficient chemistry on fermentation broths.

Several projects will be described to help illustrate how we can apply green chemical technologies to the valorisation of different wastes. These projects are usually carried out in consortia often involving industry and on many occasions ranging across more than one country.

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For background reading see:

J.H. Clark, T.J. Farmer, L. Herrero-Davila & J. Sherwood, Circular economy design considerations for research and process development in the chemical sciences. Green Chemistry, 2016, 18, 3914-3934.

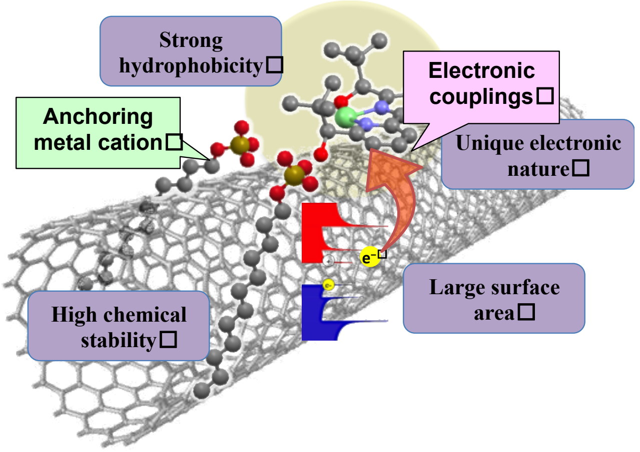
Paper No. KS-0083

DEVELOPMENT OF NOVEL CATALYST SYSTEMS TOWARDS SUSTAINABLE SOCIETY

Shū Kobayashi*

Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku,
Tokyo 113-0033, Japan

Synthetic organic chemistry has contributed a lot to modern society. Towards sustainable society, we are investigating on environment, human health, and energy issues from viewpoints of synthetic organic chemistry. Among them, the development of highly reactive and stereoselective catalyst systems is required not only to improve existing synthetic methods but also to invent epoch-making chemical reactions. Herein, a homogenized combination of nickel-based Lewis acid–surfactant-combined catalysts (LASCs) and single-walled carbon nanotubes (SWCNTs) is shown to exhibit excellent activity in water. The electrochemical behavior of the central metal was modified to address the inherently low Lewis acidity of metal cations. In addition to the enhanced reactivity, stereoselective performance and long-term stability were demonstrated in asymmetric conjugate addition reactions of aldoximes to furnish chiral nitrones in high yields with excellent selectivities. The practical and straightforward application of the designed catalysts in water provides an expedient, environmentally benign, and highly efficient pathway to access optically active compounds.[1]



Another topic is hydrogenation of arenes, which is an important reaction not only for hydrogen storage and transport but also for the synthesis of functional molecules such as pharmaceuticals and biologically active compounds. Here, we describe the development of heterogeneous Rh-Pt bimetallic nanoparticle catalysts for the hydrogenation of arenes with inexpensive polysilane as support. The catalysts could be used in both batch and continuous-flow systems with high performance under mild conditions and showed wide substrate generality. In the continuous-flow system, the product could be obtained by simply passing the substrate and 1 atm H_2 through a column packed with the catalyst. Remarkably, much higher catalytic performance was observed in the flow system than in the batch system, and extremely strong durability under continuous-flow conditions was demonstrated (>50 days continuous run; turnover number $>10^6$). Furthermore, details of the reaction mechanisms and the origin of different kinetics in batch and flow were studied, and the obtained knowledge was applied to completely selective arene hydrogenation of compounds containing two aromatic rings toward the synthesis of an active pharmaceutical ingredient.[2]

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Paper No. KS-0091

ENGINEERING BIOCATALYTIC CASCADE REACTIONS FOR REGIO- AND STEREO-SELECTIVE CHEMICAL SYNTHESIS

Zhi Li

Department of Chemical & Biomolecular Engineering, National University of Singapore,
4 Engineering Drive 4, Singapore 117585

Biocatalysis is an attractive tool for one-pot multi-step synthesis *via* cascade reactions, which could avoid the expensive, yield-reducing, and waste-generating isolation of the intermediates in conventional multi-step synthesis and enable green, selective, and useful synthesis of high-value chemicals from simple substrates. Great progress has been achieved in this field. Nevertheless, it is still necessary to develop new biocatalytic cascade reactions, engineer robust and efficient biocatalysts, and expend the scope of cascade biotransformations for chemical synthesis.

We recently established several new types of non-natural regio- and stereo-selective biocascades, engineered recombinant *Escherichia coli* cells expressing the necessary enzymes as active catalysts for these reactions, and demonstrated the synthetic potential of the developed cascade biotransformations. Some representative examples will be presented in this talk, including asymmetric *trans*-dihydroxylation of alkenes to 1,2-vicinal diols,[1] asymmetric aminohydroxylation of alkenes to 1,2-aminoalchols,[2] asymmetric transformation of alkenes to α-hydroxyacids[2] and α-aminoacids,[2-3] conversion of meso- or racemic epoxides to (*R*)-hydroxyketones,[4-5] transformation of 2-alkylidenecyclopentanones to (*R*)-δ-Lactones or (*R*)-2-alkyl-cyclopentanones,[6-7] selective oxidation of alkenes to acids,[8] anti-Markovnikov hydroamination and hydration of aryl alkenes,[9] and conversion of bio-derived *L*-phenylalanine to some of the above mentioned high-value chiral chemicals.[10]

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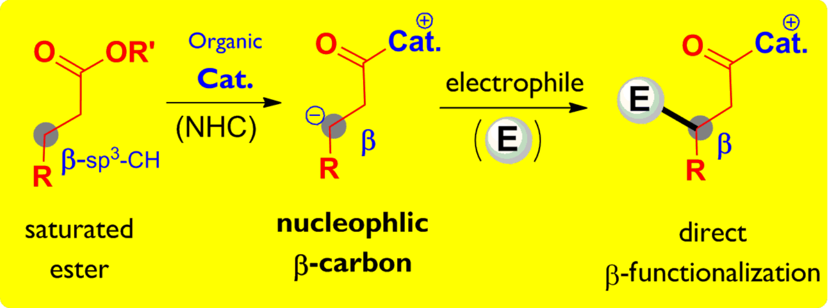
Paper No. KS-0125

CARBENE ORGANIC CATALYSIS: NEW ACTIVATION MODES and RAPID ACCESS to FUNCTIONAL MOLECULES

Yonggui Robin Chi*
Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore
E-mail: robinchi@ntu.edu.sg

The Chi laboratory is committed in state-of-art research that addresses synthetic chemistry challenges of scientific, economic, and social significance. Our essential objective is to develop fundamentally novel (organo) catalytic activation/reaction modes and synthetic strategies for the rapid (short route) synthesis of pharmaceuticals and other functional molecules that include polymer materials. Over the years, we have realized significant advancements in the design, discovery, and development of new basic activation modes enabled by N-heterocyclic carbenes (NHCs) as the key organic catalysts. With the new catalytic activation modes we hope to create new understanding of chemical reactivities and chemistry. Immediate applications of our new catalytic activation modes and synthetic strategies include concise and green processes for bioactive molecules and natural products. We have also taken significant efforts in designing new molecular scaffold for applications in agriculture chemicals, and develop scalable methods for the synthesis and manufacturing of medicinal, agricultural, and other functional molecules.



Examples of our research activities include: (1) Carbene (NHC) organic catalyst-enabled activation of carboxylic esters (including the inert beta-sp3-carbon activation of saturated esters); (2)New reaction controls of aldehydes under (oxidative) carbene catalysis; (3) Cooperative catalysis combining carbene organic catalysts with other catalysts (such as transition metal catalysts, Lewis acid catalysts, and other organic catalysts); (4)Biomimetic single-electron-transfer (SET) radical reactions enabled by carbene organic catalysts; (5) Multi-disciplinary collaborative research penetrating to the conversion of biomass and sustainable raw materials, antimicrobial polymer materials, chemistry/materials for 3D printing, Chinse medicine modifications, and agricultural chemicals (antivirus and antibacterial agents for agriculture use); (6) Research efforts toward scale up and manufacturing.

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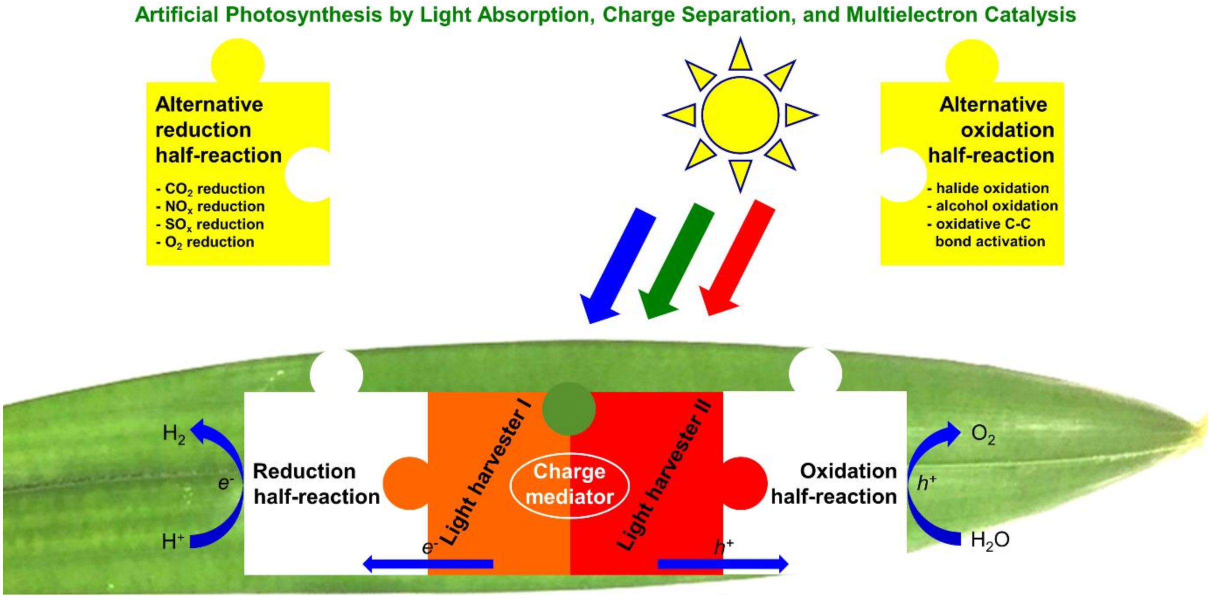
Paper No. IS-0012

ARTIFICIAL PHOTOSYNTHESIS BY HETEROGENEOUS CATALYSIS AND PHOTOREDOX C-C BOND CLEAVAGE

Milos Dokic, Kek Foo Chin, Dwaipayan Ghosh, Xian Liang Ho, Zonghan Hong, Han Sen Soo*

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore
hansen@ntu.edu.sg; http://www.ntu.edu.sg/home/hansen/Webpage/Public/Main.htm

Artificial photosynthesis has been recognized as a sustainable approach to utilize solar energy for chemical reactions and energy storage. Some of the critical functions of artificial photosynthetic systems include light absorption, charge separation, and multi-electron catalysis.[1] In this presentation, I will summarize my team's early contributions to these elementary components. I will describe our efforts in the development of interfacial anchoring groups to create metal oxide nanoparticles for heterogeneous epoxidation catalysis.[2] For the multi-electron reductive half-reaction, my team has recently reported new salicylaldimine nickel complexes bearing ether pendant arms that perform as hydrogen evolution electrocatalysts, even in seawater.[3] Regarding the multi-electron oxidative half-reaction, I will describe my team's discovery of a new selective, photoredox C-C activation reaction, which occurs under ambient, atmospheric conditions using visible light. We have conducted detailed kinetic measurements to identify the fastest catalyst.[4,5] Our efforts to expand the substrate scope will be presented.


Artificial Photosynthesis by Light Absorption, Charge Separation, and Multielectron Catalysis

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Paper No. IS-0014

SUSTAINABLE POLYMER CHEMISTRY BY FREE RADICAL APPROACH TO PRODUCE BIODEGRADABLE AND RESPONSIVE SYSTEMS

Praveen Thoniyot[1]*, Lohitha Rao Chennamaneni[1], Alexander William Jackson[1],
Freda C. H. Lim[2], Alexander M. van Herk[1]

[1]Institute of Chemical and Engineering Sciences, Sciences (ICES), Agency for Science, Technology and Research (A*STAR), 1 Pesek Road, Jurong Island, Singapore 627833
[2]Institue of High Performance Computing, Agency for Science, Technology and Research (A*STAR) 1 Fusionopolis Way, #16-16 Connexis, Singapore 138632

Non-degradable polymers in consumer care applications are expecting tougher regulations in the near future, due to unsustainable source and production methods and well understood negative impacts of these polymers in the environment. Currently, industry is showing very strong interest in degradable analogs of non- degradable polymer additives and particles in many areas of applications. Conventional anionic ring opening and step-growth approaches need demanding conditions to create such degradable polymers and are industrially less feasible. The most industrially feasible approach in terms of simplicity and cost effectiveness is free radical polymerization. However, there are not enough free radical polymerization based approaches for producing degradable and environmentally friendly polymers.[1,2] Hence the developing synthetic approaches to produce complete or partially degradable backbones of free radical polymers is of immense importance since it offers new solutions to the current problems solved by non-degradable polymers. In our approach we adopt the ring opening polymerization of novel and conventional cyclic ketene acetal monomers and co-polymerizations with a variety of common monomers. The presentation will highlight some of the findings of our new project on environmentally friendly free radical route to produce biodegradable and responsive polymers.

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Paper No. IS-0034

HYDRO-PROCESSING OF STRAIGHT VEGETABLE OILS (SVO) TO PRODUCE GREEN-DIESEL

E.L. Dewi*,[1], G. W. Murti[2], SD. Sumbogo M[2], B. Dwiratna[2]

[1]Deputy Chairperson for Technology of Information, Energy and Material (TIEM)
Agency for the Assessment and Application of Technology (BPPT)
[2]Center for Energy Resources and Petrochemical Industry Development Technology (PTSEIK)
Agency for the Assessment and Application of Technology (BPPT)
*Email: eniya.listiani@bppt.go.id

The Indonesia's energy consumption is still supplied mainly from fossil resources. However, some regulations have been issued as a form of government commitment for reducing the impact of global warming and ensuring of national energy supply security. In addition, MEMR Regulation 12/2005 regarding biodiesel mandatory has targeted the utilization of biodiesel (B100) maximum 30% in 2025. Recently, 20% biodiesel in petro-diesel (B-20) has been implemented. However, there are still many obstacles in B-20 implementation such as too viscous, reactive to rubber material, requiring modification for engine and storage, low heating value. Therefore, this 10% gap will be fulfilled by other renewable diesel or green-diesel from hydro-processing reactions. Palm, nyamplung, and kepuh oils can be used as alternative raw materials for green-diesel production since the majority of fatty acids are C-18. Palm kernel oil produced more C-11 for bio-avtur production due to more lauric acids in the structure. Palm oil seems to be the best alternative feedstock since Indonesia has huge surplus palm oil production about 33 million kilo litres per annum.

Key words: hydro-processing, green-diesel, SVOs

Paper No. IS-0044

MEMBRANE GAS SEPARATION TECHNOLOGIES FOR INNOVATION OF CHEMICALS PRODUCTION

Masahiko Matsukata[1,2]*, Motomu Sakai[3]

1 Department of Applied Chemistry, Waseda University, Tokyo, Japan
2 Research Institute of Advanced Science and Engineering, Waseda University
3 Research Organization for Nano & Life Innovation, Waseda University
mmatsu@waseda.jp

Chemical industries consumed a large amount of energy in their production processes, resulted in large CO_2 emission. In particular, distillation separation requires 40% of total energy consumption. Basic chemicals, such as ethylene, propylene, butanes and butenes, and aromatic hydrocarbons, are generally produced by cracking of naphtha and ethane and a series of substantial number of distillation towers.

Once we replace and/or hybridize with distillation columns with membrane separation processes, energy demands in chemical industries would greatly be reduced [1]. Thus, the development of membrane separating gas mixtures of hydrocarbons produced in ethylene center is essentially important to mitigate CO_2 emission problem. Since process should be operated at relatively higher pressure up to 2 MPa, membrane materials have to possess pressure resistance. In some applications like aromatics separation, organic solvent resistance and temperature resistance are also important. Therefore, promising candidates of membrane materials would be microporous inorganic materials such as zeolite, carbon, silica and MOFs.

Zeolites are crystalline inorganic materials having ordered microporous channels in the range of 0.3-0.7 nm in their structure. We have developed various types of zeolite membrane for these 25 years and recently found that a sort of zeolite membrane containing Ag^+ shows excellent separation properties for alkane/alkene mixtures.

For instance, we found that the micropore of Ag^+-loaded FAU-type zeolite membrane with about 0.7 nm of pore mouth diameter was preferentially occupied with propylene against propane, since Ag^+ located on the ion exchange site strongly adsorbs π electron in alkene. Thus, this type of membrane shows a high selectivity to propylene from propane/propylene mixtures.

Engineering calculation based on the permeation properties of propane and propylene suggested that membrane separation propane/propane gas mixture produced from ethylene center would contribute to as large as 60% of energy saving. Similarly, a variety of basic chemicals production are possible to decrease energy demand by introducing membrane separation technology.

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Paper No. IS-0054

EMULSION-BASED CRYSTALLIZATION PROCESSES FOR NOVEL API-EXCIPIENT MICROPARTICLE FORMULATIONS

Eunice W. Q. Yeap, Denise Z. L. Ng and Saif A. Khan*

Department of Chemical and Biomolecular Engineering, National University of Singapore
saifkhan@nus.edu.sg

In the pharmaceutical industry, active pharmaceutical ingredients ('API's) or drug *substances* undergo a series of crucial 'secondary' manufacturing operations, such as crystallization and formulation with additives and excipients, to obtain drug *products* of varying types, such as orally ingestible tablets or injectables. Traditionally, drug substances crystallized in batch vessels allow poor and coarse control over crucial crystal attributes, which tremendously impacts the number of subsequent processing steps required to arrive at the final drug product. We have recently developed a microfluidics-based technique which allows for crystallization and formulation of drug substances to be carried out in a single processing step, leading to monodisperse spherical granules with unprecedented control over crystal attributes such as shape, size and polymorphism [1-4]. This technique couples the usage of microfluidics for emulsion generation and thin film evaporative crystallization where, by tuning the various process parameters, we are able to crystallize and formulate a wide range of hydrophilic and hydrophobic model and commercial drugs into monodisperse spherical microparticles with tunable properties. These particles hence allow realization of the idea of *drug product intermediates* that bridge the traditional gap between primary and secondary drug manufacturing processes. This presentation will focus on our recent progress towards single-step fabrication of pharmaceutical drug-excipient microparticles with tunable structures from emulsions. Firstly, the versatility of emulsion-based processing for formulating particles with tunable structures will be showcased with two different drug-excipient systems. An interplay of phase separation, drug crystallisation and polymer vitrification in drug-polymer droplets during evaporative crystallisation leads to a plethora of microparticle structures which exhibit different drug release profiles [5]. Also, the co-formulation of drug-colloidal silica within water-in-oil droplets subject to evaporative crystallisation yields tunable crystal sizes at the nanoscale. These new formulations and processes enabled by microfluidic emulsion-based crystallisation provide valuable insights into drug(-composite) microparticle design and manufacturing, and challenge the conventions of secondary pharmaceutical manufacturing.

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Paper No. IS-0061

ELECTROCHEMISTRY ENABLED RADICAL REACTIONS

Hai-Chao Xu*

Department of Chemistry, Xiamen University, China

Organic electrochemistry, which employs electrons as the traceless oxidizing or reducing reagents, is an innately sustainable method for organic synthesis.[1] Because of its reagent-free feature and tunability, electrochemistry is useful for the generation of radical and radical ion intermediates in a controllable fashion through clean single electron transfer (SET). In the presentation, our recent progress on the electrooxidative generation of radical and radical ion intermediates and their synthetic applications in oxidative cross-coupling reactions will be discussed (Scheme 1).[2] In these electrochemical reactions, the electrons collected at the anode from the substrates move to the cathode to combine with protons to produced hydrogen gas, which obviates the need for oxidizing reagents and proton acceptors.

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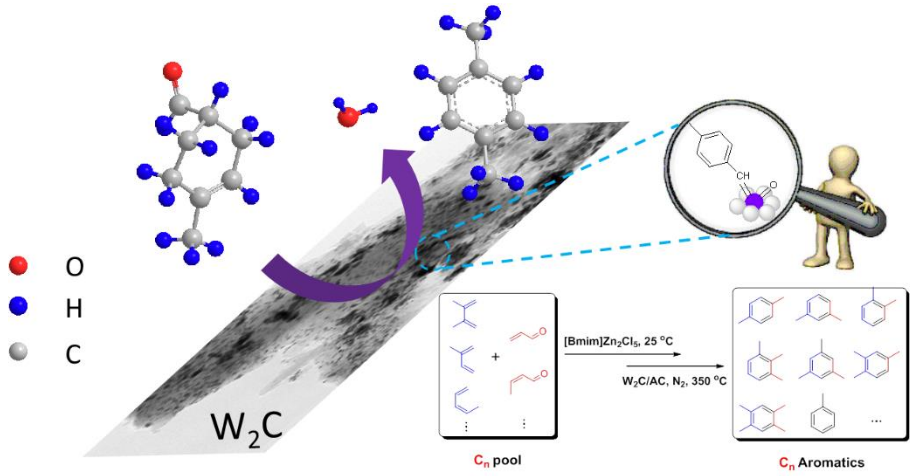
Paper No. IS-0064

SELECTIVE PRODUCTION OF RENEWABLE AROMATICS VIA TUNGSTEN CARBIDE CATALYZED ATOMECONOMIC CASCADE REACTIONS

Changzhi Li*, Aiqin Wang, Tao Zhang

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. Email: licz@dicp.ac.cn

The challenge of lowering our society's dependence on oil is upon us. Major efforts have been devoted to devising bio-based routes to those chemicals currently being made from fossil resources. As one of the key bulk chemicals in industry, para-xylene (PX) is the precursor to terephthalic acid and dimethyl terephthalate that used in making plastics and a wide array of industrial products. Currently PX is produced from petroleum chemicals at over 40 million tons per year. Therefore, developing a renewable route to PX is highly desirable for both economic and environmental concerns. In this talk, an atom-economic and renewable route is devised for continuous production of para-xylene (PX) from bio-based 4-methyl-3-cyclohexene-1-carbonylaldehyde (4-MCHCA) by using tungsten carbide (W_2C) as the catalyst. Results suggested that 4-MCHCA underwent a novel dehydroaromatization-hydrodeoxygenation cascade pathway via intramolecular hydrogen transfer without involving any extra hydrogen species, and that hydrodeoxygenation occurred through direct dissociation of the C=O bond on W_2C surface. Notably, the new process was readily applicable to synthesize various (multi)methylated benzenes from bio-based building blocks, thus providing a potentially petroleum-independent solution to those valuable aromatics.



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Paper No. IS-0065

POTENTIAL AND CHALLENGES OF WASTE VOLARISATION BY SUPERCRITICAL FLUID PROCESSING

Lai Yeng Lee[a,b]*, Soon Hong Soh[b]

[a]Newcastle University in Singapore; SIT Building @ NP, #06-01 537 Clementi Road,
Singapore 599493
[b]Newcastle Research & Innovation Institute (NewRIIS); 80 Jurong East Street 21, #05-04
Devan Nair Institute for Employment and Employability, Singapore 609607
*Corresponding author: laiyeng.lee@ncl.ac.uk; Tel: +65 6908 6016

Several supercritical fluid processes have been developed for food and pharmaceutical ingredients as a clean alternative. This include extraction, purification, micronisation, micro-encapsulation, drying, sterilization and etc. Supercritical carbon dioxide is a widely used in food and pharmaceutical processes due to its clean and versatile nature. Supercritical carbon dioxide can be used to treat bioactive compounds and biopolymers in various forms such as a solvent, an anti-solvent, as well as a foaming agent [1], to produce functional ingredients for the food and pharmaceutical industry.

In recent years, there has been increasing attention in developing processes to extract useful material from waste streams such as food-processing by-products [2]. This include spent grain (such as spent coffee or spent soy bean, *okara*), fruit and vegetable peels and by-products from fishery industry. Useful ingredients that can be recovered using supercritical fluid extraction (SFE) include caffeine, isoflavones, lycopene, polyunsaturated fatty acids (PUFAs), and etc. Preservation of spent grain by drying using supercritical carbon dioxide from beverage production industry using malt and soybean has also been demonstrated in our recent studies [3].

This presentation will introduce and discuss several applications of supercritical fluid techniques that can be applied for waste volarisation. The potential and challenges faced when using supercritical fluid processing for scale-up applications will be evaluated and discussed.

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Paper No. IS-0068

GREEN POLYMERS – PHOTO-DEGRADABLE POLYMERS TO LIGNIN BASED POLYMERS

Kei Saito*

School of Chemistry, Monash University, Clayton, VIC 3800, Australia
e-mail: kei.saito@monash.edu

Reversible polymers represent a relatively new class of materials that possess bonds capable of reversibly connecting and disconnecting monomers in response to stimuli such as heat or light. These reversible bonds can be used to construct a recyclable polymer via material polymerization and depolymerisation, on demand. Photo-chemical reactions, on the other hand, are considered to be greener synthetic pathways because photons do not leave residues, they can be conducted at ambient temperature, and often in the solid-state. Using the green chemical principles, our reversible-polymer designs centre on a biologically-inspired mechanism. Thymine, one of the nucleic acid bases of DNA, has the propensity to reversibly photo-dimerize in the solid-state. Our research exploits this reversible dimerisation to develop novel reversible polymers using di-thymine monomers. The design and synthesis of various di-thymine monomers, determination of monomer crystal structures, and characterization of the photoproducts using NMR, UV-vis, GPC, and other polymer characterisation techniques will be discussed in the presentation.

Catalytic "chemical" depolymerisation of lignin will also be discussed. A new lignin chemical depolymerisation was developed using redistribution mechanism with phenols and copper catalysts under mild condition in water. The advantage of the technology is not just producing oligomers as a source of aromatics but also producing monomers for thermoprocessable lignin based polymers.

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Paper No. IS-0069

GREEN FLUORINATION TECHNOLOGY: ENGINEERING OF THE FLUORINASE AND A COUPLED TRANSHALOGENATION SYSTEM

Huihua Sun[1], Wan Lin Yeo[1], Xinying Chew[1], Derek John Smith[2], Kok Ping Chan[1], Bo Xue[3], Robert Robinson[3], Edward G. Robins[4], Huimin Zhao[1, 5], Yee Hwee Lim[1],and Ee Lui Ang[1]*

[1] Institute of Chemical and Engineering Sciences, Agency for Science, Technology and Research (A*STAR), Singapore
[2] Biotransformation Innovation Platform, A*STAR, Singapore
[3] Institute of Molecular and Cell Biology, A*STAR, Singapore
[4] Singapore Bioimaging Consortium, A*STAR, Singapore
[5] Departments of Chemical and Biomolecular Engineering, Chemistry, Biochemistry, and Bioengineering, Carl R. Woese Institute for Genomic Biology,
University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

Fluorinases offer an environmentally friendly alternative for selective fluorination under mild conditions. However, their diversity is limited in nature and their high specificity for the S-adenosyl-L-methionine (SAM) substrate has restricted their applications as biocatalysts. Herein, I will present our efforts at engineering the enzyme to expand its substrate range and improve its activity on a non-native substrate, 5′-chloro-5′-deoxyadenosine (5′-ClDA), to produce 5′-fluoro-5′-deoxyadenosine (5′-FDA). The molecular determinants of fluorinase specificity were probed using 5′-chloro-5′-deoxyadenosine (5′-ClDA) analogs as substrates and active site mutants. Modifications at key residues were found to be beneficial towards these modified substrates, including 5′-chloro-5′-deoxy-2-ethynyladenosine, ClDEA (>10-fold activity improvement), and conferred novel activity towards substrates not readily accepted by the wild-type fluorinase. We also discovered two new S-adenosyl-L-methionine (SAM)-dependent chlorinases, ClA1 and ClA2, from soil bacteria by genome mining. These chlorinases are several orders of magnitude more efficient in SAM synthesis from 5′-ClDA than a fluorinase. A coupled chlorinase-fluorinase system was developed for highly improved trans-halogenation of 5′-ClDA to 5′-FDA. The chlorinase also demonstrated the tolerance to the modification at the C-2 position of the adenosine substrate and acted coorperatively with the fluorinase to accelerate the trans-halogenation of ClDEA to 2-ethynyl-FDA (FDEA). The improved enzymes and coupled-enzyme system developed offer the prospect of developing rapid radiolabelling protocols under mild and aqueous conditions.

Paper No. IS-0071

NEW NONTOXIC PRESERVATIVE FOR NATURAL RUBBER LATEX AND THE PROPERTIES OF THE LATEX DIPPED FILMS

C.C. Ho[1*], Rani Bushra[2,3] and J. T. Sakdapipanich[2,3]*
[1]Faculty of Science, Engineering and Technology, University of Tunku Abdul Rahman, Malaysia
[2]Department of Chemistry and Center of Excellence for Innovation in Chemistry,
Faculty of Science, Mahidol University, Bangkok 10400, Thailand
[3]Institute of Molecular Biosciences, Mahidol University, Nakorn Pathom 73170, Thailand
Email: cchoho2001@yahoo.com (C.C. Ho)
E-mail address: jitladda.sak@mahidol.ac.th (J. T. Sakdapipanich)
Fax: +66-2889-3116. Telephone no: +66(0)28893116

Commercial natural rubber (NR) latex is preserved with ammonia alone (high ammonia latex, HA) or low ammonia with a tetramethyl disulfide (TMTD) – zinc oxide system (LA-TZ latex). Ammonia is pungent, corrosive and the vapor causes irritation to the eyes whereas TMTD is a known carcinogen. A benign or less obnoxious substitute would be most welcomed by the latex dipped goods industry for products such as gloves, balloons and condoms.

1,2-Benzisothiazolin-3-one or BIT is a known biocide which has been recognized by the Environmental Protection Agency, USA in not posing serious health hazards. However, its use in preserving NR latex has not been widely reported previously. This work presents a systematic study on the suitability of BIT as an alternative to TMTD in inhibiting bacterial growth as well as stabilizing NR latex in the presence of low concentration of ammonia.

The inhibitory behavior of BIT was monitored with respect to volatile fatty acid number and bacteria counts. The stability of NR latex in the presence of 0.025 % BIT, 0.075 % ammonium laurate and 0.3 % ammonia was evaluated in terms of mechanical stability time, particle size and zeta potential. The morphology of the dipped latex film was visualized using Atomic Force Microscopy (AFM) and scanning electron microscope (SEM).

It was found that NR latex concentrate preserved with the above system was colloidally stable, without undergoing any putrefaction when stored up to 6 months. The tensile properties of vulcanized latex film dipped using latex preserved with the above system are comparable to those obtained from normal commercial NR latex concentrate. It shows BIT is an effective biocides and the above preservative system can preserve and stabilize NR latex concentrate.

Keywords: Concentrated Natural rubber latex; Preservatives; Gloves; Colloidal stability; bactericide

Paper No. IS-0084

WATER SUSTAINABILITY BY DESIGNING POLYMER MEMBRANES FOR WATER REUSE, SEAWATER DESALINATION AND OSMOTIC POWER GENERATION

Prof. (Neal) Tai-Shung Chung

Department of Chemical and Biomolecular Engineering, National University of Singapore,

Clean water, clean energy, global warming and affordable healthcare are four major concerns globally resulting from clean water shortages, high fluctuations of oil prices, climate changes and high costs of healthcare. Clean water and public health are also highly related, while clean energy is essential for sustainable prosperity.

Among many potential solutions, advances in membrane technology are one of the most direct, effective and feasible approaches to solve these sophisticated issues. Membrane technology is a fully integrated science and engineering which consists of materials science and engineering, chemistry and chemical engineering, separation and purification phenomena, environmental science and sustainability, statistical mechanics-based molecular simulation, process and product design.

In this presentation, we will introduce our efforts on membrane development for water reuse, seawater desalination and osmotic power generation. In the beginning, we will introduce the basic science of hollow fiber fabrication, then talk about the ultrafiltration membrane development as a pre-treatment for seawater RO. After that, focuses will be shifted to nano-filtration, forward osmosis and osmotic power generation. Various material and fabrication strategies to enhance membrane performance will be discussed.

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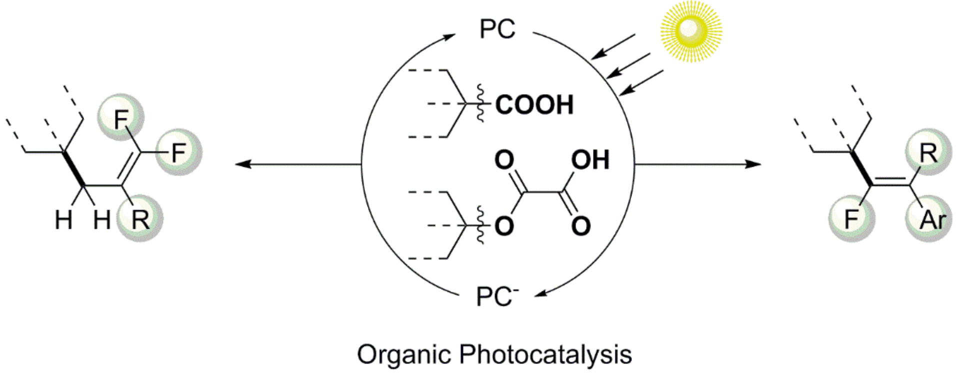
Paper No. IS-0112

ORGANIC PHTOREDOX CATALYTIC DECARBOXYLATIVE CROSS-COUPLING OF ALIPHATIC CARBOXYLIC ACIDS WITH CARBON NUCLEAPHILES

Guanghui An,* Hui Yang, Haitao Tian, Guangming Li*

Key Laboratory of Functional Inorganic Material Chemistry (MOE), School of Chemistry and
Materials Science, Heilongjiang University, No. 74, Xuefu Road, Nangang District, Harbin
150080 (P.R. China), E-mail: chemagh@163.com; gmli@hlju.edu.cn
College of Materials Science and Chemical Engineering, Harbin Engineering University,
Harbin, 150001;

Since seminal publications by Lei,[1] Nishibayashi[2] and MacMillan,[3] the decarboxylative reactions *via* photoredox catalysis[4] has become a commanding method to generate alkyl radicals. In contrary to carboxylic acids containing a heteroatom at the *α*-position, generation of alkyl radicals for coupling reactions directly from unactivated alkyl carboxylic acids or oxylic mono esters normally leads to unsatisfactory decarboxylation (Scheme 1, middle). This might be attributed to their higher oxidation potentials and the transient nature of generated acyl or alkyl radicals which are unfavorable for the radical recombination process. External oxidants with high energy irradiation (LED instead of CFL) are normally required, leading to the limited functionality compability and problematic application in late-stage functional group of complicated molecules.[5] An alternative strategy involving presynthesized redox-active ester has been developed, allowing access to the coupling reactions of secondary and tertiary acids.[5] However, this requires additional synthetic steps with combination of reductants and generates waste products. Additionally, all these processes normally involved utilization of expensive Ir catalysts. To address these issues, we developed a series of organocatalytic redox-neutral direct decarboxylation approaches and applied them to the fluorine containing compound synthesis.



Scheme 1. Photoredox decarboxylation enabled by organocatalysts.

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Paper No. IS-0113

ATOM EQUIVALENTS BASED METRICS TO BRIDGE GREEN CHEMISTRY AND SUSTAINABILITY

István T. Horváth*

Department of Chemistry, City University of Hong Kong

Atom economy or efficiency [1,2] and the environmental factor [3] have been key metrics of green chemistry [4], which can provide mass balances of reactions and processes at the molecular level. Contrarily, sustainability was poorly defined [5], as the key requisite to accurately predict the needs of future generations has been impossible to meet. Consequently, sustainability was replaced with suitability by some stake holders, as they had vested or conflicts of interests to label suitable developments erroneously sustainable, e. g. to make profits for businesses, get funding for NGOs, or to be elected/reelected as politicians and political organizations. The UN's 17 sustainable development goals and 169 targets [6] may serve as a "roadmap to happiness", but not as a metrics to set deliverables and achieve accountability. In order to avoid vested or conflict of interests, a simple definition of sustainability was suggested [7]: *resources, including energy, should be used at a rate at which they can be replaced, and the generation of waste cannot be faster than the rate of their remediation*. The *Ethanol Equivalent* (EE) [7] was also introduced to calculate the *sustainability values of resource replacement* ($\mathbf{SV_{rep}}$) and the *sustainability values of fate of waste* ($\mathbf{SV_{waste}}$) [8], which were combined to establish the *sustainability indicator* ($\mathbf{SUS_{ind}}$) for carbon-based chemicals [8] and renewable energy [9].

$$\mathbf{SV_{rep}} = \frac{\dfrac{\dfrac{\mathbf{ERoE}}{\mathbf{1+ERoE}} \cdot \dfrac{\mathbf{ERoE}}{\mathbf{2.3}} \cdot \mathbf{EE_{available\ resource}} + \mathbf{EE_{secondary\ resource}}}{\mathbf{t_{replacement}}}}{\dfrac{\mathbf{EE_{necessary\ resouce}}}{\mathbf{t_{consumption}}}}$$

$$\mathbf{SV_{waste}} = \frac{\dfrac{\mathbf{EE_{treated\ waste}} + \mathbf{EE_{untreated\ waste}}}{\mathbf{t_{waste\ treatment}} + \mathbf{t_{waste\ natural\ decomposition}}}}{\dfrac{\mathbf{EE_{generated\ waste}}}{\mathbf{t_{waste\ generation}}}}$$

$$\boxed{\mathbf{SUS_{ind}} = \frac{\mathbf{SV_{rep}} \cdot \mathbf{SV_{waste}}}{\mathbf{SV_{rep}} + \mathbf{SV_{waste}}}}$$

In order to expand the applicability of the *sustainability indicator* to all elements of the periodic table, the $\mathbf{SV_{rep}}$ and $\mathbf{SV_{waste}}$ were modified with the corresponding *Atom Equivalent* (AE) for each constituent element of a chemical or a material. A new term addressing the sustainability of the associated energy requirements for $\mathbf{SV_{rep}}$ and $\mathbf{SV_{waste}}$ was also included.

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Paper No. IS-0116

SYNTHESIS OF UNSYMMETRICALLY SUBSTITUTED *P*-TER-PHENYLS AND SUBSTITUTED 1,3-*BIS* (2,5 DIHYDRO-*1H* PYRROLES) BY BATCH, FLOW AND SPINNING DISC REACTOR METHODS: COMPARATIVE STUDIES.

Shahid A. Kazi, Eva M Campi, Peter Clark, W. Roy Jackson and Milton T.W. Hearn
Centre for Green Chemistry,
School of Chemistry,
Monash University, Clayton, Australia, 3800

Terphenyl compounds are widely found in Nature, predominantly as *p*-terphenyl derivatives with a wide range of significant biological activities with therapeutic potential, including potent immune-suppressant, neuro-protective, antithrombotic, anticoagulant, specific 5-lipoxygenase inhibitory, and cytotoxic activities. In addition, the unique photo-physical properties of terphenyl compounds have been exploited in the design of organic electroluminescent (OEL) devices, liquid-crystalline materials, charge transporting agents, charge generating agent, and photo-responsive polymers. Similarly, substituted 1,3-*bis* (2,5 dihydro-*1H* pyrroles) represent useful building blocks in the development of important medicinal hetero-aromatics, natural products and other biologically active compounds, whilst these precursors have also found wide application in the development of novel polymers due to their novel electrical and electronic properties.

This presentation documents the different attributes of batch and flow chemical synthetic procedures for the "one-pot" preparation of unsymmetrically substituted *p*-ter-phenyls utilising sequential chemo-selective Suzuki-Miyaura cross-coupling of substituted 2,5-di-bromo-benzenes with a variety of arylboronic acids and a ligand-less palladium catalyst. Similarly, metathesis reactions at the laboratory scale have been developed with porous silica particles impregnated with the Grubbs (I) and Hoveyda–Grubbs (II) catalysts as a surface coating in a low cost spinning disk system. The technology provides an efficient and relatively inexpensive alternative to batch procedures for the preparation of substituted 1,3-*bis* (2,5 dihydro-*1H* pyrroles). Collectively, these comparative studies have provided new opportunities to efficiently conduct reactions at lower temperatures, minimizing the need for high energy processes, with reduced solvent use and the potential to operationalise these reactions essentially as continuous production modes.

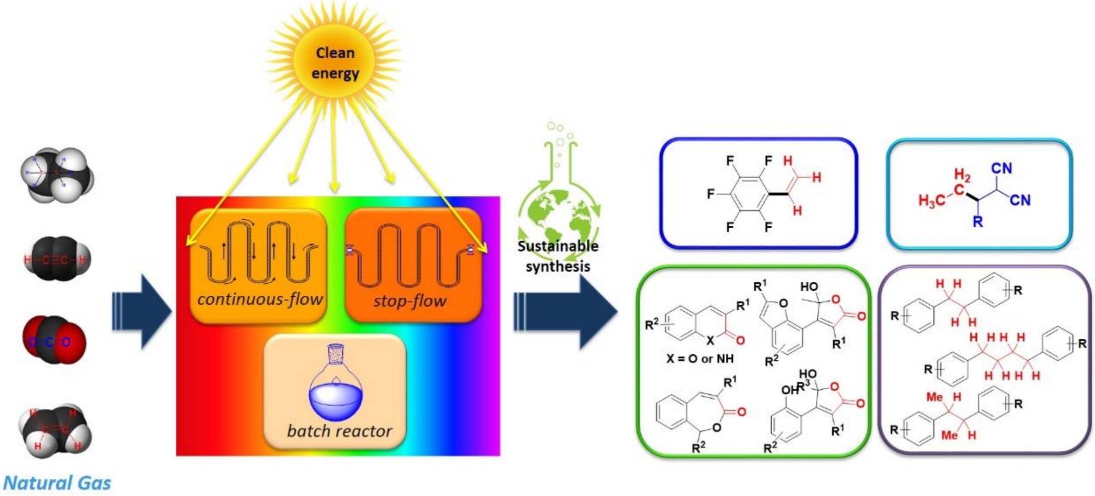
These studies were supported by the Australian Research Council.

Paper No. IS-0117

VISIBLE-LIGHT-DRIVEN FINE CHEMICAL SYNTHESIS USING NATURAL GASES AS FEEDSTOCKS IN BATCH AND FLOW REACTORS

Jie Wu,* Hongping Deng, Jing Hou, Jiesheng Li, and Fei Xue
Department of Chemistry, National University of Singapore, Singapore

The use of photons as "traceless and green reagents" renders photochemical processes green and sustainable. Light activation of molecules provides access to reaction pathways which are otherwise impossible to reach with classical thermochemical activation. In conventional batch reactors, scalability of photo-reactions is hampered due to the attenuation effect of photon transport, which prevents the use of a dimension-enlarging strategy for scale-up. The use of continuous-flow micro-tubing reactors for photochemical applications allows these issues to be overcome, by ensuring uniform irradiation of the entire reaction mixture and scaling-up of photochemical reactions via scaling-out or numbering-up strategies. In this context, my research group at NUS has invented a "stop-flow" micro-tubing (SFMT) reactor platform, which represents an ideal laboratory bench model for reaction discover applications.



The conventional stainless-steel high-pressure reactors are incompatible with photo-mediated reactions, and the development of new reactions using gaseous reagents under photo-mediated conditions is limited, usually requiring a complicated special apparatus. We thus envision that the SFMT system provides an effective tool for developing visible-light promoted gas/liquid reactions and would be more suitable than continuous-flow technique for screening as visible-light promoted photoredox transformations are slow in many cases. Assisted by SFMT reactors, a photocatalytic vinylation of fluorinated aryl bromides using acetylene gas was developed, which represents the first example of the vinylation of aryl halogen compounds utilizing acetylene gas. Following this research line, we developed synthetic methodologies to convert CO_2, ethylene, and ethane into fine chemicals. Gram-scale synthesis can be easily achieved by the SFMT reactors, and the reaction can be further scale-up by using continuous-flow technology.

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Paper No. IS-0129

CONTINUOUS MANUFACTURING - FROM R&D TO PRODUCTION

Steven Tan
(GlaxoSmithKline, boon-hong.b.tan@gsk.com)

Batch Processes have and will continue to fulfill an important role in the manufacture of Active Drug Substance; they allow multiple recipes to be executed in the same core equipment. However, the compromise is, batch fails to deliver the precision, speed of manufacture and intensification of a flow process.

At GSK, we are developing flow processes for organometallic chemistry. Using process understanding generated using batch methods, and a combination of insilico simulation and physical demonstration we can redefine conventional operating parameters for this type of chemistry and industrialize processes which are not feasible in batch due to risk of scale.

We believe this will allow us to deliver more medicines of value to patients, both in affordability and function.

Paper No. OR-0033

MICROBIAL STRAIN DEVELOPMENT FOR SUSTAINABLE PRODUCTION OF FUEL AND CHEMICALS FROM LIGNOCELLULOSIC BIOMASS

Geng Anli*

School of Life Sciences and Chemical Technology, Ngee Ann Polytechnic, Singapore 599489
Email: Geng_Anli@np.edu.sg

Lignocellulosic biomass such as forestry and agricultural wastes is the most abundant resource of polymer for fermentable sugars. It is therefore a sustainable resource for fuel and chemical production.

In the first part of this presentation, the isolation and strain improvement of wild-type filamentous fungal strains for cellulase production is reported. Both random mutagenesis and genetic engineering approaches were applied for enhanced enzyme production with comparable enzyme titer to that by commercial cellulase-producing strains. The produced cellulolytic enzyme cocktail was able to effectively hydrolyze lignoellulosic biomass, such as oil palm empty fruit bunch (OPEFB) to fermentable sugars, such as glucose and xylose with comparable performance to commercial enzymes.

In second part of this presentation, the metabolic engineering of the baker's yeast, *Saccharomyces cerevisiae*, for the utilization and conversion of biomass sugars, glucose and xylose, to fuel and chemicals is reported. Xylose-utilizing yeast was developed through the overexpression of xylose isomerase from a mammal gut bacterium. Further metabolic engineering of this yeast followed by adaptive evolutionary engineering made this yeast able to ferment xylose to ethanol. Subsequent engineering of this yeast strain made it resistant to biomass inhibitors and enable it to be a cell factory for both ethanol and muconic acid production by using OPEFB hydrolysate.

Paper No. OR-0013

SLUG-FLOW TUBULAR REACTOR WITH DIELECTRIC BARRIER DISCHARGE PLASMA

Motonobu Goto*, Motoki Yamada, Kakeru Mano, Yui Hayashi, Noriharu Takada, Wahyudiono, Hideki Kanda

Department of Materials Process Engineering, Nagoya University, Nagoya 464-8603 Japan
goto.motonobu@material.nagoya-u.ac.jp

Discharge plasma in contact with aqueous solution has been attracted attention in the application of wastewater treatment, nanoparticles generation, and medical application [1-3]. Although various methods of electric discharge over aqueous solution surface were studied, interfacial area between gas and aqueous solution where discharge plasma generated is limited. Generation of discharge plasma inside bubbles to enlarge interfacial area is one method to improve plasma reaction. However, bubbles were difficult to control because of sheer force and buoyancy, resulting in temporal change of discharge conditions.

We propose the plasma reaction process with discharge using gas-liquid slug flow in tube [4]. Slug flow has size-controlled bubbles separated by liquid phase. The discharge plasma was generated inside bubbles in gas-liquid slug flow and applied to chemical reaction system.

Gas-liquid slug flow was formed in glass capillary by mixing gas and liquid at T-junction. Glass capillary has 2mm in inside diameter and two pieces of cupper plate were attached outside the capillary as electrodes. AC pulsed voltages at ±10 kV were applied. Aqueous solution including coomassie brilliant blue (CBB) was used as a reactant. When discharge plasma was generated, plasma emission was observed in all bubbles between the electrodes. The reactive solution was efficiently circulated by convection flow. Since total amount of reactive oxidation species had correlated with CBB decomposition, oxidation species such as OH radicals must have caused decomposition reaction. When gas containing oxygen was used, decomposition rate was enhanced compared to the other gases.

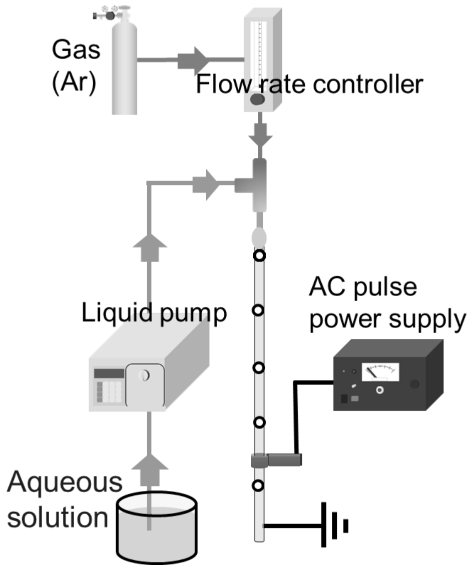

Fig. 1 Experimental apparatus for plasma reaction.

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Paper No. OR-0014

SUSTAINABLE POLYMER CHEMISTRY BY FREE RADICAL APPROACH TO PRODUCE BIODEGRADABLE AND RESPONSIVE SYSTEMS

Praveen Thoniyot[1]*, Lohitha Rao Chennamaneni[1], Alexander William Jackson[1],
Freda C. H. Lim[2], Alexander M. van Herk[1]

[1]Institute of Chemical and Engineering Sciences, Sciences (ICES), Agency for Science, Technology and Research (A*STAR), 1 Pesek Road, Jurong Island, Singapore 627833
[2]Institue of High Performance Computing, Agency for Science, Technology and Research (A*STAR) 1 Fusionopolis Way, #16-16 Connexis, Singapore 138632

Non-degradable polymers in consumer care applications are expecting tougher regulations in the near future, due to unsustainable source and production methods and well understood negative impacts of these polymers in the environment. Currently, industry is showing very strong interest in degradable analogs of non- degradable polymer additives and particles in many areas of applications. Conventional anionic ring opening and step-growth approaches need demanding conditions to create such degradable polymers and are industrially less feasible. The most industrially feasible approach in terms of simplicity and cost effectiveness is free radical polymerization. However, there are not enough free radical polymerization based approaches for producing degradable and environmentally friendly polymers.[1,2] Hence the developing synthetic approaches to produce complete or partially degradable backbones of free radical polymers is of immense importance since it offers new solutions to the current problems solved by non-degradable polymers. In our approach we adopt the ring opening polymerization of novel and conventional cyclic ketene acetal monomers and co-polymerizations with a variety of common monomers. The presentation will highlight some of the findings of our new project on environmentally friendly free radical route to produce biodegradable and responsive polymers.

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Paper No. OR-0018

A TWO-PHASE PHOTOCATALYTIC SYSTEM UTILIZING A MODIFIED METAL-ORGANIC FRAMEWORK FOR PRODUCTION OF HYDROGEN PEROXIDE

Yusuke Isaka,[1] Yudai Kawase,[1] Yoshifumi Kondo,[1] Yasutaka Kuwahara,[1,2] Kohsuke Mori,[1,2,3]
Hiromi Yamashita*,[1,2]

[1]Grad. Sch. of Eng., Osaka Univeristy, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
[2]Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University,
Katsura, Kyoto 615-8520, Japan
[3]JST, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

Hydrogen peroxide (H_2O_2) has attracted much attention as an ideal fuel for compact one-compartment fuel cells because it can be handled as a liquid under ambient conditions.[1] On the other hand, metal-organic frameworks (MOFs) are interesting class of materials composed of metal oxide clusters interconnected by organic linkers. Particularly, amine-functionalized MOFs are of our interest due to their photocatalytic activities. We herein report application of a MOF composed of $Ti_8O_8(OH)_4$ clusters and 2-aminoterephthalic acid, MIL-125-NH_2, to photocatalytic H_2O_2 production. The modification of the amine-functionalized linkers realized its selective dispersion in an organic phase for facile isolation of synthesized H_2O_2.

MIL-125-NH_2 was synthesized according to a reported method. Synthesis of H_2O_2 together with benzaldehyde was observed when MIL-125-NH_2 was dispersed in O_2-saturated acetonitrile solution of benzylalcohol and irradiated with visible light ($\lambda > 420$ nm). In this system, however, it was difficult to isolate synthesized H_2O_2 from the reaction solution.

Following the procedures reported for another amine-functionalized MOF, we have successfully synthesized MIL-125-NH_2 modified with various carboxylic anhydrides.[2] The modified MOFs were found to disperse selectively to organic phase of water/benzylalcohol two-phase system (Fig. 1). When the the modified MOFs dispersed in the two-phase system was irradiated with visible light ($\lambda > 420$ nm), simultaneous formation of H_2O_2 and benzaldehyde was observed. Here, H_2O_2 and benzaldehyde were observed only in aqueous and organic phase, respectively, to realize facile separation of the products. Only limited amount of H_2O_2 was formed when unmodified MIL-125-NH_2 was employed for the reaction.

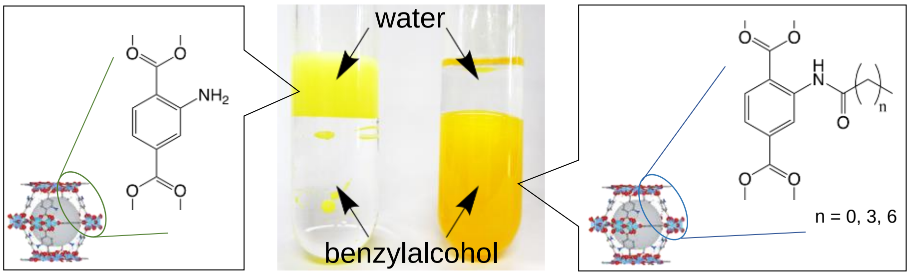

Fig. 1 Photocatalytic H_2O_2 production in a two-phase system utilizing modified MOFs.

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Paper No. OR-0020

PROCESS PARAMETERS INFLUENCING FUCOIDAN DEPOLYMERIZATION OVER GRAPHENE OXIDE UNDER MICROWAVE CONDITIONS

Elaine G. Mission[1], Armando T. Quitain[2,3]*, Mitsuru Sasaki[3], Tetsuya Kida[4]
[1]Graduate School of Science and Technology
[2]Faculty of Advanced Science and Technology
[3]College of Cross-Cultural and Multidisciplinary Studies
[4]Institute of Pulsed Power Science
Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555, Japan
* Corresponding author: Fax: 81-96-342-3679, E-mail: quitain@kumamoto-u.ac.jp

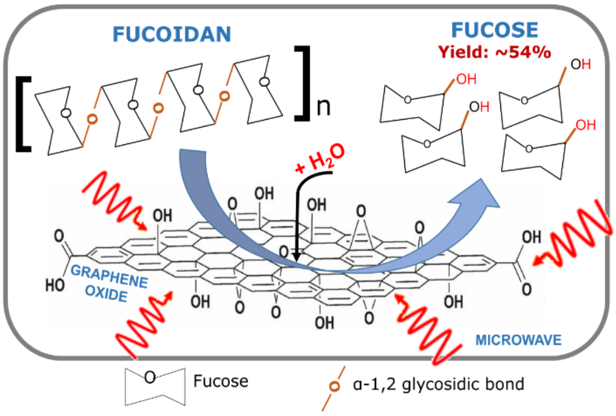

FIGURE 1 SYNERGISM OF MICROWAVE and GRAPHENE OXIDE FOR FUCOIDAN DEPOLYMERIZATION

Introduction. Brown algae such as Undaria Pinnatifida (wakame), has been regarded as an invasive specie in the Europe, North America and New Zealand. It contains fucoidan, a polysaccharide that is composed mainly of L-fucose units which are sulfated in the 4-position and connected through α-(1,2) linkages. Having fucose as its major constituent, fucoidan is a promising and potential substrate for biofuel and biochemical production. Petit et al. [1] reported that the metabolism of fucose by E. coli, S. enterica, and other bacteria produced 1,2-propanediol which can be converted into propanol and proprionate. The high moisture and oxygen content and low bulk density inhibits the use of conventional processing techniques on macroalgae, thus hydrolytic depolymerization would be a more suitable path to take. Presently, there is a scarcity of research that focuses on the depolymerization of fucoidan. Rodriguez-Jasso et al. [2] utilized trifluoroacetic acid and 121^{O}C for 2 hrs for hydrolysis of fucoidan from Fucus vesiculosus with a yield from about 9-12 mol%. On the other hand, Malihan et al. [3] made use of ionic liquid and hydrochloric acid to generate 10wt% fucose yield at 130^{O}C and 150 min from Undaria pinnatifida. But since homogeneous acids are difficult to separate from the hydrolysate and may also leave residues that affect final product quality and ionic liquids are expensive, an alternative which do not use toxic chemicals is necessary. Herein we report on the depolymerization of fucoidan into fucose under the synergy of MW and GO (Fig. 1). Specifically, this study aims to ascertain process parameters influencing fucoidan hydrolysis, which includes catalyst loading and form, substrate loading, microwave power, reaction time and temperature.

Results and Discussion. It was found that temperature and MW power have significant contributions in increasing fucose yields. The temperature is a critical factor in weakening bonds in the molecules for hydrolysis to easily occur. Higher MW power would have induced rapid rotation of molecules that facilitated faster hydrolysis process. The highest fucose yield of 54% was achieved at 15 min and 600 W under reflux conditions. These results demonstrate that MW and GO can be an effective system to depolymerize fucoidan.

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Paper No. OR-0021

BASE-FREE AEROBIC OXIDATION OF 5-HYDROXYMETHYL-2-FURFURAL TO PRODUCE 2,5-FURANDIMETHYLCARBOXYLATE

Dinesh Kumar Mishra,[a] Yong Jin Kim [a,*]

[a] Green Chemistry & Material Group, Korea Institute of Industrial Technology (KITECH), 89
Yangdaegiro-gil, Ipjang myeon, Cheonan-si 31056, Republic of Korea.
* E-mail: yjkim@kitech.re.kr

Base-free aerobic oxidation of 5-hydroxymethyl-2-furfural (HMF) to produce 2,5-furan dimethylcarboxylate (FDMC) has been carried out in the presence of gold (Au) nanocatalyst. Au nanocatalyst with particles size (2~4 nm) was prepared by standard homogeneous deposition-precipitation (HDP) method [1]. As prepared hydroxyapatite (HAP) supported Au nanocatalyst (Au/HAP) afforded 89.3% yield of FDMC which is attributed to stronger basic sites on the surface of Au/HAP nanocatalyst. For comparison point of view, the catalytic activities of various metal-based nanocatalysts have also been tested. To explain the catalytic behaviour of Au/HAP nanocatalyst, the effect of reaction variables such as time, temperature, pressure (synthetic air), and the amount of catalyst has been studied comprehensively. Au/HAP nanocatalyst was fully characterized by various techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen (N_2)-physisorption (adsorption-desorption) method, inductively coupled plasma-optical emission spectroscopy (ICP-OES), and X-ray photoelectron spectroscopy (XPS). Moreover, the surface properties of HAP and various supported Au catalysts were investigated by temperature-programmed desorption of ammonia (NH_3-TPD) and temperature-programmed desorption of carbon dioxide (CO_2-TPD) techniques. Furthermore, it is worth to mention that Au/HAP nanocatalyst could be also easily recovered by simple filtration method and reused up to five times without a notable change in original activity.

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Paper No. OR-0023

USE OF IONIC LIQUIDS AS NOVEL REAGENT FOR PRODUCING 2,5-FURANDICARBOXYLIC ACID

Cong Chien Truong[a], Yong Jin Kim[a,b]*

[a] Department of Green Process and System Engineering
Korea University of Science and Technology (UST), 217 Gajeong-ro, Yuseong-gu, Daejeon, 34113, Republic of Korea.
[b] Green Chemistry and Material Group
Korea Institute of Industrial Technology (KITECH), Cheonan 31056, Korea
E-mail: yjkim@kitech.re.kr

2,5-Furandicarboxylic acid (FDCA), one of the most important bio-based molecules, is considered as the potential alternative monomer for terephthalic acid for polyethylene terephthalate (PET) and polybutylene terephthalate (PBT). Compared to these fossil-based polymers, polyethylene furanoate (PEF) and other FDCA-derived polymers were found to display superior gas barrier properties, which have attracted much attention. Currently, the production of FDCA is mainly based on the oxidation of 5-(hydroxymethyl)furfural (HMF). Although various improvements for the synthesis of FDCA have been made, drawbacks such as uneconomical efficacy and the formation of impurities which cause chain terminations during the polymerization hamper the commercial production of FDCA. Recently, C-H carboxylation of 2-Furoic acid (FA) with CO_2 to FDCA in high yield through the utilization of alkali metal furoate has been reported as a potential alternative route. In our continuous efforts in advancing FDCA synthetic protocol, well-defined furoate-based ionic liquids (ILs) were prepared and firstly used as novel reagent for the direct carboxylation of FA with CO_2 to FDCA. These ILs were well characterized via NMR spectroscopy, IR, differential scanning calorimetry (DSC), and thermogravimetry (TGA). In this study, we found that tuning the cations of ILs could deliver FDCA from moderate to excellent yields under optimized conditions.

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Paper No. OR-0024

PALLADIUM-CATALYZED OXIDATIVE CARBONYLATION OF AROMATIC AMINES FOR GENERATING URETHANES

Thanh Tung Nguyen[1, 2], Yong Jin Kim[1, 2, *]

[1] Green Chemistry and Material Group, Korea Institute of Industrial Technology (KITECH), 89 Yangdaegiro-gil, Ipjang-myeon, Cheonan, 31056, Republic of Korea.
[2] Korea University of Science and Technology (UST), 217 Gajeong-ro, Yuseong-gu, Daejeon, 34113 Republic of Korea.
*E-mail: yjkim@kitech.re.kr; Phone: +82 41 589 8469; Fax: +82 41 589 8580.

Abstract. Organic isocyanates (R–NCO) have achieved great commercial importance as chemical intermediates in the manufacture of many useful chemicals as well as polyurethanes. Accordingly, synthesis of isocyanate via a phosgene-free route has attracted much interest due to the drawbacks originated from conventional protocol of using phosgene. Preparing isocyanate by thermal decomposition from carbamate is commended as a promising way. As a simplest aryl carbamate, Methyl *N*-phenyl carbamate (MPC) has been prepared through various methods such as oxidative carbonylation of aniline, reductive carbonylation of nitrobenzene, alcoholysis of 1,3-diphenyl urea, and methoxy carbonylation of aniline with DMC. In this research we synthesized the complexes of palladium and some other transition metals with phosphine type ligands, then applied them to the oxidative carbonylation of aniline to produce MPC. With this strategy, high TOF around 2200 h^{-1} for the synthesis of MPC in the presence of the catalyst system comprising palladium complex and KI at 160 ^{o}C and 1200 psi for 2 h.

Keywords. Carbon monoxide. Palladium catalysts. Phosphine Ligands. Oxidative carbonylation. Aniline. Methyl *N*-Phenyl Carbamate

Paper No. OR-0025

PALLADIUM-CATALYZED CARBONYLATION OF BROMINATED FUROATE FOR GENERATIONG2,5-FURANDIMETHYLCARBOXYLATE

Hye Jin Lee,[a]Yong Jin Kim[b,*]

[a] Korea University of Science and Technology (UST), 217 Gajeong-dong, Yuseong-gu,
Daejeon 34113, Republic of Korea
[b]Green Chemistry & Material Group, Korea Institute of Industrial Technology (KITECH), 89
Yangdaegiro-gil, Ipjang myeon, Cheonan-si 31056, Republic of Korea.
* E-mail: yjkim@kitech.re.kr

2,5-furan dimethylcarboxylate (FDMC)is promising replacement of dimethyl *p*-phtalate in polymer industry. Conventional process for producing FDMC involves oxidation of 5-hydroxymethyl-2-furfural (HMF) to FDCA and subsequent esterification of FDCA with alcohol. However, using HMF as starting material has some drawbacks such as problems of difficult to purify and limited production capacity therefrom. Furfural, as representative to biomass, has gained much attention because it is being produced as liquids form from the inedible bulky raw bio-materials in a large scale un China, furthermore, has an additional advantage of purifying.

In this session, we present an alternative route to FDMC from methyl 2-furancarboxylate which is produced from furfural by oxidation process. The catalytic process consists of two step; 1) bromination of methyl 2-furancarboxylate, 2) carbonylation of methyl 5-bromo-2-furancarboxylate using CO gas. The effect of time, temperature, CO pressure, variation of base, catalyst loading were studied. Various analysis techniques such as nuclear magnetic resonance (NMR) and fourier-transform infrared spectroscopy (FT-IR) were employed for the characterization of the catalyst.

Paper No. OR-0026

CUSE$_2$-CATALYZED REDUCTIVE CARBONYLATION OF NITROBENZENE: MECHANISTIC STUDY

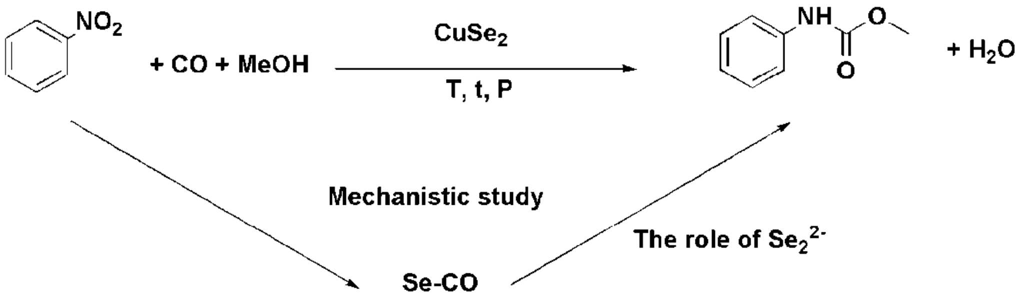
VyAnhTran[1], Yong Jin Kim[1,2]*

[1]Graduate School, Korea University of Science and Technology (UST), 217 Gajeong-ro,
Yuseong-gu, Daejeon-si 34113, Republic of Korea.
[2]Green Chemistry & Material Group, Korea Institute of Industrial Technology (KITECH), 89
Yangdaegiro-gil, Ipjang myeon, Cheonan-si 31056, Republic of Korea.

E-mail: yjkim@kitech.re.kr

Abstract

$CuSe_2$ and $CuSe_2@CeO_2$, as the highly active and cheap heterogeneous catalysts are synthesized and applied to the reductive carbonylation of nitrobenzene to produce methyl *N*-phenylcarbamate (MPC). The structure, morphology, and crystallography of $CuSe_2$ and $CuSe_2@CeO_2$ were investigated by scanning electron microscopy (SEM), transmission electron microscopic (TEM), and X-ray diffraction (XRD). To characterize the surface composition and oxidation states of elements on the surface of catalysts, X-ray photoelectron spectroscopy (XPS) was also studied. For mechanistic studies, the effects of reaction time, pressure, and temperature on the reductive carbonylation were evaluated. The results showed that 97.5 % yield of MPC was obtained at 160 ^{0}C, 1200 psi for 4 h, suggesting that they are promising and new catalyst as a cheap and effective for the reductive carbonylation compared to conventional Pd-based catalyst[1][2]. Moreover, a plausible reaction intermediate is proposed, which is supported by FTIR spectroscopy obtained from high- pressure gas cell.



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Paper No. OR-0027

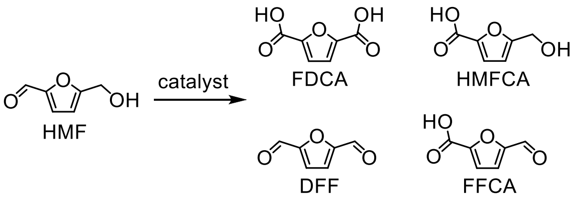
AEROBIC OXIDATION OF 5-HYDROXYMETHYLFURFURAL TO 2,5-FURANDICARBOXYLIC ACID OVER MANGANESE DIOXIDE CATALYST

Eri Hayashi, Keigo Kamata, Michikazu Hara*

Laboratory for Materials and Structures, Institute of Innovative Research, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, JAPAN
e-mail: hayashi.e.ac@m.titech.ac.jp

2,5-Furandicarboxylic acid (FDCA), which is obtained by the oxidation of 5-hydroxymethyl furfural (HMF), has attracted much attention as a raw material of bio-polyesters such as polyethylene furanoate. While effective supported noble metal catalysts for the oxidation of HMF to FDCA have been reported, most systems typically require 2–4 equivalents of strong base with respect to HMF to obtain high FDCA yield. Non-precious metal catalyst systems are promising candidates but they have disadvantages such as low yield and selectivity for FDCA, harsh reaction condition requirements, the use of specific oxidants, and poor recyclability. In this work, We report a simple, efficient, and non-precious-metal-based $MnO_2/NaHCO_3$ system for aerobic oxidation of HMF to FDCA.[1]

Table 1. Effect of catalysts for oxidation of HMF to FDCA[a]



Catalyst	Conv. (%)	Yield (%)			
		FDCA	HMFCA	DFF	FFCA
MnO_2	≥99	91	–	–	–
$SrMnO_3$	≥99	58	1	–	16
Mn_2O_3	58	5	12	1	34
Mn_3O_4	17	1	1	–	–
Fe_2O_3	16	–	1	0	1
Co_3O_4	17	1	1	1	–
NiO	19	–	1	2	1
CuO	19	1	1	1	1
–	23	1	1	1	1

[a] Reaction conditions: Catalyst (0.1 g), HMF (0.2 mmol), $NaHCO_3$ (0.6 mmol), water (5 mL), pO_2 (1 MPa), 100 °C, 24 h. Conversion and yield were determined by HPLC.

First, the oxidation of HMF to FDCA catalyzed by various metal oxides in the presence of $NaHCO_3$ (3 equivalents with respect to HMF) at 1 MPa O_2 was investigated (Table 1). Among the catalysts tested, MnO_2 showed the highest yield of FDCA (91%). The hexagonal $SrMnO_3$ catalyst gave a moderate activity with 58% FDCA yield. While other manganese oxides showed extremely low yields of FDCA (1–5% yield) and HMF conversion of 17–58%. Other metal oxide catalysts were almost inactive. The effect of base was also investigated. Regardless of the cation, bicarbonates were the most effective. In the presence of 2–3 equivalents of $NaHCO_3$, FDCA was obtained in high yield whereas 5-formyl-2-furancarboxlic acid (FFCA) and leaching of manganese species was not observed.

The used MnO_2 catalyst could be recovered from the reaction mixture by simple filtration, washing with water, and drying at 80 °C. The recovered MnO_2 catalyst could be reused without leaching of manganese species. In addition, the present $MnO_2/NaHCO_3$ system was applicable to the seletive oxidation of other biomass-derived substrates and large-scale oxidation of HMF to FDCA.

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Paper No. OR-0028

FACILE MECHANOCHEMICAL SYNTHESIS OF NICKEL/INDUSTRIAL-QUALITY GRAPHENE OXIDE NANOCOMPOSITES WITH HIGHLY UNIQUE AND TUNABLE MORPHOLOGY: APPLICATIONS IN ENERGY STORAGE AND CATALYSIS

Dian Deng[1], Mayakrishnan Gopiraman[2], Michikazu Hara[1*]
[1]Laboratory for Materials and Structures, Institute of Innovative Research, Tokyo Institute of Technology, Nagatsuta-cho 4259, Midori-ku, Yokohama 226-8503, Japan
E-mail: hara.m.ae@m.titech.ac.jp
[2]Department of Applied Bioscience, College of Life & Environment Science, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, South Korea
Email: gopiramannitt@gmail.com

Recently, graphene/metal nanoparticle composites have been much focused due to their use in numerous practical applications[1]. However, synthesis of supported nanoparticles often relies on chemical reduction. The majority of synthetic methods employ the use of reducing agents such as $NaBH_4$or stabilizers[2]. In this work, we report a simple and facile route to afford Industrial-quality graphene oxide (GO) anchored with monodispersed NiO nanoparticles without the use of any additional reducing agents or stabilizers.

The schematic synthesis procedure of Ni/GO nanocomposites is illustrated in Figure 1. For the typical preparation of Ni/GO, certain amount of $Ni(acac)_2$ was dissolved in DMF. The prepared $Ni(acac)_2$/DMF solution was mixed with GO, and the mixture was ground manually in a pestle and mortar. The resultant mixture was placed in a ceramic boat and heat treated at 400 °C for 3 h in a tubular furnace under flowing nitrogen to facilitate the decomposition of the acetate salts to form metal particles.

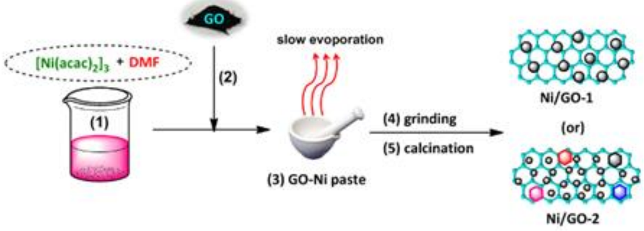

Figure 1. Schematic diagram of the preparation process.

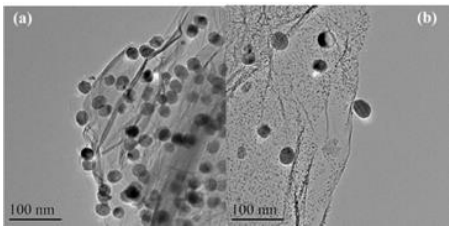

Figure 2. TEM images of Ni/GO-1(a) and Ni/GO-2(b)

Figure 2 shows the TEM images of Ni/GO-1 and Ni/GO-2. Interestingly, regardless of metal loadings, the Ni particles size was dispersed homogeneously on the GO surface.

To evaluate the catalytic activity of the as-prepared Ni/GO catalysts, the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) was carried out as a benchmark reaction. The kinetic reaction rate constant k was calculated to be $6.81 \times 10^{-3}\ s^{-1}$ and $2.73 \times 10^{-2}\ s^{-1}$ for the reduction of 4-NP catalyzed with 2mg Ni/GO-1 and 0.75mg Ni/GO-2, respectively, which compares favorably to other reported Ni NP-based catalysts.To demonstrate the as-synthesized Ni/GO nanocomposites can act as potential electrode materials for supercapacitors, the cyclic voltammetry (CV) analysis for Ni/GO-1 and Ni/GO-2 were performed at different scan rates with 1.0 M KOH electrolytes,Maximum capacitances of 67, 311 and 461 F/g at a scan rate of 5 mV/s were obtained for the pristine GO, Ni/GO-1 and Ni/GO-2, respectively.

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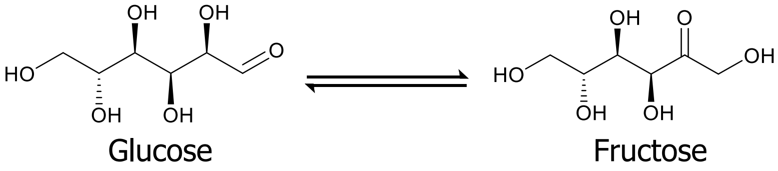
Paper No. OR-0029

ISOMERIZATION OF GLUCOSE TO FRUCTOSE BY SOLID BASE CATALYSTS

Natsumi Shibayama, Mizuho Yabushita, Kiyotaka Nakajima, Atsushi Fukuoka*

Institute for Catalysis, Hokkaido University, Japan (natsumi@cat.hokudai.ac.jp)



Scheme 1. Glucose isomerization to fructose.

Fructose has been used as a sweetener and starting material for producing value-added chemicals.[1] Although enzymatic isomerization of glucose (Scheme 1) can synthesize fructose in 50% yield, which is a maximum yield due to equilibrium between these two sugars in water at moderate temperatures, such processes always involve serious issues (e.g., short lifetime of enzymes). A chemocatalytic process with an easily-separable and reusable heterogeneous catalyst is thus more suitable for large-scale production of fructose. The glucose isomerization is known to proceed in the presence of base via the Lobry de Bruyn–Alberda van Ekenstein (LdB–AvE) mechanism. In this study, we thus examined fructose production from glucose in ethanol with solid base catalysts to obtain both high fructose yield and selectivity.

Table 1 summarizes the results of glucose isomerization by various solid base catalysts at 363 K for 2 h in ethanol. Among the catalysts tested, hydrotalcite (HT, Mg/Al = 3) shows the highest catalytic activity and produces fructose in 50% yield with 83% selectivity, while the fructose yield in water is only 16%. The reaction at 393 K for 30 min with HT gives 56% fructose yield with 80% selectivity. The high catalytic performance of HT originates from its high density of base sites whose properties are suitable for the isomerization.

Table 1. Glucose isomerization at 363 K for 2 h in ethanol.

Catalyst	Fructose /%	
	Yield	Selectivity
None	1.3	8.0
HT	50	83
HT[a]	16	57
HT[b]	56	80
MgO	4.5	25
γ-Al_2O_3	17	60
CaO	23	59

[a]In water. [b]At 393 K for 30 min.

After any reactions shown above, the color of HT turned to yellowish or even brown from white, which indicates the deposition of insoluble humins on the catalyst surface. Humin formation on solid surface resulted in the decrease in original activity of HT in the subsequent reactions. Taking advantage of "memory effect",[2] we proposed the two-step regeneration process for reusing HT, which consists of calcination and reconstruction in an $(NH_4)_2CO_3$ aqueous solution. By using this two-step regeneration, HT can be used repeatedly for the isomerization in at least three times, where the total turnover number for fructose production is 46.

We also confirmed whether base sites of HTs function as active sites for this reaction by isotope tracer analysis using glucose-2-d_1 as a substrate. Our data of ^{2}H NMR spectroscopy revealed that deuterium atom involved in glucose-2-d_1 was removed by HT, while the fructose production was confirmed by separate HPLC analysis. We have thus concluded that base sites of HT work as active sites to promote the isomerization through the LdB–AvE mechanism.

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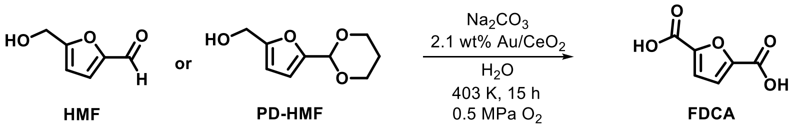
Paper No. OR-0031

A NEW ROUTE FOR THE FORMATION OF FURAN 2,5-DICARBOXYLIC ACID FROM A CYCLIC HMF-ACETAL WITH A SUPPORTED AU CATALYST

Kiyotaka Nakajima[1,2,*], Atsushi Fukuoka[1]
[1] Institute for Catalysis, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo 001-0021, Japan, [2] Advanced Low Carbon Technology Research and Development Program (ALCA), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi 332-0012, Japan.

The utilization of 5-(hydroxymethyl)furfural (HMF) for the large-scale production of essential chemicals has been largely limited by the formation of solid humin as a by-product, which prevents the operation of step-wise batch-type processes and continuous flow-type processes. The reaction of HMF with 1,3-propanediol produces an HMF-acetal derivative (PD-HMF) that exhibits excellent thermal stability. The aerobic oxidation of HMF and PD-HMF in water was examined with a CeO2-supported Au catalyst. When the oxidation was performed using dilute HMF or PD-HMF (1 wt%) solutions in water, FDCA yields for both reactants exceeded 90% (entries 1 and 2). This confirms the utility of the supported Au catalyst for the efficient oxidation of the cyclic acetal of PD-HMF into the carboxylic acid. When the concentration of the HMF or PD-HMF reactants was increased to 10 wt%, the results were very different. The FDCA yield from HMF decreased to 28%, whereas it remained as high as 80% with PD-HMF as the reactant. The FDCA yield by PD-HMF oxidation could be further increased to 94% by optimization of the base concentration (entry 6); however, a similar increase in the base concentration did not further improve the FDCA yield from HMF (entry 5). It was noted that the higher FDCA yield is largely due to a more complete mass balance, which indicates that by-product formation is significantly suppressed in the presence of two equivalents of base relative to PD-HMF. A further increase of the PD-HMF concentration to 20 wt% only slightly affected the FDCA yield (91%) (entry 7). These results demonstrate that the cyclic HMF-acetal with 1,3-propanediol reported here is a promising intermediate for selective FDCA production from highly concentrated solutions in excess of 10 wt%. The present results represent a significant advance over the current state of the art, overcoming an inherent limitation of the oxidation of HMF to an important monomer for biopolymer production.

Table 1. Catalytic activity of Au/CeO_2 toward aerobic oxidation of HMF or PD-HMF in the presence of Na_2CO_3 in water.[a]



Entry	Conc.[b] /wt%	Substr.	Base /equiv	Conv.[c] /%	Yield /%		M.B[e] /%
					FDCA	Others	
1	1	HMF	0.2	>99.9	91	5	96
2		PD-HMF		>99.9	95	3	98
3	10	HMF	0.2	>99.9	28	25	53
4		PD-HMF		>99.9	80	10	90
5	10	HMF	2.0	>99.9	28	28	56
6		PD-HMF		>99.9	94	3	97
7	20	PD-HMF	2.0	>99.9	91	0	91

[a] Reagents and conditions: HMF or PD-HMF, 50 mg; Catalyst, Au (2.1 wt%)/CeO_2; catalyst weight, 50 mg (molar ratio of HMF/Au=78 and PD-HMF/Au=53); Na_2CO_3, 0.2 or 2.0 equiv to HMF and PD-HMF on a molar basis; H_2O (solvent), 0.25, 0.5, and 5 mL; Oxygen pressure, 0.5 MPa; Temperature, 413 K; Time, 15 h; Stirring rate, 500 rpm. [b] Substrate concentration, [c] Conversion of HMF or PD-HMF estimated by HPLC, [d]

Paper No. OR-0036

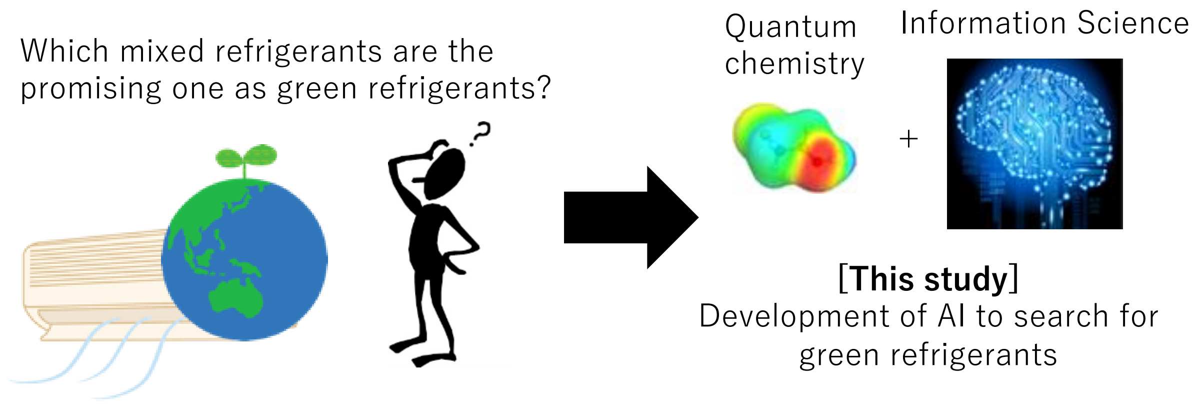
MATERIALS INFORMATICS TOWARD GREEN COOLING

Hirotoshi MORI*

Faculty of Core Research, Natural Science Division, Ochanomizu University Tokyo, Japan

Refrigerants are substances that can be used in the refrigeration cycle of air conditioning and refrigeration equipment because of their thermodynamic properties. Among various chemical compounds, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) had been utilized as refrigerants since their cooling efficiency are very high. However, as is well known, usage of these compounds is being phased out under the Montreal Protocol, an international agreement to protect the ozone layer. To develop substituent materials with high cooling efficiency and low environmental loads, many researchers and engineers have been working very hard to search for such materials. However, no better materials than those currently used have not been found. One of the most effective strategy to search for novel green refrigerants is using mixed refrigerants. In mixed materials, however, intermolecular interactions among different species cause non-linear thermodynamic property change to molar fraction. It had been considered difficult to predict candidate mixed green solvent prior to performing a number of experiments, which are expensive and time consuming.

With the above backgrounds, we have tried to develop a novel database that combine theoretical and experimental thermodynamic data for applying artificial intelligence in the field of refrigerants development. In this talk, a novel approach to find out green solvent materials which is based on quantum chemical calculations and information science will be introduced.



Acknowledgments

Some of the presented calculations were performed at the Research Center for Computational Science (RCCS), the Okazaki Research Facilities, and the National Institutes of Natural Sciences (NINS). This study was supported in part by the Precursory Research for Embryonic Science and Technology programs (PRESTO; Grant number: JPMJPR16NC) from the Japan Science and Technology (JST) Agency.

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Paper No. OR-0037

THE CHEMICAL RECYCLING OF POLYMERIC WASTES IN HIGH TEMPERATURE FLUID

Hideyuki Tagaya[1]*, Daisuke Yamashita[1], Nozomi Sakuma[1], Keizo Akutagawa[2],
Masahiro Hojo[2], Katsuaki Hironaka[2], Taichi Sugeno[1]

[1]Yamagata University, Yonezawa, Yamagata, Japan
[2]Bridgestone Corporation, Kodaira, Tokyo, Japan

The feedstock recycling of waste plastics into their monomers has been gaining greater attention as a technique to obtain valuable products from waste plastics. Thermosetting resin is stable thermally and not easy to recycle mechanically because thermosetting resin do not melt to mold again. Also tire is composite materials of organic compounds having different thermal properties, and waste tires are difficult to recycle mechanically. Anyway, we have already confirmed the liquid phase decomposition of plastics including thermosetting resin and tire into their monomer and oligomers. In these reactions at over 350 °C, bond scission reaction between carbon and carbon bond occur easily, and solvents play important roles as the hydrogen donor to stabilize carbon radicals. To evaluate the solubilization ability of the solvents, model compounds of the plastics were reacted at wide temperature range, and it was confirmed that the decomposition reaction occur at below 350 °C. Actually, effective decomposition reactions of phenol resin and tire were attained at 300 °C by using phenols such as cresols. In this study polymeric compounds such as phenol foam resin, tire and their model compounds were reacted in various solvents containing hydrogen donating solvents and alcohol compounds. Reactions were carried out by using 10ml tubing bomb reactor and the solubilization rate was calculated from the amount of THF or diethyl ether insoluble part. Products were analyzed by TG, GC and GC/MS. In the reactions of phenol foam resin at 300°C in aliphatic alcohol such as 1-heptanol, productions of monomeric compounds such as phenol, cresol and dimethylphenols were confirmed. Also, in the reaction of waste tire at 300°C, solubilization was attained and the ratio depended on the kind of solvents. These results suggested the occurrence of solvolysis reaction in which solvents contribute to the bond scission reaction as agents to attack cross-linking.

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Paper No. OR-0050

SYNTHESIS OF FURFURAL FROM GLUCOSE OVER MESOPOROUS SILICA SUPPORTED TIN CATALYST

Miyuki Asakawa[1, 2], Abhijit Shrotri[1], Atsushi Fukuoka[1, *]

[1]Institute for Catalysis, Hokkaido University, Sapporo, 001-0021, Japan
[2]Graduate School of Chemical Science and Engineering, Hokkaido University, Sapporo, 060-8628, Japan
fukuoka@cat.hokudai.ac.jp

1. Introduction

Furfural is a versatile chemical precursor used for the synthesis of furan resins, fuels, and plastics. Practically, furfural is produced by dehydration of xylose, obtained from biomass, in the presence of sulfuric acid. However, biomass also contains a large amount of cellulose that can be converted to glucose. Therefore, use of glucose as feedstock along with xylose can increase the yield of furfural from biomass. Furthermore, use of sulfuric acid as catalyst is undesired because it produces a lot of neutralization waste. In this study, we use supported Sn catalyst for the conversion of glucose to furfural in sulfolane.

2. Results and discussion

The catalyst containing 1 wt% Sn was prepared by impregnation of $SnCl_4 \cdot 5H_2O$ over SBA-15 support followed by calcination. The Sn particles were well dispersed on the catalyst surface as no peaks were observed in XRD, and the individual Sn particles were not visible in high resolution TEM. EXAFS analysis showed the Sn atoms were coordinated with 4.7 oxygen atoms and were structurally similar to octahedrally coordinated Sn in SnO_2. Reaction of glucose in the presence of this catalyst with sulfolane as the solvent (160 °C for 2 h) gave 28% yield of furfural. The catalytic activity decreased by increasing the Sn content to 10% owing to the formation of large SnO_2 crystals. Furfural yield was only 4% when unsupported SnO_2 was used as the catalyst. These results show that well dispersed amorphous particles of Sn, octahedrally coordinated with oxygen atoms, were the active sites for the reaction.

The reaction pathway from glucose to furfural was elucidated by analyzing products obtained from isotopically labelled substrates by ^{13}C NMR and GC-MS. Glucose was first isomerized to fructose in the presence of Sn catalyst. Fructose spontaneously underwent dehydration and decarbonylation at the C6 position in sulfolane, even in the absence of Sn catalyst, to produce furfural.

In conclusion, we demonstrate that well dispersed Sn catalyst supported on SBA-15 promotes isomerization of glucose to fructose in sulfolane, which is followed by dehydration and decarboxylation of fructose to yield furfural.

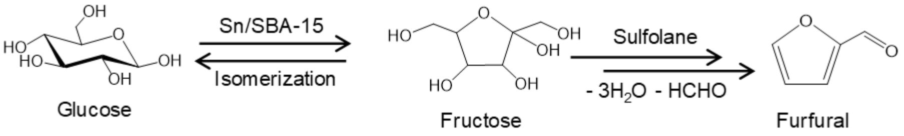

Figure: Conversion of glucose to furfural by Sn/SBA-15 in sulfolane.

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Paper No. OR-0051

NOVEL HETEROGENEOUS PHOTOCATALYSTS FOR CROSS-DEHYDROGENATIVE COUPLINGS

C. P. Ross[1†‡], R. Rios[2‡], R. Raja[3‡*]

[†‡]Institute of Chemical and Engineering Sciences (ICES), Agency for Science and Technology Research (A*STAR), Singapore
[‡]University of Southampton, United Kingdom
[1]C. P. Ross@soton.ac.uk [2] R. Rios-Torres@soton.ac.uk [3]R.Raja@soton.ac.uk

Cross-dehydrogenative couplings (CDCs) use two different C-H bonds to form a nucleophile and electrophile *in situ*, mitigating the need for prefunctionalisation of the substrates.[1] The aza-Henry reaction shown in Fig. 1 is an excellent example of this, with facile and selective addition of nitromethane adjacent to a tertiary amine, it is of industrial and academic interest. Zeolitic imidazolate frameworks (ZIFs), combine the highly desirable properties of zeolites and metal-organic frameworks (MOFs).[2] We have identified ZIF-9 and ZIF-67, two structures of cobalt with different imidazolate linkers, as efficient photocatalysts in the aza-Henry reaction. As heterogeneous materials, they offer a more sustainable alternative to the transition metal complexes[3] and organic dyes[4] that have so far dominated reports.

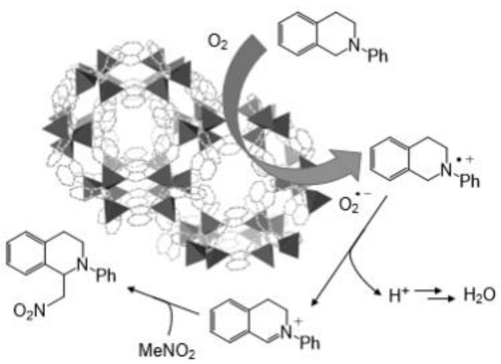

Fig. 1: CDC between nitromethane and *N*-phenyl-tetrahydroisoquinoline using heterogeneous ZIF-9.

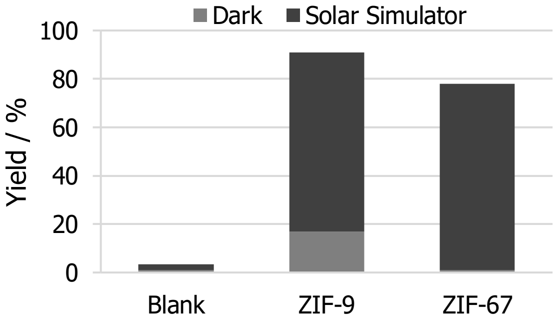

Fig. 2: *N*-phenyl-tetrahydroisoquinoline (0.11 mmol) with nitromethane (1 mL) and catalyst (6 mol%) under a solar simulator.

Catalytic performance was analyzed alongside a range of characterization techniques, including SEM, BET and UV-Vis, to discern structure-property relations. Fig. 2 shows that despite the great similarity between the two materials, the differences observed in the characterization play a vital role in the catalytic activity observed. The heterogeneous nature of both Co-ZIFs mean easy separation from the reaction mixture, whilst recyclability tests revealed excellent yields continue after five cycles.

We would like to thank the VC scholarship of the University of Southampton and A*STAR for funding.

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Paper No. OR-0053

VISIBLE-LIGHT DRIVEN CARBOXYLATION WITH CO_2 WITH THE SYSTEM OF BIOCATALYST AND PHOTOCATALYTIC DYE

Yutaka Amao[1,2,3*], Takayuki Katagiri[3], Shusaku Ikeyama[2]
[1]Research Center for Artificial Photosynthesis, Osaka City University, Osaka 558-8585, Japan
[2]Advanced Research Institute for Natural Science and Technology, Osaka City University, Osaka 558-8585, Japan
[3]Graduate School of Science, Osaka City University, Osaka 558-8585, Japan

Recently, CO_2 utilization (CDU) technology has received much attention. In catalysts for the CDU, some biocatalysts for CDU have received much attention. For example, malic enzyme (ME) catalyzes the reaction of pyruvate and CO_2 to malate with co-enzyme NADPH[1]. Thus, ME is attractive biocatalyst for carboxylation due to building carbon-carbon bonds from CO_2 as a feedstock. Some studies on the visible light-driven malate production from pyruvate and CO_2 with the system consisting of an electron donor (D), a photocatalytic dye (P), an electron mediator (C), ferredoxin-NADP$^+$ reductase (FNR), NADP$^+$ and ME as shown in Fig. 1 (system 1) are reported [2-5].

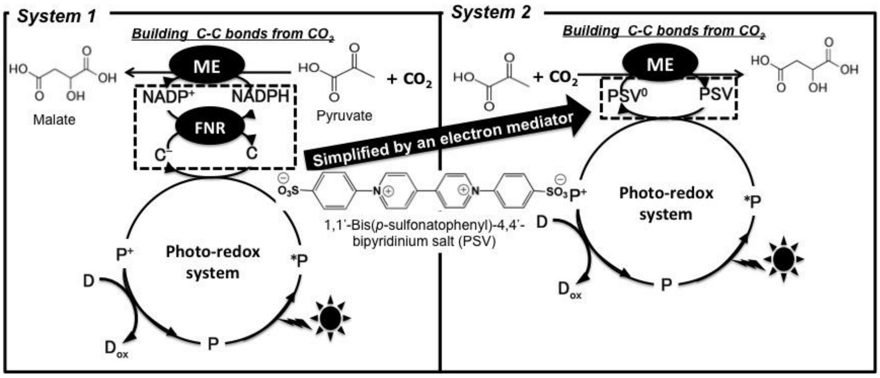

Fig. 1. Visible-light driven malate production from pyruvate and CO_2 with ME

Since this system is very complicated, it is necessary to simplify using a simple electron mediator 1,1′-bis(*p*-sulfonatophenyl)-4,4′-bipyridinium salt (PSV) as shown in Fig. 1 (system 2)[6,7].

In this work, the visible-light driven malate production from pyruvate and CO_2 with ME using the reduction of PSV with water soluble porphyrin (PS) in the presence of triethanolamine (TEOA) is developed. When a sample solution containing TEOA (0.2 M), PS (40 μM), PSV (0.4 mM), pyruvate (6.0 mM) and ME (4.0 units) in CO_2 saturated buffer aqueous solution was irradiated, 0.6 mM of malate was produced after 3 h irradiation.

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Paper No. OR-0060

EFFICIENT PHOTOCHEMICAL RECOVERY OF RHENIUM FROM AQUEOUS SOLUTIONS: A GREENER APPROACH FOR RHENIUM METALLURGICAL PROCESSING

Hisao Hori*, Takafumi Otsu

Department of Chemistry, Faculty of Science, Kanagawa University, 2946 Tsuchiya,
Hiratsuka, 259-1293, Japan, E-mail: h-hori@kanagawa-u.ac.jp

Rhenium, a minor metal in the Earth’s crust and has a high melting point (3180 ºC), is used in superalloys for turbine blades for aircraft and thermal power plants, and in petroleum reforming catalysts for the production of high-octane gasoline [1]. The utility of rhenium for these applications arises from its high heat resistance, high corrosion resistance, and high hardness. Molybdenum and copper ores are the sole economically viable mineral sources of rhenium, which is obtained as a by-product of the metallurgical processing of these ores; specifically, the rhenium component is oxidized to volatile Re_2O_7 in the flue dusts and then collected in aqueous solution in the form of perrhenate ion (ReO_4^-). In addition, during processing of secondary raw materials (spent catalysts and alloys), the rhenium is also transformed into ReO_4^- in aqueous solutions. The recovery of ReO_4^- from aqueous solutions is difficult because of its low concentration and high solubility at all pH values. Two techniques for this purpose—solvent extraction and ion exchange—are currently used in industrial processes [2]. However, solvent extraction produces large volumes of extractant waste (mainly amines). In addition, both techniques require subsequent steps to separate the collected ReO_4^- from the solvent or the ion-exchange resin and transfer it to an aqueous phase, as well as recrystallization to precipitate a salt (typically NH_4ReO_4, generated by addition of NH_4OH), and the mother liquor generally contains a non-negligible amount of ReO_4^-. Furthermore, ion-exchange technique requires toxic thiocyanate to elute the ReO_4^- from the resin. Under the circumstances, a method for recovery of rhenium from aqueous solutions with high yield, accompanying with no environmentally harmful waste is strongly desired.

We report herein that irradiation of aqueous ReO_4^- with UV–visible light in the presence of 2-propanol and acetone (which concentration was comparable to the initial ReO_4^-), leads to formation of a precipitate consisting of amorphous ReO_2 and ReO_3, and that 95% of initial rhenium is recovered within 6 h of irradiation [3]. In this photochemical process, 2-propanol donates an electron to an excited-state of ReO_4^- species and acetone increases absorption of light by ReO_4^- via precomplexation. Characterization of the precipitate, selectivity of rhenium from aqueous mixed metal solutions, and extension of this method to industrial scale are also presented.

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Paper No. OR-0062

SCAPP: FRAMEWORK DEVELOPMENT FOR SUSTAINABLE CHEMISTRY ASSESSMENT

Iskandar Halim*, Khoo Hsien Hui, Naraharisetti Pavan Kumar,
Algin Oh Biying, Thoniyot Praveen

Institute of Chemical and Engineering Sciences
A*STAR (Agency for Science, Technology and Research)
1 Pesek Road, Jurong Island, Singapore 627833

Sustainable chemistry goes beyond green chemistry concept and can be defined as the application of scientific principles to drive the design, manufacture, and use of chemical products and processes that are safe, environmentally-benign, resource-efficient, and economically sound at the same time. While a unified set of indicators for sustainable chemistry has not been established, numerous metrics have been proposed to measure the level of resource utilization during a chemical synthesis. These include atom economy, E-factor, reaction yield, and process mass intensity. Such metrics need to be augmented with other indicators that measure the environmental impacts as well as economic viability of the upstream and downstream stages of product development in order to deliver a more comprehensive assessment.

We propose a framework, called SCaPP (Sustainable Chemical Products and Processes), to evaluate the sustainability of any given chemical product or process. SCaPP framework is designed to integrate different computer tools: knowledge-based system, process simulator, environmental impact assessment tool, and economic evaluation tool to enable fast calculation of various sustainability metrics and also help compare and screen between alternative process chemistries. Therefore, SCaPP allows evaluation of potential sustainability impacts during the early stages of product and process development. SCaPP incorporates user friendly interface such as drag-and-drop features. To test the framework, we have applied it to a case study involving chemistry synthesis of a 'green product'.

Paper No. OR-0070

SYNTHESIS OF BIO-ACRYLICS POLYMERS FROM RENEWABLE RESOURCES: A TRANSITION OF RENEWABLE CHEMICALS TO GREEN POLYMERS

Parijat Ray[1], Craig Smith[2], George Simon[1], Kei Saito*

[1] Department of Materials Science and Engineering and New Horizons Research Centre and
* School of Chemistry, Monash University, Clayton, Victoria 3800, Australia
[2] PPG Industries, Pittsburg, USA

Dihydro-5-hydroxyl furan-2-one (2H-HBO), a renewable-sourced chemical containing the hydroxyl functionality is converted into its acrylic counterpart for the first time through a green chemical procedure. This newly-synthesized acrylic monomer is able to be polymerized using different techniques such as bulk, solution and emulsion polymerization. To check the capability of this monomer to polymerize with different other commercially-available acrylates, copolymerizations are studied based on emulsion techniques. The pendent lactone ring remains unopened during the polymerization and makes the polymer highly polar to be polymerized in a polar solvent like dimethyl sulfoxide (DMSO). This monomer is suitable to copolymerize with other commercially available acrylic monomers such as methyl methacrylate (MMA), hydroxyethyl methacrylate (HEMA), styrene etc. RAFT emulsion polymerization is also studied with the same monomer in a simple way which gives a steady conversion (~60%) with a low dispersity of 1.06. The homopolymer produced from emulsion polymerization shows higher molecular weight from all the methods, with a glass transition temperature of around 108°C which is showing the potentiality of this monomer as an interesting, green replacement for methyl methacrylate in certain field of applications. Along with this, another bio-acrylics monomer has been discovered from a green solvent which is believed to be a strong alternative of an existing methacylic monomer widely used in acrylics resin manufacturing for automotive coatings.

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Paper No. OR-0072

PHOTO-RESPONSIVE SELF-HEALING EPOXY COATINGS

Timothy Hughes[1], George Simon[2]*, Kei Saito[1]*

[1]School of Chemistry, Monash University, Clayton, VIC, Australia
[2]Department of Materials Science and Engineering, Monash University, Clayton, VIC, Australia

Photo-healable self-healing polymers (SHP) have the ability to heal damage by the use of an appropriate light irradiation to trigger a reversible reaction that causes a transition between a rigid state and a flowable state. This transition leads to healing that can restore the mechanical properties of a damaged polymer allowing for the return to service after a suitable healing treatment. When used as a coating, a SHP can ensure the continued protection of the underlying structure after damage with minimal downtime of the component and no replacing of the coating being necessary effectively saving resources by not requiring additional coating material and no loss of the underlying substrate. Several polymers were made through different approaches in an effort to produce a variety of high performing coating materials that had the ability to heal at room temperature. The photo-reversible mechanism from which the self-healing ability arises was confirmed by IR, UV-Vis and solubility tests and the self-healing ability demonstrated for several different polymer systems.

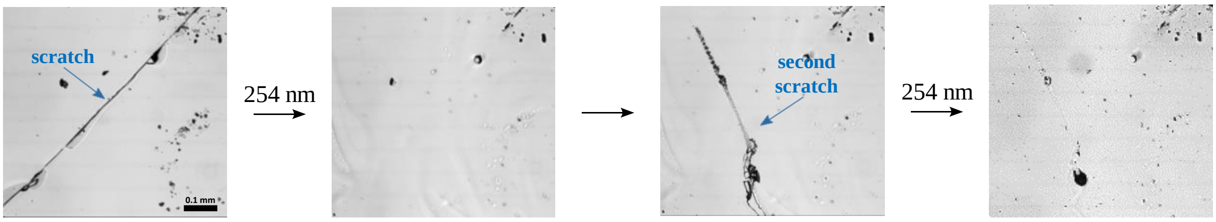


FIGURE 1: REPEATABLE SELF-HEALING OF A SURFACE SCRATCH ON ONE OF THE SYNTHESISED EPOXY COATINGS

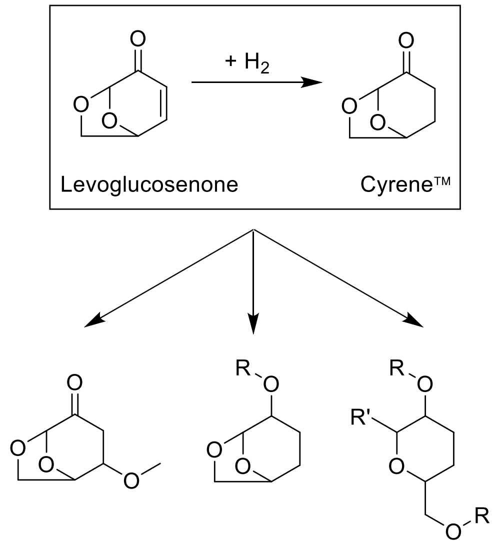
Paper No. OR-0073

SOLVENT APPLICATIONS OF LEVOGLUCOSENONE DERIVATIVES

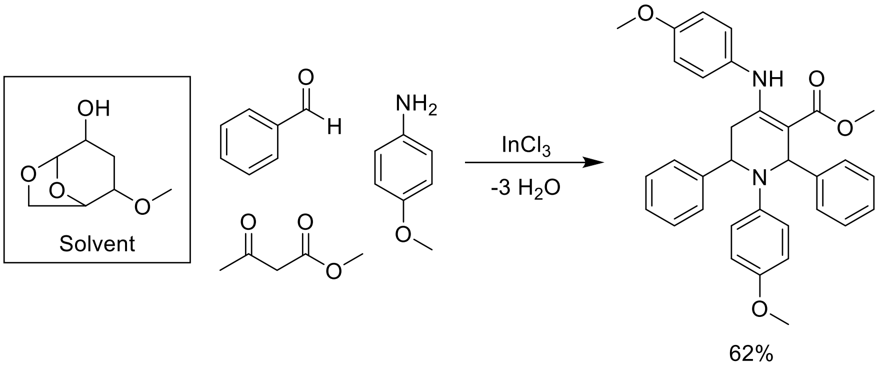
James Sherwood*

Green Chemistry Centre of Excellence
Department of Chemistry
University of York, UK
james.sherwood@york.ac.uk

Many common dipolar aprotic solvents are reprotoxic, and subject to regulatory controls limiting their uses. The response from research groups has been to develop new solvents without the amide and sulfone functionalities that are associated with chronic toxicity. One such example is Cyrene™, the hydrogenated analogue of levoglucosenone. Since the first report of Cyrene™ being used as a solvent in 2014,[1] numerous international research efforts have been dedicated to its applications. The multifunctional levoglucosenone lends itself to other chemical modifications. Michael addition, ketone reduction, and acetal opening were performed to provide novel solvents (examples given to the right) and tested alongside Cyrene™ in various applications.



Cyrene™ and its 5-methoxy derivative were found to act as hydrotropes, improving the solubility of pharmaceuticals (e.g. acetaminophen and thiamphenicol) for intravenous treatments, replacing reprotoxic *N*-methyl pyrrolidone (NMP). The exfoliation of graphite and subsequent dispersion of the resulting graphene in Cyrene™ was an order of magnitude more effective than NMP.[2] The higher viscosity of Cyrene™ also lead to more pristine graphene flakes. Finally, levoglucosenone was subject to an oxa-Michael addition with methanol and reduced to an alcohol to provide a bespoke solvent for the synthesis of tetrahydropyridines in a one-pot reaction from amine, aldehyde, and acetoacetate reactants (see scheme to the left). Yields were comparable to conventional dipolar solvents.



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Paper No. OR-0077

MICROWAVE ASSISTED HYDROLYSIS OF BIOMASS

Vincent Valette, Florent P. Bouxin, Hannah Briers, Vitaly Budarin, James H. Clark, Jiajun Fan*

Green Chemistry Centre of Excellence, Department of Chemistry, University of York,
Innovation Way, Heslington, York, YO10 5DD, United Kingdom

Organic acids are major secondary products of any cellulose thermal depolymerisation processes. These organic acids promote auto-hydrolysis of biomass, therefore systematic investigation of acid influence on biomass hydrolysis is very important for future biorefinery technologies. Due to its very heterogeneous and complex structure, biomass is not ideal for the mechanistic study. In this case cellulose, as major component of biomass, has been selected to mimic general behaviour of biomass in acid-catalysed hydrolysis processes. Recently it has been found that microwave irradiation is very efficient tool of cellulose activation. According to the previous work morphology of cellulose is critical for the microwave activation process[1]. However, there are no studies of the structural effects on cellulose during the microwave hydrothermal reaction in the presence of bio-derived acids. To investigate how cellulose morphology impacts on its acid-catalysed hydrolysis, cellulose with crystallinity ranging from 0.5 to 0.8 were submitted to various organic acids. Cellulose mass losses, glucose yields and degrees of crystallinity were measured after microwave-assisted hydrolysis at temperature ranging from 180°C to 230°C. Results suggested that, independently of the nature of acid catalyst, both low degree of crystallinity and crystallite size of cellulose led to higher glucose yield; likely due to the increase in rate of hydrolysis. A fourfold increase of the glucose yield could be observed when the degree of crystallinity was decreased from 0.73 to 0.53. Kinetic phenomena also influenced the degree of crystallinity of solid residue produced during hydrolysis. In most cases, cellulose crystallinity increased after the reaction due to the hydrolysis of the amorphous region was faster than cellulose conversion from crystalline to amorphous phase. However, in cases of low hydrolysate yields, decrease of the crystallinity was also observed.

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Paper No. OR-0079

MULTICOMPONENT SYNTHESIS OF 5-AZA-ADENINES AND THEIR ANALOGUES ASSESSED THROUGH THE PRISM OF GREEN CHEMISTRY METRICS

Felicia Phei Lin Lim[1*], Anton V. Dolzhenko[1], Milton T.W. Hearn[2]

[1]School of Pharmacy, Monash University Malaysia, Jalan Lagoon Selatan, Bandar Sunway, Selangor Darul Ehsan 47500, Malaysia. E-mail: fplim1@student.monash.edu
[2]Green Chemical Futures, School of Chemistry, Faculty of Science, Monash University, Scenic Blvd & Wellington Road, Clayton VIC 3800, Australia.

1,3,5-Triazine based purine isosteres have been recognised as privileged scaffolds in medicinal chemistry.[1] Purine isosteres have also attracted significant interest as leads in the development of new agents acting on several pharmacologically important targets. Inspired by the need to explore the therapeutic potential of these compounds, our group has focused efforts towards the development of practical and efficient methods for the synthesis of 5-azapurines and their analogues. We have developed multicomponent reactions (MCRs) that utilizes aminoazoles, orthoesters and cyanamide for the synthesis of 5-aza-adenines and structurally related molecules. Exploration of the scope of this MCR using a variety of aminoazoles and orthoesters has led to the preparation of libraries of 1,2,4-triazolo[1,5-*a*][1,3,5]triazines[2], pyrazolo[1,5-*a*][1,3,5]triazines[3], and imidazo[1,2-*a*][1,3,5]triazines[4].

MCRs satisfy many principles of Green Chemistry. We have thus investigated the "greenness" of our developed multicomponent protocols based on the Green Chemistry metrics. The efficiency and sustainability of our reactions were quantified, and the potential environmental impact of these protocols evaluated. We found that the overall efficiencies of these reactions were linked to variations in the molecular structures of the aminoazole precursors used in the MCR. Usage of different orthoesters to introduce another point of diversity in the reaction product also affected reaction efficiency. Employing microwave irradiation in our MCR was paramount in reducing the overall energy intensity of the reaction. We confirmed quantitatively that the MCR was a more sustainable and efficient approach compared to the step-wise synthesis of 5-aza-adenines and their analogues. In general, the MCRs showed lower E-factors, higher atom economies and higher energy efficiencies. Quantification of the efficiency and sustainability of these chemical processes enables new avenues to be identified for the future improvement in these methodologies.

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Paper No. OR-0082

SUSTAINABLE SYNTHESIS OF NATURAL PRODUCTS FROM SUGARS

Congqiang Zhang[1], Xixian Chen[1], Sudha Devi[1], Nic Lindley[1], Heng-Phon Too[1,3]

1. Biotransformation Innovation Platform, Agency for Science, Technology and Research (A*STAR), Singapore
2. Department of Biochemistry, Yong Loo Lin School of Medicine, National University of Singapore, Singapore

Modern chemistry has been driven by green and sustainability. Compared to metal catalysts, biocatalysts are intrinsically green, sustainable, and superior in selectivity and flexibility. Here, we developed a microbial platform as a whole-cell bioreactor for effective conversion of sugars into various natural products. To overcome biological complexity in regulation and metabolic networks, we developed a multidimensional heuristic process (MHP). MHP provides a focused and systematic approach to balance the different modules (transcription) and within specific module (translation and enzymes). MHP adopts 'modular design' that significantly reduces experimental workload yet without losing the flexibility by simultaneously control different functional dimensions. Thus, MHP expands the dimensions in control and solution space and simultaneously improves resolution.

As a proof-of-concept, we effectively enhanced the production of the 15-step heterologous biosynthetic route of astaxanthin, a high-value carotenoid with multiple clinical benefits from glucose. Currently, this is the highest reported productivity (184 mg/L/day) and titer (320 mg/L), paving the way for a sustainable, commercial production of astaxanthin. In addition, we have successfully applied MHP to optimize other natural products, such as α and β-ionone (a C13 fragrance molecule) with a titer of 0.5 g/L in bioreactors, retinol (a C20, vitamin A) of 0.5 g/L in bioreactors, viridiflorol (C15 antimicrobial fragrance) of 1 g/L in flasks, nerolidol (C15 fragrance molecule) of 0.3 g/L in flasks, linalool (C10 fragrance molecule and pesticide) of 0.1 g/L in flasks. Collectively, these examples lend further evidence that MHP is an effective workflow for designing and optimizing complex biocatalytic systems to synthesize natural products sustainably.

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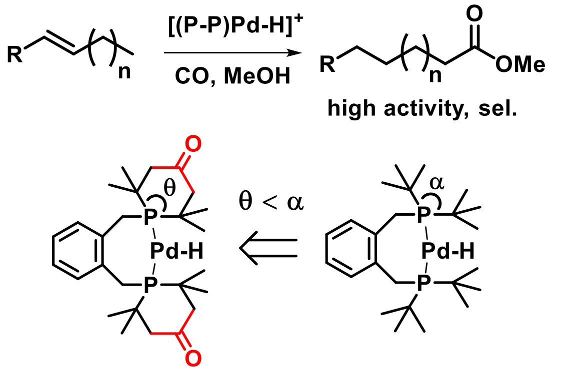
Paper No. OR-0087

TANDEM ISOMERIZING CARBONYLATION REACTIONS USING HETEROCYCLIC PHOSPHINE LIGANDS

Martin van Meurs,* James D Nobbs, Ludger P Stubbs, Cun Wang, Low Choon Heng, Eite Drent‡

Institute of Chemical & Engineering Sciences, Agency for Science Technology & Research, 1 Pesek Road, 627833 Singapore. ‡ Leiden University, Gorlaeus Laboratories, Einsteinweg 55, 2333 CC Leiden, the Netherlands
martin_meurs@ices.a-star.edu.sg

Phosphorus heterocycles have found applications in catalysis with often dramatically different properties compared to their acyclic analogues. In our recent work we have shown that bis(phosphorinone) ligands [1,2] produce a significantly more active isomerising methoxycarbonylation catalyst compared to its more well-known *tert*-butyl analogue (DTBPX) while at the same time maintaining a high selectivity to the terminal ester. This catalyst has been successfully applied to produce bio-derived monomers both from natural oil derivatives as well as cellulose-based platform chemicals.[3]



Sterically similar but electronically different ligands!

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Paper No. OR-0088

RATIONAL MUTAGENESIS OF STRUCTURAL HOT-SPOTS FOR ENHANCED SOLUBLE EXPRESSION AND ACTIVITY OF NON-MEVALONATE PATHWAY ENZYMES

Xixian Chen[1]*, Sudha Devi D/O Manbahal Shukal[1], Lim Chin Chin[1], Congqiang Zhang[1], Sebastian Maurer-Stroh[1,3], Heng-Phon Too[2]*

1. Biotransformation Innovation Platform (BioTrans), Agency for Science, Technology and Research (A*STAR), Singapore
2. Department of Biochemistry, Yong Loo Lin School of Medicine, National University of Singapore, Singapore
3. Bioinformatics Institutes (BII), Agency for Science, Technology and Research (A*STAR), Singapore

Increasing the metabolic flux through a biochemical pathway is highly desirable for metabolic engineering. One strategy is to enhance the solubility of overexpressed pace-making enzymes. Accurate theoretical prediction of target mutation sites is instrumental to reduce the experimental efforts and speed up the optimization process. In this study, the rate-limiting steps along the non-mevalonate (DXP) pathway, namely *E. coli* Dxs and IspG, were used as the model enzymes to learn and develop a set of bioinformatics tools that would enable rational optimization of enzyme solubility. Preliminary results shown that mutating the aggregation-prone sequences, identified by TANGO, would result in an increase in solubility. *In vivo* activity measurement suggested that SIFT score would be able to sieve out the non-tolerable amino acids to a certain extent. Taken together, the solubility of both Dxs and ispG were enhanced by ~2-fold without affecting their activities. The information gained would be useful for rational engineering of over-expressed pathway enzymes and improve pathway efficiencies.

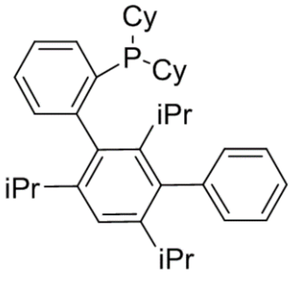
Paper No. OR-0095

CY*PHINE GOES SNORKELING: Pd CROSS COUPLING REACTIONS IN AQUEOUS MEDIA

Valerio Isoni*

Institute of Chemical and Engineering Sciences (ICES, A*STAR)
(1 Pesek Road, Jurong Island, Singapore 627833. *Email: isoniva@ices.a-star.edu.sg)

In recent years, evolutionary meta-terarylphosphine ligand Cy*Phine has been reported in literature to enable a series of palladium mediated reactions including Mizoroki-Heck, copper free Sonogashira, Suzuki-Miyamura, borylation and Buchwald-Hartwig type reactions.[1-3] Different protocols using organic solvents as reaction media are available in literature where reaction conditions have been optimized to demonstrate the performances against the state-of-the art ligands and catalysts in the respective reactions and/or reaction cascades. However, moving towards safer and more environmentally benign reaction media such as aqueous systems, we tested the waters with Cy*Phine for both copper free Sonogashira and Suzuki-Miyamura reactions. Four different commercially available additives were tested in water in combination with low palladium loadings in the range of 1000s ppm under mild conditions, achieving good to excellent yields. The results will be discussed more in details during the presentation.



Cy*Phine

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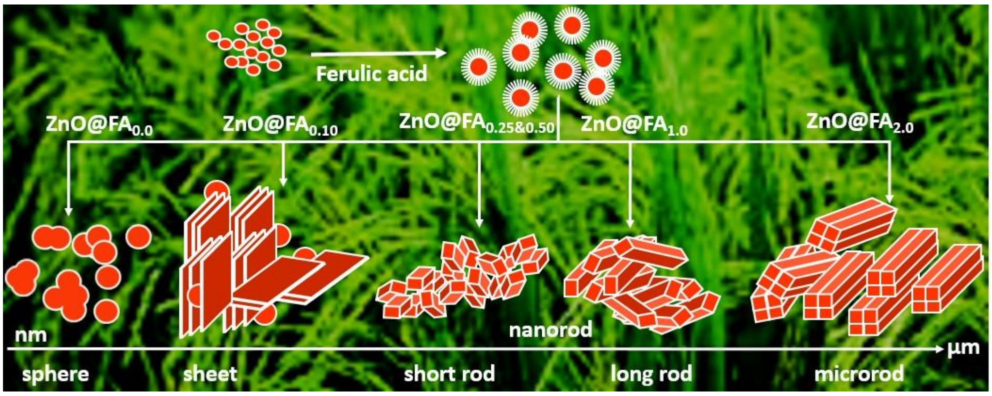
Paper No. OR-0104

FERULIC ACID FUNCTIONALIZED ZINC OXIDE ARCHITECTURES: A SUSTAINABLE SUNSCREEN

Vivek Arjunan Vasantha* and Anbanandam Parthiban

Institute of Chemical and Engineering Sciences (ICES),
Agency for Science, Technology and Research (A*STAR), Singapore 627833
E-mail: vivek_vasantha@ices.a-star.edu.sg

The effect of solar radiation on human skin can be deleterious causing sunburn, photoaging, erythema, and inflammation.[1] Due to these facts, sunscreen substances (organic and inorganic UV filters) are now incorporated into everyday products such as creams, lotions, and skin preparations. The sunscreen incorporated materials may help to reduce the chance of the harmful effects of UV-B and UV-A through blocking, reflecting and scattering sunlight. However, to achieve broad spectrum, use the high level of actives – the problem arises such as limited range of UV spectrum, aesthetic, whiteness, and photocatalyst (react with other chemicals). [2] Here we have designed the greener approach for fabricating zinc oxide (ZnO) architectures using bio-derived ferulic acid. Ferulic acid (FA) acting as structural direction and capping agent for tunable ZnO nanostructure via the solvothermal process.[3] The optical behavior and sunscreen performance of functionalized ZnO-FA was investigated. The result suggests that ZnO-FA have strong absorption and the high degree of UVA protection (λcric= 388 nm) with unique antioxidant, and suppressed photocatalytic activity. The sustainable UV filters for the broad range of solar spectrum through encapsulation will also be highlighted in the presntation.[4]



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Paper No. OR-0106

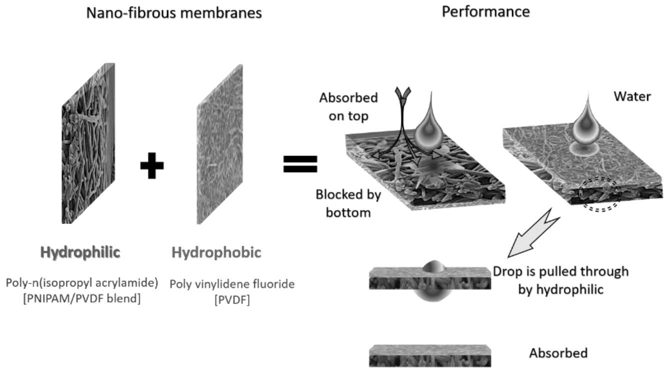
ELECTROSPUN JANUS MEMBRANE: PUSHING THE PERFORMANCE LIMITS

Anupama Sargur Ranganath*, Avinash Baji

Division of Engineering Product Development, Singapore University of Technology and Design (SUTD), Singapore - 487372

Membrane technology has been researched extensively to improve the performance by leaps and bounds since its first advent in early 1900 [1]. Intensive research on the membrane science has achieved constant improvement in the performance. However, there is always a quest for new ways of improvement, which increases efficiency and energy consumption. We show the development of the Janus structure by combining in-compatible chemistry that provides new direction to the membrane science and technology.

Janus membrane with opposite chemistry on either side has attracted immense attention during recent years for its unique functionalities in directional water flow and oil spill cleanup [2, 3]. The most popular one is a separation of the oil-water emulsion with a switchable performance that selectively allows one of the liquids to transmit through. However, the influence of physical properties, such as Janus thickness on functionality is yet to be fully understood. Properties of water diode, unidirectional water flow is unique to Janus membranes. Our research studies the influence of Janus thickness on the water diode, and oil-water separation under gravity. We electrospun the Janus construct using polyvinylidene fluoride (PVDF) and its blend with poly-n-isopropylacrylamide (PVDF/PNIPAM). For a successful water diode, the membrane requires a critical thickness of PVDF and no air gap between hydrophobic and hydrophilic. It is interesting to observe that the water diode functions even when the thickness of the hydrophobic is greater than hydrophilic. In oil-water separation experiments, the effect of Janus structure on the pure water transmission became evident with applied pressure difference across the membrane. This structure had twice the separation efficiency and the flux than the blend membrane alone, which is the functional component of the system.



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Paper No. OR-0107

IRON- AND COBALT-CATALYSED CROSS-COUPLING REACTIONS

Wenqin Wu,[a] Qiaoqiao Teng,[b] Yi-Yuan Chua,[a] Han Vinh Huynh,*[b] Hung A. Duong*[a]

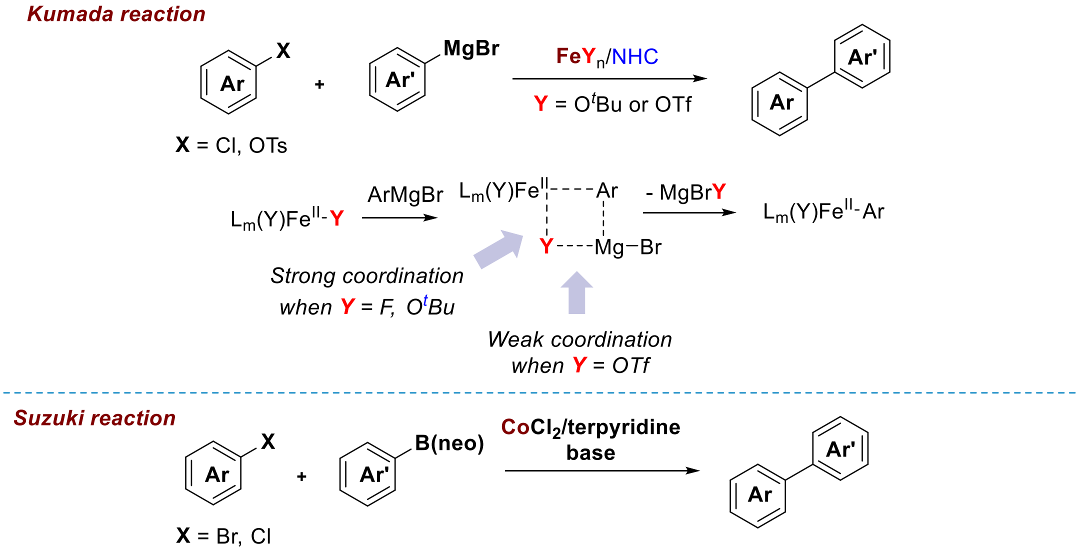
[a] Institute of Chemical and Engineering Sciences (ICES, A*STAR)
duong_hung@ices.a-star.edu.sg;

[b] Department of Chemistry, National University of Singapore
chmhhv@nus.edu.sg

The palladium-catalysed cross-coupling reactions have become an indispensable tool in contemporary organic synthesis. There has been, however, a strong interest in replacing palladium with base metals in these reactions due to their great abundance and inexpensiveness. We are in particular interested in developing iron and cobalt catalysts for aryl-aryl coupling since biaryls constitute a prevalent structural motif in numerous natural products, pharmaceuticals and materials.

We have explored the effect of the counterion of iron and the stereoelectronic properties of *N*-heterocylic carbene ligands in the iron-catalysed Kumada cross-coupling reaction. The understanding obtained led us to establish highly efficient iron catalyst systems for the coupling of aryl Grignard reagents with aryl chlorides and tosylates.[1]

While iron and cobalt catalyst are well-studied in the Kumada and Negishi reactions, much less success has been achieved in the Suzuki-Miyaura reaction, presumably due to the difficulty associated with transmetalation from boron to these metals. We recently discovered a cobalt/terpyridine catalyst system that enables the coupling of a broad range of aryl halides and aryl boronic esters.[2]



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Paper No. OR-0108

BIO-DERIVED MATERIALS FOR UV BLOCKING APPLICATIONS

Balamurugan Ramalingam,[1]* Lim Jieyan,[1] Ranganathan Krishnan,[1] Nguyen Tuan Minh[1]
Satyasankar Jana,[1] Jayasree Seayad[1] and Farid John Ghadessy[2]

[1] Institute of Chemical and Engineering Sciences, 8 Biomedical Grove, Singapore 138648
[2] p53 Laboratory, 8A Biomedical Grove, Singapore 138 648

Protection of materials against photo-degradation from natural or artificial light is important for sunscreen, coating, packaging and plastic industries. To address this technological challenge, small organic compounds (SOCs) such as benzophenones, triazines and benzotriazoles are added as UV stabilizers to maintain the performance of the materials. However, synthetic SOCs are prone to leaching or skin penetration leading to environmental and/or health hazards. To address this common problem, we have developed a new series of oligomeric and bio-derived UV blocking oligomers that are potentially less vulnerable to leaching and skin penetration.

The bio-derived oligomeric materials were obtained by laccase catalyzed oxidative polymerization[1] of lignin model compounds and natural phenols under environmentally benign reaction conditions. The oligomers were characterized by matrix-assisted laser desorption ionisation time of flight mass spectroscopy (MALDI-TOF-MS) analysis and gas permeation chromatography (GPC). The oligomers exhibited good UV absorbing properties with high molar extinction coefficients. Analysis of the oligomers indicated that the oligomerization mainly occurs through C5-C5′ linkages, one of the linkages present in the lignin. The oligomers were blended with commercial polymers such as polyvinyl chloride (PVC) and polystyrene to evaluate the compatibility and photostability. The oligomer embedded films found to exhibit good UV blocking characteristics[2] and their potential application as UV stabilizers was demonstrated. It was also established that the oligomers show minimum leaching from the formulated polymers under various food simulants tested.

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Paper No. OR-0111

GREEN AND SUSTAINABLE PRODUCTION OF ACRYLIC ACID FROM LACTIC ACID

Lili Zhang,[a] De Sheng Theng[a] , Feng Gao[a], Lin Huang[a], Chuan Wang[b], Luwei Chen[a] and Armando Borgna*[a]

[a]Institution of Chemical and Engineering Sciences, A*STAR (Agency for Science, Technology and Research), 1 Pesek Road, Jurong Island, Singapore 627833

[b]Institution of Advanced Synthesis, Nanjing Tech University, China.

Email: Armando_Borgna@ices.a-star.edu.sg

Shifting from fossil fuels to biomass derived feedstocks for the production of valuable chemicals has been an important aspect in heterogeneous catalysis for achieving sustainable and environmentally friendly processes. Acrylic acid, a widely used commodity chemical in the manufacture of paint additives, adhesives, textiles and super-absorbent materials, is mainly produced from petrochemical industry nowadays by partial oxidation of propylene. The general drawback of this route is the total dependence on the nonrenewable fossil resource. Therefore, finding an alternative and sustainable route to produce acrylic acid would be of great importance. In this regard, we have developed efficient catalysts capable to achieve high yield of acrylic acid from dehydration of lactic acid. Alkali and alkaline-earth metal cation modified zeolites have been systematically studied as catalysts for gas-phase dehydration of lactic acid to acrylic acid. Long-term reaction-regeneration cycles, reaction and deactivation mechanisms have been investigated. The strong acidic adsorbate/catalyst surface interaction (base property), hydrothermal stability and the acidity of the catalyst are responsible for the catalyst deactivation. The formation of a stable intermediate shifts the dynamic equilibrium to the dehydration reaction. A high AA selectivity of ~ 84% with 100% LA conversion is obtained while the AA selectivity reaches 82% with 100% LA conversion after four consecutive long-term reaction-regeneration cycles [1].

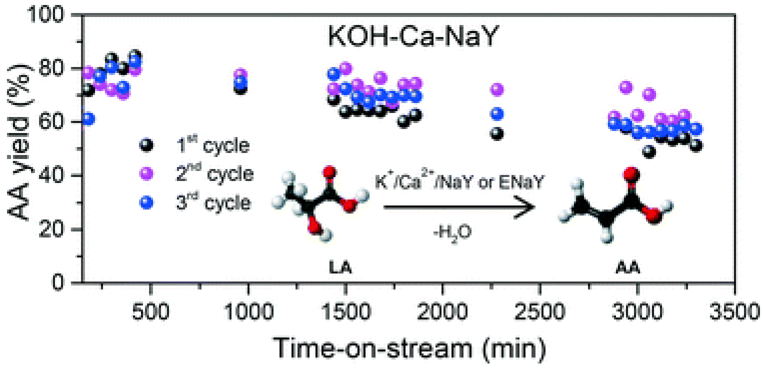

Figure. Long-term reaction-regeneration cycles of modified zeolite catalyst

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Paper No. OR-0120

THE SYNTHESIS OF MALEIC ACID/ANHYDRIDE FROM RENEWABLE BIOMASS

Xiukai Li, Yugen Zhang*

Institute of Bioengineering and Nanotechnology, 31 Biopolis Way, The Nanos #08-01(J), Singapore 138669, Singapore. Email address: xkli@ibn.a-star.edu.sg; ygzhang@ibn.a-star.edu.sg

Maleic acid (MA) and its anhydride (MAnh) are important intermediates in chemical industry that represent millions of tons of market demands. The synthesis of MA and MAnh from renewable biomass resources such as furfural and 5-hydroxymethylfurfural (HMF), which can be derived from cellulosic biomass, is highly desirable for the sustainability. Most of the reported processes for MA/MAnh synthesis from biomass suffer from low efficiency, complicated conditions and poor catalyst recyclability. In this talk, we demonstrate several heterogeneous catalytic systems (batch or continuous gas phase reactions) for the synthesis of MA and MAnh from HMF and furfural.

In heterogenous catalytic systems using supported or unsupported vanadium oxide catalysts, up to 79% yield of MA was achieved from HMF under 5 bar of oxygen. The one-pot two-step conversion of fructose to MA via the HMF intermediate in this system afforded 50% overall yield of MA. The vanadium oxide catalysts are recyclable for several times. Furfural is a cheaper starting material than HMF. With heterogenous Mo-V-O catalysts and 20 bar of O_2 as oxidant, about 65% yield of MA was achieved for furfural oxidation in acetic acid solvent. The catalysts could be recycled; the leaching of the vanadium species into the solution was observed. To solve the problem of poor catalyst recyclability in the batch conversion of furfural and HMF, a catalyst-free system was developed. In this simple system which requires only H_2O_2 as an oxidant in formic acid solvent, an excellent yield (95%) of MA was achieved under mild conditions (RT to 100 °C). Under similar conditions, good yield (89%) of MA was achieved from HMF. The continuous flow gas phase reactions have some advantages over the batch reactions. We developed a plate vanadium phosphorous oxide (VPO) catalyst for furfural oxidation to MAnh in gas phase. The plate VPO catalyst has a preferentially exposed 200 crystal plane and exhibited enhanced activity, selectivity and stability as compared to conventional VPO catalysts and other state-of-the-art gas phase catalytic systems. At 360 °C reaction temperature with air as an oxidant, about 90% yield of MAnh was achieved at 10 vol% of furfural in the feed, a furfural concentration that is much higher than those (< 2 vol%) reported for other catalytic systems. The catalyst showed good long term stability and there was no decrease in activity and selectivity for MAnh in the time-on-steam duration of 25 h.

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Paper No. OR-0122

DEHYDRATIVE ALLYLATION USING ALLYL ALCOHOL IN THE PRESENCE OF METAL OXIDE CATALYST

Yoshihiro Kon, Tadahiro Fujitani, Takuya Nakashima, Toru Murayama, Wataru Ueda*

Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.
Institute for Catalysis, Hokkaido University, N21W10, Sapporo, Hokkaido 001-0021, Japan.
Research Center for Gold Chemistry, Tokyo Metropolitan University, 1-1-F203 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan.
Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University, 3-27, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan.

Allyl compounds are widely used as important building blocks of value-added chemicals that are indispensable to our daily life. A synthetic method that can form various allyl compounds is needed to obtain wide varieties of functional chemicals. Due to growing demand for environmentally benign organic synthesis[1], allyl alcohol is known as one of the best substrates for allylation because it is a source of other allylating agents such as allyl esters or allyl carbonates. In recent years, such a process has been reported using homogeneous catalysts (Pd, Ru, Pt, Ni).[2,3] However, homogeneous catalysts are soluble in the reaction solution and it is difficult to reuse the spent catalyst. Therefore, it is needed to use a reusable heterogeneous catalysis that can be applied to a wide variety of substrates for the efficient synthesis of allyl compounds.[4]

We demonstrate a sustainable method to synthesize allyl ethers and/or allyl amines from allyl alcohol with various substrates over a 90% yield in the presence of titanium oxide supported molybdenum oxide catalyst (MoO_3/TiO_2), with water as the sole by-product. [5] To the best of our knowledge, the development of MoO_3/TiO_2-catalyzed dehydrative allylation of alcohol and/or amine was proposed as the first high-yielding synthetic method to produce various allyl amines using a MoO_3 solid catalyst. The developed catalytic reaction was applicable to various alcohols and amines, and MoO_3/TiO_2 catalyst was easily reused without decreasing its catalytic activity. This catalyst shows excellent catalytic activity by virtue of the highly dispersed nature of MoO_3 supported on TiO_2, which is reusable at least five times. In this reaction, the nucleophilic attack of substrate to allyl molybdenum species on the surface of MoO_3/TiO_2 might be a key step to achieve the highly selective dehydrative allylation under heterogeneous reaction conditions.

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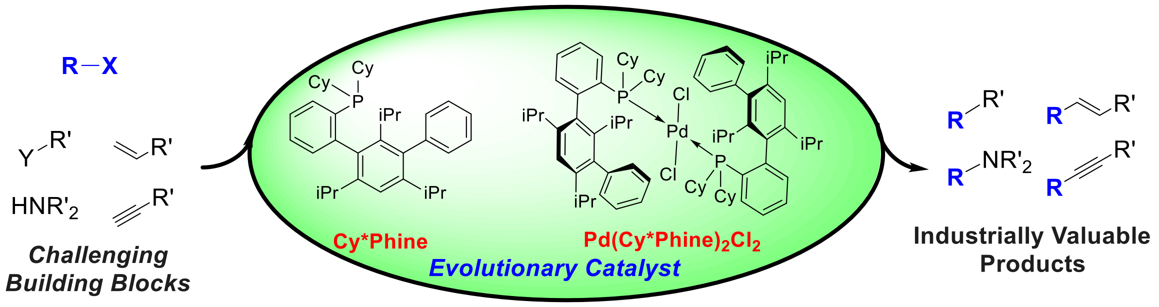
Paper No. OR-0123

DESIGN & APPLICATION OF A PALLADIUM CATALYST WITH MULTI-ARYL PHOSPHINE LIGAND FOR CROSS-COUPLING REACTIONS

Yee Hwee Lim,[a]* Howard Jong,[a] Yong Yang,[a] Fui Fong Yong,[a] Adrian M. Mak,[b] Daniel Weiliang Tay,[c] Wenqin Wu,[a] Xinying Chew,[a] Edward G. Robins,[c] Michael B. Sullivan,[b] Charles W. Johannes[a]

[a]Organic Chemistry, A*STAR Institute of Chemical and Engineering Sciences (ICES);
[b]A*STAR Institute of High Performance Computing (IHPC);
[c]A*STAR Singapore Bioimaging Consortium (SBIC)
lim_yee_hwee@ices.a-star.edu.sg

Cross-coupling reactions are one of the most versatile and valuable transformation to forge chemical bonds efficiently. After decades of development, there are many catalysts capable of this feat but few catalyst systems exhibit both effectiveness and versatility. A couple of years back, our group uncovered impactful evolutionary design element in the ligand architecture that enabled the catalyst performance and scope to surpass many of the modern phosphine-based palladium systems. Herein, the presentation will describe the conceptualization, insights and development of a *meta*-teraryl architecture based ligand, Cy*Phine and its application in multiple palladium-catalyzed cross-coupling reactions including the copper-free Sonogashira coupling,[1,3,5] the Mizoroki-Heck reaction[2] and the Buchwald-Hartwig[7] amination. Both experimental and computational[4,7] evidence will be presented to rationalize the tangible catalytic enhancements. Finally, an example a one-pot, cross-coupling treble of borylation, Suzuki, and amination[6] will be highlighted to showcase how the insights may help catalyst selection and can be leveraged to develop novel reaction sequences.



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Paper No. OR-0126

CARBENE-CATALYZED NEW ACTIVATION MODE AND SYNTHETIC APPLICATIONS

Xingkuan Chen，Yonggui Robin Chi

[1]Nanyang Technological University, Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, Singapore 637371, Singapore

Breakthroughs in methodology development often come from the discoveries of new basic activation modes. For instance, a new intermediate can subsequent lead to the development of many reactions. The field of N-heterocyclic carbene organic catalysis has primarily focused on the activation of non-aromatic carbon atoms in acyclic/non-aromatic aldehydes (Figure 1 on the right). Several intermediates and many reactions based on these intermediates and the reactive carbons have been developed. In contrast, little is known for (a) activation of aromatic sp2-carbon or benzylic sp3-carbons and (b) activation of hetero atoms for asymmetric reactions. It remains challenging for the stereo-electronic power of the carbene catalyst to go across the conjugated bonds of the aromatic frameworks to induce activation and selective reactions.

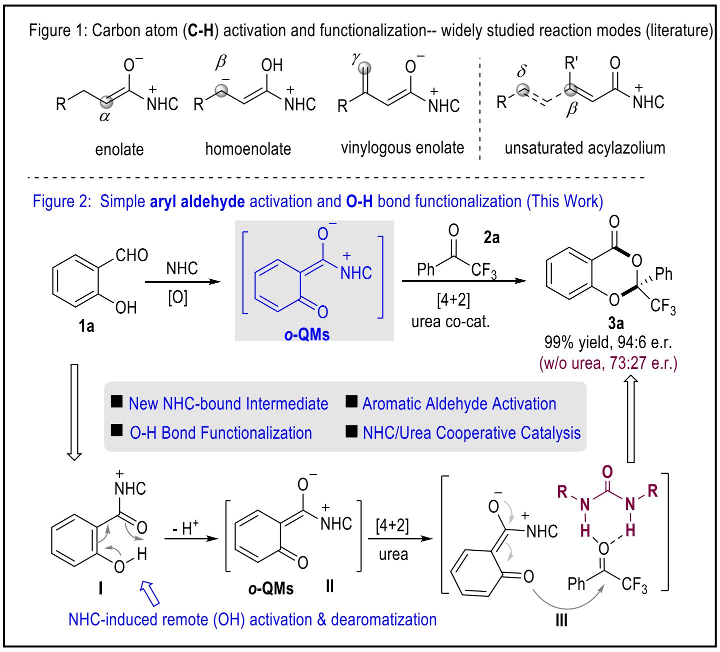
Figure 1: Carbon atom (**C-H**) activation and functionalization-- widely studied reaction modes (literature)

Figure 2: Simple **aryl aldehyde** activation and **O-H** bond functionalization (This Work)

Here we report a new mode of carbene catalysis that allows for aromatic aldehyde activation and remote oxygen atom functionalization (Figure 2). The addition of a carbene catalyst to the aldehyde moiety of a 2-hydroxyl aryl aldehyde eventually enables dearomatization and remote OH activation. The catalytic process generates a new type of carbene-derived intermediate with an oxygen atom as the reactive center (azolium-bound ortho-quinone methides intermediate II (o-QMs), Figure 2). Inexpensive achiral urea co-catalysts work cooperative with the carbene catalysts, leading to consistent enhancements of the reaction enantioselectivities.

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Paper No. P-0019

APPLICATION OF MICROWAVE-CARBOCATALYSIS FOR BIOMASS UTILIZATION

Elaine G. Mission[1], Armando T. Quitain[2,3]*, Mitsuru Sasaki[3], Tetsuya Kida[4]

[1]Graduate School of Science and Technology
[2]Faculty of Advanced Science and Technology
[3]International Research Organization for Advanced Science and Technology
[4]Institute of Pulsed Power Science
Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555, Japan
* Corresponding author: Fax: 81-96-342-3679, E-mail: quitain@kumamoto-u.ac.jp

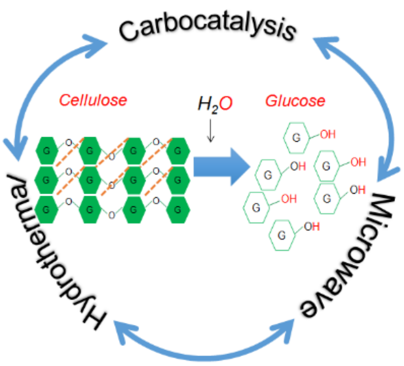

Figure 2 Synergism of MIcrowave, carbocatalysis and pressurized water

Introduction. Significant attention has been accorded to lignocellulosic biomass (LCB) as a cheap and stable resource for the synthesis of biochemical and biofuels precursors. Its valorization offers not only a wide array of platform molecules, but also the reduction of carbon dioxide being emitted into the atmosphere due to open burning. However, the rigidity and recalcitrant structure of cellulose due to an extensive hydrogen network in its surface poses a major barrier towards hydrolysis. Pursuant to a green, sustainable, energy efficient and environmentally benign biomass conversion process, we leveraged the synergism between graphene-based catalysts and microwave irradiation (MW) for one-pot microcrystalline cellulose (MCC) depolymerization process with water as the sole solvent (Fig. 1). The findings reported herein provided insights on the utilization of carbon-based catalysts and their appropriate design that would be crucial in extending the technology to other biopolymers and reaction pathways towards a biobased economy.

Results and Discussion. In synergy with MW, graphene oxide (GO) thru the oxygenated functionalities on its surface, overcame the extensive hydrogen bonding networks which protected the β-glycosidic bond, as evidenced by the reduction in post-reaction crystallinity index (from 68 to 60) and crystalline sizes (from 5.3 to 4.5 nm) of MCC. MW facilitated conformational changes for effective molecular interaction and delivering the necessary energy to cleave the hydrolytic bond, significantly cutting down reaction time and energy use. With the optimization of process parameters, MCC was efficiently hydrolyzed into glucose with a yield 61% at 453 K, 200 W and 60min, following the surface attrition mechanism as observed via scanning electron microscopy. With fewer surface functionalities, we integrated reduced GO (rGO) with MW-subcritical water, to avoid functionalization with strong acids. The hydronium/hydroxyl ion concentration under subcritical conditions is high enough to facilitate acid-base reactions. For example, by elevating the temperature to 493 K and 513 K, additional 13% and 22% glucose was obtained bringing the overall yield to ~74% and 83%, respectively, with a 5 min holding time. The shorter reaction time compensates for the high reaction temperature. The MW-GO synergism was also applied to the esterification of fatty acids. Under this process, 99.2 % fatty acid methyl ester was achieved at 3 min, methanol/oleic acid molar ratio of 12. The carbon backbone of GO has potentially adsorbed the oleic acid which enabled the highly reactive methanol to easily access the oleic acid's carboxylate head towards alcoholysis.

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Paper No. P-0030

CE-SILICALITE-1/PDMS COMPOSITE MEMBRANE IN ISOPROPYL ALCOHOL RECOVERY: THE ROLE OF CERIUM IN AFFECTING MEMBRANE HYDROPHOBICITY AND PERFORMANCE

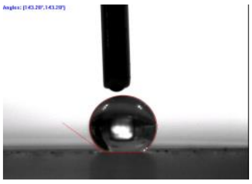
Eng Toon SAW[1], Kun Liang ANG[1], Wei HE[1#], Xuecheng DONG[1]*, Seeram RAMAKRISHNA[2]

*1 Singapore Institute of Manufacturing Technology, A*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, Singapore 138634
2 Department of Mechanical Engineering, Faculty of Engineering, National University of Singapore, Blk EA, #07-35, 9 Engineering Drive 1, Singapore 117576

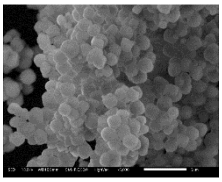
*Corresponding Author 1; #Corresponding Author 2
Email address: xcdong@simtech.a-star.edu.sg; hewei@simtech.a-star.edu.sg

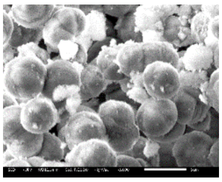
Solvent recovery has been a common practice in most of the Active Pharmaceutical Ingredient (API) manufacturing sites when the recovery process is technically feasible, economically justified and acceptable product quality. Isopropyl alcohol (IPA) is a generally used solvent in pharmaceutical industries with the composition of 10 to 20% present in the effluent of solvent waste [1]. In general practice, solvent waste is incinerated without undergo solvent recovery process due to the low feasibility of current biological treatment technology as solvent is toxic to microbes. Additionally, the high disposal cost and environmental pollution concerned have drawn significant interest to recover IPA in the solvent waste or wastewater stream. To recover IPA in the solvent waste, membrane pervaporation process is considered as a promising technology owing to the low energy intensive, low cost and low footprint. At present, based on the literature data, the membrane separation performance is still not met the commercialization stage. It is essentially needed to develop an IPA selective membrane to increase the membrane separation performance. Cerium element is chosen due to the selective adsorption of IPA on CeO_2 (100) surface based on DFT calculations [2].

In this study, cerium element is substituted into silicalite-1 zeolite particle to increase IPA selective adsorption and increase hydrophobicity to recover IPA from aqueous solution. A series of Ce-substituted silicalite-1 zeolite was synthesized and used as selective adsorption filler. The zeolite particle was dispersed into PDMS (Polydimethylsiloxane) as filler. It was observed that with cerium substituted into silicalite-1 zeolite particle, causing the unit cell of silicalite-1 crystal lattice expansion. Furthermore, the substituted of cerium into silicalite-1 zeolite resulting the increase of zeolite particle size drastically with high loading of cerium. In addition, it causes the water contact angle to increase from ~117° (only PDMS) to ~143° with 20wt% of zeolite loading. This provides a good indication of the potential of IPA-water separation based on hydrophobicity properties and selective adsorption of cerium.


Water CA: ~143°


IPA CA: ~0°


Silicalite-1


Ce-Silicalite-1

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Paper No. P-0032

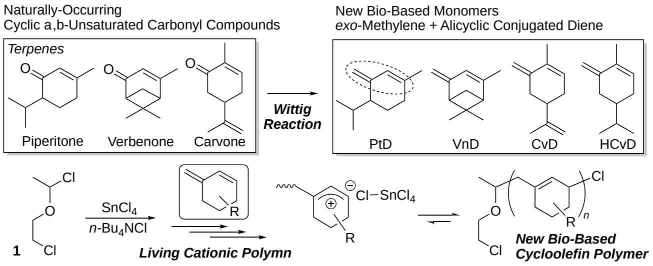
LIVING CATIONIC POLYMERIZATION OF VARIOUS ALICYCLIC CONJUGATED DIENES WITH A REACTIVE EXO-METHYLENE GROUP DERIVED FROM NATURALLY-OCCURRING TERPENES

Takenori NISHIDA, Kotaro SATOH, Masami KAMIGAITO*

Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusaku, Nagoya 464-8603,
nishida@chiral.apchem.nagoya-u.ac.jp

We have reported the synthesis of various bio-based polymers via the polymerization of naturally-occurring terpenes.[1] The cyclic terpene-based polymers exhibited good thermal and optical properties as renewable cycloolefin polymers.

In this work, we focused on naturally cyclic terpenes bearing α,β-unsaturated carbonyl groups as raw materials for novel bio-based cycloolefin polymers. The carbonyl compounds were converted into alicyclic conjugated dienes possessing a reactive *exo*-methylene group (Scheme 1). The cationic polymerizations were investigated by the initiating systems for the living polymerization of vinyl ethers. In addition, properties of the obtained polymers were also evaluated as cycloolefin polymers.



Scheme 1. Synthesis and Living Cationic Polymerization of New Bio-Based Conjugated Dienes Derived from Naturally-Occurring α,β-Unsaturated Carbonyl Compounds

The bio-based diene monomers (PtD, VnD, CvD) were prepared via Wittig reaction from naturally-occurring α,β-unsaturated carbonyl compounds, such as piperitone, verbenone, and carvone. HCvD was synthesized by selective hydrogenation of the pendent olefin in carvone prior to Wittig reaction. Living cationic polymerization of these dienes was then examined using the **1**/$SnCl_4$/*n*Bu_4NCl system, which is efficient for the polymerization of vinyl ether and a similar naturally-occurring conjugated diene, β-phellandrene (β-Phe).[2] All the monomers were consumed, whereas the polymerization rate depended on the structures. Although CvD resulted in gel at the later stage of the polymerization owing to the unconjugated pendent olefin, the SEC curves of the obtained polymers showed narrow distributions, suggesting that living cationic polymerizations proceeded (Figure 1). By DSC analysis, the glass transition temperatures (T_g) of the polymers were higher than that of poly(β-Phe) in our previous report.

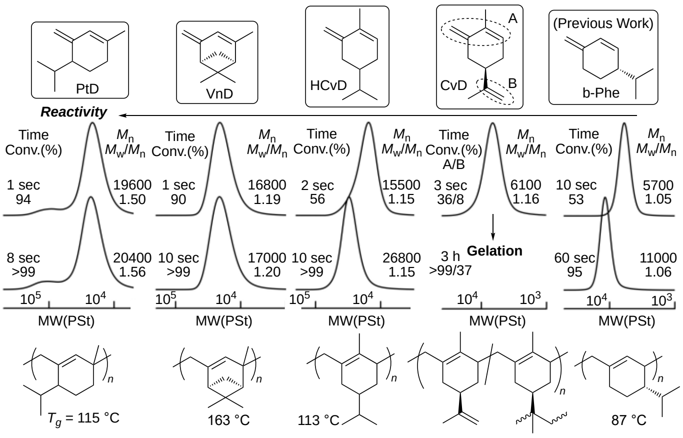


Figure 1. Living cationic polymerization of monomers: $[M]_0/[\mathbf{1}]_0/[SnCl_4]_0/[nBu_4NCl]_0$ = 100/1.0/5.0/4.0 mM, toluene/CH_2Cl_2 (1/1), −78 °C.

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Paper No. P-0038

THE EFFECTS OF SOLVENTS ON THE LIQUID PHASE DECOMPOSITION OF WASTE TIRES

Daisuke Yamashita[1], Keizo Akutagawa[2], Masahiro Hojo[2], Katsuaki Hironaka[2],
Hideyuki Tagaya[1*]

[1] Yamagata University, Yonezawa, Yamagata, Japan
[2] Bridgestone Corporation, Kodaira, Tokyo, Japan

In recent years, the number of waste tires has been increasing. Currently, recycling of waste tires is subject to thermal decomposition and conversion to liquid fuels. However, this method is expensive because of the operation at high temperature (~400 °C). As a result, these waste tires are burned without heat recovery and landfill. These treatments may adversely affect the environment in the future. It is also expected that the world population will increase and resources will be consumed. To keep resources is needed. The tire is composite and composed mainly of a part directly contacting the ground and the other part having a role to support the original shape of the tire. In addition, additives such as carbon black which is the stable material chemically for increasing the durability of the tire, and sulfur and vulcanization accelerator which increase the durability by crosslinking are also included. Further, the inside of the tire contains metal such as wires for reinforcing the tire, glass fibers and the like. Due to the complicated combination of such various materials, it is not easy to recycle. And in order to decompose to recover organic materials, it is necessary to treat it at high temperature at around 400 °C or higher, so it is not recycled from the current cost and environmental aspects. In this research, we aimed to investigate new recycling technology on the liquid phase treatment of waste tires and to obtain basic knowledge on effective treatment solvents and the reaction time. Reactions were carried out by using a tubing bomb reactor. Waste tire samples were charged into the reactor with solvent. Then, they were poured into an image furnace set to a predetermined temperature in advance, and heated at reaction temperature for predetermined time. The recovered material was subjected to suction filtration to separate products into a solid residue and a liquid recovered substance. The solid residue was sufficiently dried, and thermogravimetric analysis was performed. The liquid recovered materials, was subjected to GC and GC-MS analysis. Polymeric materials were measured by GPC analysis to determine the molecular weight distribution. TG results suggested that the waste tire is composed of rubber component with different thermal decomposition temperatures such as natural rubber, isoprene rubber, and styrene butadiene rubber. High conversion was attained in most solvents at a high temperature of 430°C. In this study possibility of new recycling technology of waste tire is shown.

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Paper No. P-0039

PREPARATION OF ORGANIC-INORGANIC NANOHYBRIDS BY THE REACTION OF METAL HYDROXIDE WITH ORGANIC COMPOUNDS.

Akane Sato, Maika Kikuchi, Hideyuki Tagaya*

Graduate School of Science and Engineering, Yamagata University, Japan

Preparation of organic-inorganic complexes were widely researched because they have many applications as attractive functional materials. We have already succeeded to prepare layered organic-inorganic nano composite by the self-assembly reaction of metal hydroxide with organic carboxylic acid. Inorganic molecular parts provide thermal stability and crystalline to organic polymer compounds which is used in various way. We have already prepared organic-inorganic complexes with carboxylic acid and zinc hydroxide. We can control the complexes' structure by varying organic compounds. In this study, metal hydroxide and alcohol were mixed in an air atmosphere, and mixture was stirred for 5h at 70°C. We can prepare organic-inorganic complexes with phenols which have chloro groups. Products were dried under reduced pressure during 3 to 4 days. The dried samples were analyzed by TG, XRD and SEM analyses. The TG pattern of these products show improvement of heat resistance. In the XRD analysis, new peaks were confirmed. In the SEM images, structures of obtained compounds were different with raw materials and fiber-formed structure was confirmed. These results suggest the complexes with metal hydroxide and phenol which has chloro groups have different structure from the complexes with metal hydroxide and carboxylic acid. Based on these result, we use aliphatic alcohol instead of chloro phenols. The reaction was suggested to advance.

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Paper No. P-0040

RECYCLING OF COMPOSITE PLASTIC MATERIALS

Shiori Yokoo, Mayuko Ishita, Nobeya Sugaya, Hideyuki Tagaya*

Graduate School of Science and Engineering, Yamagata University, Yonezawa, Japan

Recycling of waste materials is environmentally benign process on green chemistry. Laminated film is used as packaging materials such as for medical supplies and foods. The film contains some organic polymer materials and Al metal layer. They are useful materials, however the film wastes have no effective recycle method because it is not easy to separate the film into Al metal layer and organic parts. Therefore, they are mainly incinerated and landfilled. In this study, extraction operation and solvent treatment for chemical recycling of the films were carried out. By the measurement of SEM images, it was confirmed three-layer structure and thickness was 80-130 micrometer. Thermal analysis showed the film have polyolefin and polyester. The residue left by thermal analysis was Al metal and the residue reached to 10-20%. In Soxhlet extraction by cyclohexane, it was shown that part of the organic matter dissolved. However, it did not lead to perfect separation. The solvent treatment with the bio-based solvent was effective for separation at the heat treatment at 80 °C. By this treatment, the polyolefin layer was effectively separated. Also, solvent treatment was easier to detach than Soxhlet extraction.

Diapers are also composite materials. The diaper market in the world grows year by year. Diapers contain various components so its treatment method is mainly incineration and there is no effective recycling method. In this research, diaper is also treated.

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Paper No. P-0041

THE LIQUID PHASE DECOMPOSITION OF RUBBER WASTES

Itsuki Oyama[1], Daisuke Yamashita[1], Keizo Akutagawa[2], Masahiro Hojo[2],
Katsuaki Hironaka[2], Hideyuki Tagaya[1*]

[1]Graduate School of Science and Engineering, Yamagata University, Yamagata, Japan
[2]Bridgestone Corporation, Kodaira, Tokyo, Japan

The production of polymer materials has been increasing rapidly since the 1950's, and it exceeded 335 million tons in 2016. Therefore, the recycling of polymer wastes has attracted great interest. Thermosetting resin especially cannot be recycled mechanically even after separation because the resin dose not melt at the molding process. It is considered that disposal by burning and landfill of the resin has a negative influence on the environmental. Organosilicon polymers such as silicone rubber have been produced several million tons for a year and the polymer wastes have caused same issues with other polymers. Therefore, the development of recycling technology which is friendly to the environment is expected. In this study, rubber wastes such as waste tire and waste silicone rubber were treated in high temperature liquid phase. In the typical reaction, rubber wastes were treated with solvents in the absence or presence of additives by using 10cc autoclave. After the reaction, obtained solid residue was weighed to calculate solubilization and measured by TG and FT-IR. Solubilization depended on the solvent, temperature and reaction time. Anyway, solubilization occurred at the temperature lower than 350°C indicating that the carbon-carbon bond scission producing radicals was not important and suggests that the solvolysis reaction was important.

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Paper No. P-0042

SOLVENT TREATMENT AND CHEMICAL RECYCLING OF COMPOSITE WASTE PLASTIC FIBER

Nobuya Sugaya, Hideyuki Tagaya*

Graduate School of Science and Engineering, Yamagata University, Yonezawa Japan

Recycling of waste materials is environmentally beneficial process on green chemistry. Composite plastic fiber materials are blended materials of different thermal properties and functionalities such as polyolefin and polyester containing polyethylene terephthalate (PET). Various functionalities and strong strength are realized by these mixtures, and these composite fibers are used as insulation and sound absorbing material such as for car interior and clothes. However, it is difficult to separate the fibers because different fibers are complicatedly entangled. In this study, solvent treatment for chemical recycling of the fiber wastes was carried out.

The presence of two endothermic peaks were confirmed at near 150 °C and at 250 °C by TG-DTA of the fiber samples. Melting of each fiber was confirmed at that temperature by melting point measurement. It was found that about 25 micrometer and 10 micrometer thickness fibers are tangled from the SEM images. We attempted separation by extracting these components using Soxhlet extraction apparatus at distillation temperature for 3-12h. During the Soxhlet extraction, polymer fiber solubilized and white extraction residue was recovered by the distillation of solvent. 12h was effective to separate different components in the treatment at high temperature. Organic and terpene type solvents were particularly effective in this treatment, however, reduction of reactivity was confirmed by stirring at a lower temperature. This treatment of the composite waste plastic fiber is effective and contribute to green chemistry sufficiently.

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Paper No. P-0043

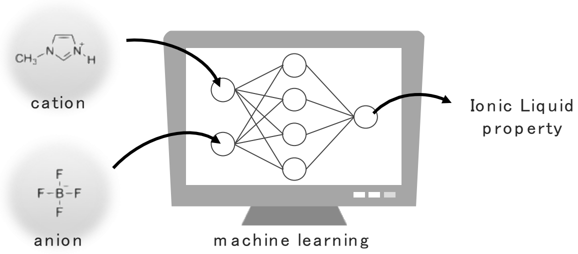
EXPLORING IONIC LIQUIDS FOR EFFICIENT CO_2 CAPTURE AND STORAGE BY ELECTRONIC STRUCTURE CALCULATION AND MACHINE LEARNING

Nahoko KUROKI,*,1 Hirotoshi MORI*,2

[1] Department of Chemistry and Biochemistry, Graduate School of Humanities and Sciences,
Ochanomizu University, 2-1-1 Otsuka, Bunkyo-ku, Tokyo 112-8610, Japan
[2] Faculty of Core Research Natural Science Division,
Ochanomizu University, 2-1-1 Otsuka, Bunkyo-ku, Tokyo 112-8610, Japan

*E-mail: g1670603@edu.cc.ocha.ac.jp, mori.hirotoshi@ocha.ac.jp

Ionic liquids are non-volatile and highly stable solvents, which consisted only pair of cations (mostly organic) and organic/inorganic anions. Due to the unique liquid properties of ionic liquids, they have used to a wide range of applications such as cellulose dissolution, energy storage, electrolytic solution, and so on. Since Blanchard found that ionic liquids have CO_2 absorption abilities, [1] large amounts of theoretical studies based on electronic structure calculations and molecular dynamics simulations have been reported for exploring novel ionic liquids with better CO_2 absorption abilities. However, due to the high computational costs of quantum chemical calculations, it has been considered difficult to predict such a novel ionic liquids only with the quantum chemistry based methods. In this study, using an interdisciplinary approach of quantum chemistry and information science, we will introduce a new prediction scheme for designing ionic liquids with higher CO_2 absorption abilities. We will present the method how to describe ionic properties as much compact as possible toward inverse design of ionic liquids.



Acknowledgments

Some of the presented calculations were performed at the Research Center for Computational Science (RCCS), the Okazaki Research Facilities, and the National Institutes of Natural Sciences (NINS). This study was supported in part by the Advanced Information and Communication Technology for Innovation (ACT-I; Grant number: JPMJPR16UB) Precursory Research for Embryonic Science and Technology programs (PRESTO; Grant number: JPMJPR16NC) from the Japan Science and Technology (JST) Agency, and JSPS KAKENHI (Grant Number: 16K13928).

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Paper No. P-0045

ELASTIC AND SELF-HEALABLE POLYELECTROLYTE COMPLEX FROM LIGNOSULFONATE

Kazunori Ushimaru, Tomotake Morita, Tokuma Fukuoka*

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan
k-ushimaru@aist.go.jp, t-fukuoka@aist.go.jp

Introduction

Lignin is a major component of plant biomass and has attracted the attention to use as an ingredient for sustainable materials. Lignosulfonate is one of major industrial lignin, which is produced in pulping processes of wood biomass and is commercially available.

We tried to produce unique moldable material from lignosulfonate by using its sulfo group. Specifically, lignosulfonate was complexed with cationic polyelectrolytes and its mechanical properties were evaluated.

Material and methods

Aqueous solution of sodium lignosulfonate (L-SO_3Na, 40 w/v%, Tokyo Chemical Industry) was mixed with aqueous solution of cationic polyelectrolytes, then, casted on a poly(tetrafluoroethylene) (PTFE) mold. The casted samples were pealed from the mold after drying. The sample was cut into a dumbbell-shaped test piece according to International Organization for Standardization (ISO) 37-3. The cross-head speed for the test was 50 mm/min (EZ-LX, Shimadzu) and the test was performed at room temperature.

For the self-healing test, the sample was cut into two completely separate pieces by a razor blade. The cut surface of the pieces was gently pressed together, then, the contacted pieces were placed into each healing condition.

Results and discussion

We prepared complexes of lignosulfonate using three different cationic polyelectrolytes, poly(allylamine) (PAA), poly(ethyleneimine) (PEI), and poly(diallyldimethylammonium chloride) (PDADMACl). All samples were obtained as sheet-like form and could be cut into dumbbell-shaped test pieces. These samples revealed elasticity (Figure 1) except for the samples with high lignin content. As a result of tensile tests, the complex of L-SO_3Na and PDADMACl revealed the highest toughness in three complexes.

Figure 1. Dumbbell-shaped test pieces of L-SO_3Na and PDADMACl complex.

Self-healing property of the L-SO_3Na/PDADMACl complex was also evaluated. The self-healing property was improved with increasing of relative humidity due to water adsorption. In addition, the self-healing property was not observed the test piece of pure PDADMACl. It suggested that ionic interaction is essential for the self-healing property as other reported polyelectrolyte complexes [1,2].

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Paper No. P-0046

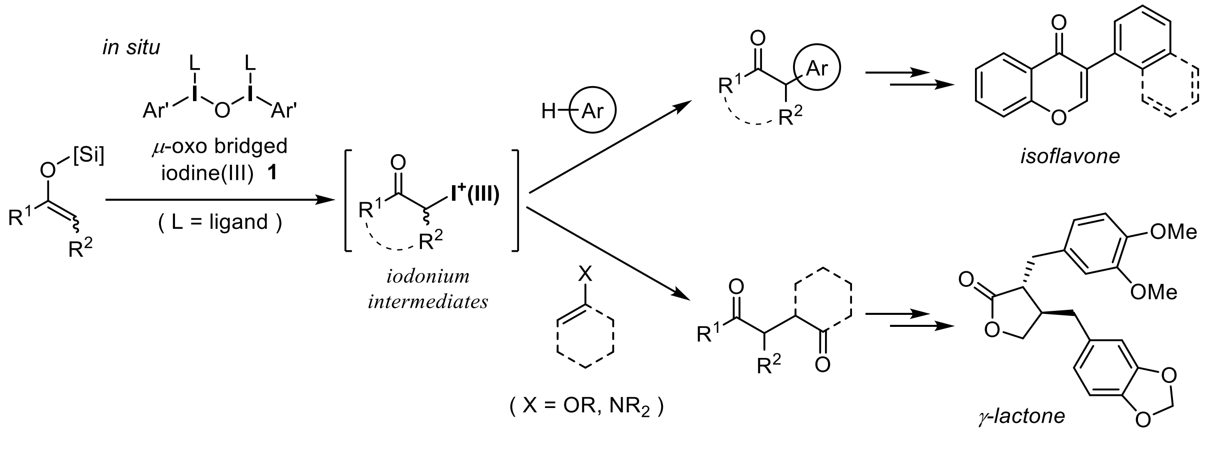
Hypervalent Iodine-Induced Oxidative Coupling of Silyl Enolates and Its Application to the Construction of Naturally-Occurring Structures

Daichi Koseki,[1] Toshiki Minakata,[1] Misako Inoue,[1] Nobutaka Yamaoka,[1] Toshifumi Dohi*,[1] Yasuyuki Kita*[2]

[1] Graduate School of Pharmacy, Ritsumeikan University
[2] Research Organization of Science and Technology, Ritsumeikan University
1-1-1, Nojihigashi, Kusatsu, Shiga, 525-8577, JAPAN
ph0021hp@ed.ritsumei.ac.jp

Oxidative coupling is an attractive transformation because of its high atom- and step-economy, in which substrate C-H bond can be directly used for C-C bond formations.[1] However, oxidative cross-coupling of two nucleophiles often suffers from over-oxidation and homodimer formation. In 2007, Baran et al reported the first oxidative cross-coupling of metal enolates with aromatic compounds using Cu^{II} as an oxidant for the synthesis of naturally-occurring compounds,[2] but the reaction required strong base and stoichiometric amount of metal oxidant, and the scope of aromatic compounds is limited to pyrroles or indoles.

Hypervalent iodine reagents are known as user-friendly oxidants, which show versatile reactivities for the synthesis of a variety of bioactive natural products and pharmaceutical compounds. Over the past few decades, our research group has engaged in developing new transformations using hypervalent iodine(III) reagents as an alternative of toxic heavy-metal oxidants. Recently, we have found a new series of reactive hypervalent iodine(III) species, in which two iodine(III) atoms are bridged with an oxygen atom. This unique μ-oxo iodine(III) species are more reactive than conventional iodine(III) reagents, such as $PhI(OAc)_2$ and $PhI(OCOCF_3)_2$, in phenolic oxidations.[3] In our attempt to apply this new reagent for oxidative C-C bond formation, herein, we report a new coupling reaction of silyl enolates with *C*-nucleophiles *via* single-electron-transfer (SET) oxidation pathway using μ-oxo bridged hypervalent iodine(III) species **1** to afford α-functionalized carbonyl compounds, such as α-aryl ketones and 1,4-diketones as a useful precursor of isoflavones and γ-lactones.



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Paper No. P-0048

THERMAL DECOMPOSITION OF POLYMERIC COMPOUNDS CONTAINING SULFIDE BOND

Ayaka Sawakami[1], Daisuke Yamashita[1], Keizo Akutagawa[2], Masahiro Hojo[2], Katsuaki Hironaka[2], Hideyuki Tagaya[1]*

[1]Graduate School of Science and Engineering, Yamagata University, Yamagata, Japan
[2]Bridgestone corporation, Kodaira, Tokyo, Japan

Polymeric wastes containing sulfide bond as represented by vulcanized rubber tires and PPS are difficult to recycle because they are thermally stable. It is considered that the thermal recycling by burning impacts on the environment because of the sulfur oxide discharge. In this study, the effective decomposition of polymeric waste containing sulfide were confirmed in the high temperature fluids. In the case of PPS, 50% conversion was attained in high temperature water at 430 degrees centigrade by adding basic compound although perfect solubilization could not be attained. However, in high temperature methanol, perfect solubilization was attained by the reaction at 430 degrees centigrade. It was also confirmed that even by reaction at 370 degrees centigrade, conversion reached to 75% by the reaction in methanol for 5h. Oligomers and monomeric compounds such as thiophenol, diphenyl sulfide, thioanisole and dibenzothiophen were mainly obtained in the reactions. Inspired by those results, we came up with an idea to decompose those polymeric wastes in alcohols and at milder temperature below 300 degrees centigrade. To clarify the underlying mechanism, the reactions by using model compounds were carried out instead of polymeric materials.

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Paper No. P-0049

PREPARATION AND CHARACTERIZATION OF NANOMOLECULAR COMPOSITE BY THE REACTION OF METAL HYDROXIDE WITH ORGANIC DICARBOXYLIC ACID

Kentaro Yumino, Takahiro Kaburagi, Hideyuki Tagaya*

Graduate School of Science and Engineering, Yamagata University, Yonezawa Japan

In recent years, organic-inorganic hybrid materials have been widely investigated as they have many applications as attractive functional materials in various fields. In our laboratory, preparation of organic-inorganic layered complexes was confirmed by the self-assembly reaction under mild conditions using a mixture of organic carboxylic acid and metal hydroxide. Layered compounds were prepared and the interlayer spacing of the nanohybrids depended on the size of organic carboxylic acids. In this study, dicarboxylic acid was reacted with calcium hydroxide, and the products were characterized. Reactions were carried out with molar ratio of dicarboxylic acid and calcium hydroxide of 1:1 or 0.5:1. In the case of dicarboxylic amino and amino acid was dissolved into mixed solvent of water and organic solvent, and calcium hydroxide was added to it. Products were dried under reduced pressure, and the dried samples were supplied to make clear their properties by TG,XRD,SEM and TEM analyses. The thermal properties of the product were confirmed by TG analysis. Since the starting temperature of the weight loss was higher than that of the raw materials, improvement in heat resistance was confirmed, suggesting the construction of the new product. In the XRD analysis, the existence of new peaks was confirmed, and it was found that a new crystal structure was constructed. They had repeat peaks suggesting the existence of a layered structure. SEM analysis showed the crystallinity of the product. These results indicated the preparation of new organic-inorganic layered composites ever by the reaction of dicarboxylic acid depending on the size of the acids.

Paper No. P-0052

PREPARATION OF RECOMBINANT RESILIN-LIKE ELASTIC BLOCK COPOLYPEPTIDES

Tokuma Fukuoka*, Kazunori Ushimaru, Azusa Saika, Shun Sato, Tomotake Morita

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan
t-fukuoka@aist.go.jp

Structural proteins such as silk, collagen, and elastin, have been receiving much attention as a promising elastic biopolymer in a wide variety of fields. Resilin is an elastic protein found in specialized regions of the cuticle of most insects, providing outstanding mechanical properties including low stiffness, high strain and resilience[1][2]. As focused on excellent elastic properties of resilin, a few research groups designed and synthesized recombinant resilin-like proteins, and their properties and mechanism of elasticity have been demonstrated[2]-[5]. Thus, resilin-like proteins are expected as a highly elastic biomaterial to replace synthetic rubbers.

Several repetitive amino acid sequences in natural resilin were identified and reported, for example, exon I (a 15-residue sequence: GGRPSDSYGAPGGGN) and III (a 13-residue: GYSGGRPGGQDLG) domains in resilin of fruit fly, *Drosophilia melanogaster*, and a 11-residue (AQTPSSQYGAP) from resilin of mosquito, *Anopheles gambiae*. All of them have tyrosine residues, which form intermolecular crosslinks through di- and tri-tyrosines connecting resilin polypeptides. Expression and purification of recombinant resilin-like polypeptides composed of a large number of these repeating motifs have been already reported[6]. In addition, comparison of properties of these recombinant resilin-like polypeptides with different repeating motifs have been carried out[6]-[8], and these studies provide important information for understanding excellent mechanical properties of resilin.

In this study, we tried to prepare block copolypeptides composed of multiple copies of the above-described three representative repeating motifs, EI = GAPGGGNGGRPSDSY, EIII = GGQDLGGYSGGRP, and Ag = GAPAQTPSSQY. We designed and synthesized various artificial genes encoding the repetitive amino acid sequences coupled different repeating motifs together, such as EIx16 + EIIIx16, EIIIx16 + Agx16, Agx16 + EIx16, and so on. Then, these genes were transformed to *Escherichia coli*, and expression of objective artificial polypeptides were investigated. More than 30 homo- and copolypeptides with different sequence and chain length have been hitherto obtained, and Ag segment-containing polypeptides showed higher productivity and water-solubility among of three repeating motifs. Here we report preparation and characterization of these novel recombinant resilin-like "hybrid" polypeptides.

This work was supported by JSPS KAKENHI for Young Scientists (B) Grant Numbers JP15K17913 and JP17K14540.

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Paper No. P-0074

Multicomponent adsorption & desorption of heavy hydrocarbons on *BEA

Gota Suzuki [1], Masahiko Matsukata [1,2]*

[1]Department of Applied Chemistry, Waseda University, 3-4-1 Okubo, Shinjuku-ku,
Tokyo 169-8555, Japan [2]Advanced Research Institute for Science and Engineering,
Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan.
*Corresponding author, e-mail mmatsu.@waseda.jp, fax +81-3-5286-3850

Since diesel cars have high torque and mileage with smaller emission of CO2, their market is expanding in developing countries. The process of hydrocarbon (HC) emission has been considered to include adsorption of HCs emitted from engine on DOC at low speed, and the desorption and oxidation of HCs the temperature rise in a moment with acceleration of engine. Based on this model, we studied adsorption, desorption and oxidation of n-hexadecane (n-C16) and decylbenzene (DB) on zeolite *BEA to evaluate the effects of aromatic ring on each step.

*BEA having different Si/Al ratios, 20, 225, 414, and 786 was sued as adsorbent. Adsorption tests were carried out in a flow reactor at 393 K. The adsorbent weighing 300 mg was packed in the reactor, the concentrations was 190 ppm each for n-C16 and DB, and the GHSV to be 55000 h-1. To analyze adsorbed species on zeolite, zeolite was dissolved with HFaq. The adsorbed HCs were extracted with CH2Cl2 and injected to GC-FID to determine the proportions of adsorbed species. The total amount of adsorbed hydrocarbons was obtained by using TG-DTA. The relationships between the amount of adsorbed HC and Si-OH was studied using dealuminated *BEA obtained by HNO3 treatment. Si/Al ratio was measured with XRF.

Fig. 1 shows the desorption profiles of DB and n-C16 mixture for *BEA with different Si/Al ratios. Clearly, the desorption temperature became higher with increasing amount of Si-OH. Fig. 2 shows the relationships between the amount of adsorbed HC species. These values were calculated by using the GC-FID results, the total amount of HC and the amount of Si-OH increased with increasing amount of Si-OH, indicating the interaction between Si-OH and aromatic ring.

Comparison of the adsorption and desorption behaviors of HCs having the same carbon number, C16, suggested that adsorption of aromatic ring was stronger than n-paraffin. The interaction between aromatic ring with acid sites would stronger than n-paraffin. In addition, Si-OH group on *BEA also acted as adsorption site. The observed higher desorption temperature of n-C16 in the presence of DB suggested that adsorbed DB inhibited the desorption of n-C16.

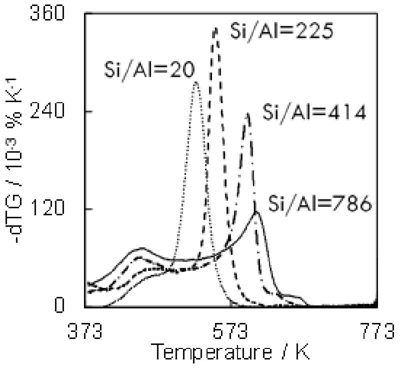

Fig. 1 Desorption profiles of HC mixture for *BEA with different Si/Al ratios.

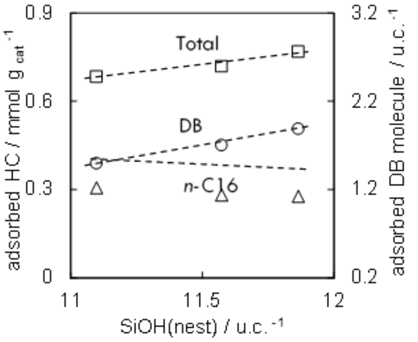

Fig. 2 Relationship between the amount of HCs in micropore and the amounts of silanol.

Paper No. P-0075

UNDERSTANDING POLYMER INTERACTIONS AND BEHAVIOR IN THE REFORMULATION STRATEGIES FOR WATER BASED COATINGS: A MOLECULAR DYNAMICS STUDY

G. S. Lim,[1] S. Chakraborty,[1] J. Ye,[1] M. Klähn,[2] W. S. Tan,[3] J. Kumar,[3] C. K. Liu,[3]
A. Parthiban,[2] B. A. Burkett,[2] A. M. van Herk,[2] M. B. Sullivan,[1] F. C. H. Lim[1]*

[1]Institute of High Performance Computing (IHPC), A*STAR
1 Fusionopolis Way, #16-16 Connexis, Singapore 138632
[2]Institute of Chemical and Engineering Sciences (ICES), A*STAR
1 Pesek Road, Jurong Island, Singapore 627833
[3]Institute of Materials Research and Engineering (IMRE), A*STAR
2 Fusionopolis Way, #08-03 Innovis, Singapore 138634

*limch@ihpc.a-star.edu.sg

Conventional solvent based nail polish contains a variety of small organic compounds which are harmful to both human and the environment. These small organic compounds, which include solvents, monomers and plasticizers, typically leave the formulation during the drying stage in order to induce film formation through a glass-liquid transition of the polymer matrix. Arising from the functional necessity of plasticizers, existing water based formulations in the market still contain a significant amount of these undesirable small organic compounds. Therefore, a radical paradigm shift is needed to reevaluate water based coating formulations in order to avoid the use of harmful small organic compounds.

In this work, we collaborate closely with our experimental partners to redesign water based nail polish formulations without small organic compounds. This is done through a manipulation of polymer design. In this novel polymer design, the maleic anhydride polymeric backbone with cross-linkable pendant groups are shielded from other cross-linkable groups by long hydrophilic and hydrophobic side chains that are concurrently grafted along the backbone. Manipulating the shielding effects will allow formulations to remain fluid during storage and application while allowing film formation to occur during drying. Our computational work facilitates the understanding of molecular interactions between the polymers with tunable hydrophilic and hydrophobic shielding behaviors.

The work presented here solely features the computational study. Our molecular dynamics simulations investigate the dynamics and interactions of the combed maleic anhydride based polymer with amphiphilic features. By tuning the length of the hydrophilic side chain units, optimization of the shielding effects has been investigated. Other properties such as the glass transition temperature and radius of gyration of the combed polymer system were analyzed. Our results have shown that varying the length of the hydrophilic side chains directly interferes with backbone separation, which affects the possibility of cross-linking among polymer strands. In addition, a study of the glass transition temperature of the systems also revealed that there are three transition points, originating from the polymer backbone, as well as the hydrophobic and hydrophilic side chains. We have also compared these combed polymer systems with the polymer blend equivalent in order to understand the effects of chemically grafting the side chains to the backbone.

Paper No. P-0076

UNDERSTANDING POLYMER-NANOPARTICLE INTERFACIAL INTERACTIONS TO GAIN INSIGHTS FOR POTENTIAL ECO-FRIENDLY EXTERIOR COATING FORMULATION

Souvik Chakraborty,[1*] Ritwik Panigrahi,[2] Melissa Prawirasatya,[2] Thoniyot Praveen, [2]
Alex M. van Herk,[2] Geraldine S. Lim,[1] Freda C. H. Lim,[1] Jun Ye,[1*]
[1]Institute of High Performance Computing (IHPC), A*STAR
1 Fusionopolis Way, #16-16 Connexis, Singapore 138632
[2]Institute of Chemical and Engineering Sciences (ICES), A*STAR
1 Pesek Road, Jurong Island, Singapore 627833

E-mail: chakraborty@ihpc.a-star.edu.sg, yej@ihpc.a-star.edu.sg

Small organic compounds (SOC) are the volatile components of paint formulation which pose hazards both in terms of environmental impact and to health. SOCs consist of hydrocarbons which have high enough vapor pressures to enable them to vaporize into the atmosphere. Present in the conventional solvents used for paint formulation, these organic compounds leave formulation during the drying stage of the coating process that leads to film formation. This process is guided by a phenomenon called the glass transition of polymer composite system present in the paint formulation. To find and establish alternative formulation approach to exclude SOCs, it is important to understand the interactions that influence glass transition of composite system. Within the context of water-based exterior coating formulations, high particle volume concentrations can be expected. Thus, the effects of polymer interactions with the high volume of particles can be significantly exploited to induce film formation as water leaves the film during drying.
In the proximity of a particle, polymer glass transition behaviour deviates from its bulk counterpart. This behaviour is also known as the nanoconfinement effect.[1] The change in the local dynamics of polymer segments at polymer-particle interface can lead to a shift in the glass transition temperature.[1-4] In addition to that, the interplay of the substrate surface chemistry and the polymer structure plays crucial role in determining the nature of interfacial interaction that affects the glass transition temperature (T_g).

In this work, all atom molecular dynamics simulation has been performed to study the glass transition behaviour of poly(vinyl alcohol) (PVA) confined by the silica substrate to resemble a PVA-silica nanoparticle composite model paint system. The chemical structure of the silica surface is varied by the extent of hydroxyl functionalization (0%, 25%, 50%, 75%, and 100%) that corresponds to silica nanoparticles prepared under different pH conditions. We have found that the amount of T_g change depends on the extent of hydrogen bonding interaction between PVA and silica surface. Free energy of adhesion determined from umbrella sampling simulations of the composite system sheds lights to the thermodynamics of interfacial interactions. Our results suggest strong attractive interactions between PVA and silica nanoparticles with higher OH coverage originated from hydrogen bonding interactions that give rise to greater T_g increase, while bare silica nanoparticle surface led to a suppression of T_g, which paves the way in designing for water-based exterior coating formulation that is free of volatile SOC

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Paper No. P-0078

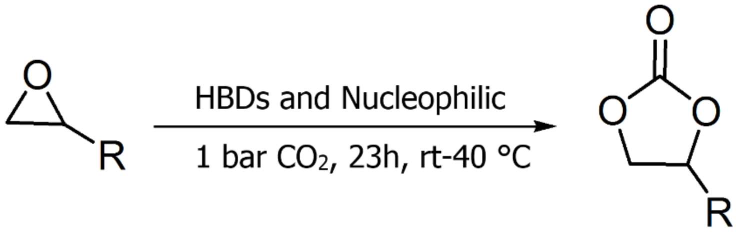
ORGANOCATALYSTS FOR THE SYNTHESIS OF CYCLIC CARBONATES FROM CO_2 UNDER AMBIENT CONDITIONS

Prapussorn Yingcharoen, Chutima Kongtes, Sunatda Arayachukiat, Valerio D'Elia*

Department of materials science and engineering, school of molecular science and engineering, Vidyasirimedhi institute of Science and technology, 21210, Payupnai, Wangchan, Rayong, Thailand

*E-mail :valerio.delia@vistec.ac.th

Dual catalytic systems composed of hydrogen bond donors (HBDs) and nucleophilic cocatalysts have been applied for the organocatalytic transformation of carbon dioxide (CO_2) to value-added cyclic carbonate. Brønsted acidity properties of HBDs have a strong effect on the efficiency of the HBDs. HBDs with acidity in the range of pK_a 9-12 displayed the highest efficiency for the synthesis of variously substituted cyclic carbonates from CO_2 and epoxides. Based on this results, the ascorbic acid scaffold has been modified by tuning its Brønsted acidity to produce a highly active HBD. Additionally, the reaction catalyzed by the newly synthesized organocatalysts can take place under ambient conditions, demonstrating high activity and selectivity for the sustainable conversion of CO_2.



Paper No. P-0089

HOW FREE AND BONDED PLASTICIZERS INDUCE CHANGES IN THE GLASS TRANSITION OF POLYMERS STUDIED WITH MOLECULAR DYNAMICS SIMULATIONS

Jia Min Phang,[a] Freda C. H. Lim,[b] Alexander M. van Herk,[a] Satyasankar Jana,[a] and Marco Klähn[a]*

[a] Institute of Chemical and Engineering Sciences, 1, Pesek road, Jurong Island, Singapore 627833.
[b] Institute of High Performance Computing, Fusionopolis Way, #16-16 Connexis, Singapore 138632.
*Correspondence: klahnm@ices.a-star.edu.sg

The effect of two different plasticizers, 1-phenoxy-2-propanol and butyl carbitol, on the glass transition temperature, T_g, of typical (meth)acrylate terpolymers is simulated. Plasticizers are considered as free additives in the polymer, i.e. as external plasticizers, but also as bonded additives that are directly integrated into the polymer, i.e. internal plasticizers.[1] Simulations are performed with all-atomistic molecular dynamics (MD) simulations in combination with a suitably parameterized molecular mechanical (MM) force field. We observe that free plasticizers are more efficient in lowering T_g than bonded plasticizers. A relation between the T_g increase that can be achieved by binding free plasticizers to the terpolymer and the size of the plasticizer is obtained. These predicted T_g-shifts from simulations are confirmed by calorimetric measurements, which also validates the used computational model. Moreover, we find that the T_g-value of the polymer is related to polymer energy barriers that need to be overcome to enable polymer segment movement. These barriers can be substantially lowered by introducing mobile free plasticizers that for their part also exhibit low energy barriers of diffusion. The results of this work prepare the design of reactive coalescing agents that could replace free coalescing agents that are typically used in coatings to lower their T_g and minimum film formation temperature.[2-3] The evaporation of such volatile additives from coatings potentially effect environment and user negatively. Therefore, it is highly desirable to develop reactive coalescing agents that react with the polymer after drying and therefore remain inside the coating.

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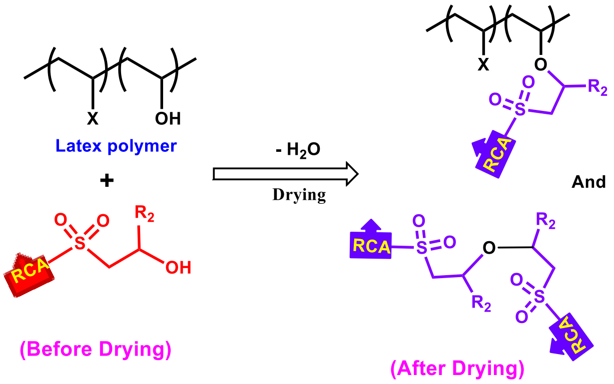
Paper No. P-0090

HYDROXYETHYLSULFONE BASED REACTIVE COALESCING AGENTS FOR WATERBORNE COATING WITH LOW ENVIRONMENTAL IMPACT

Jagjit Kaur,[1] Ranganathan Krishnan,[2] Balamurugan Ramalingam*[1] and Satyasankar Jana*[2]

[1]Organic Chemistry, 8 Biomedical grove, Institute of Chemical and Engineering Sciences, Singapore 138665
[2]Polymer Engineering & Characterization, Institute of Chemical and Engineering Sciences, 1 Pesek Road, Jurong Island Singapore 627833
*E-mail: balamurugan_ramalingam@ices.a-star.edu.sg; satyasankar_jana@ices.a-star.edu.sg

One of the successful industrial approaches for making surface coatings with low environmental impact is adopting waterborne formulations. However, present waterborne coatings still use substantial amount coalescing agent (CA) to reduce the glass transition temperature (Tg) of the binder polymer. These CAs are vulnerable to vaporize into the environment (volatile organic compounds, VOCs) and causes environmental pollution and long term health hazards. In the present work, we have developed a series of novel hydroxylethyl sulfone (HES) based RCAs and evaluated their suitability to act as reactive coalescing agents. We found that HES compounds react with alcohol and amine monomers as well as crosslink with polymers during drying process. Coalescing performance of HESs were investigated by measuring minimum film formation temperature (MFFT). Preliminary experimental studies indicated that HES undergo 'water-release-triggered equilibrium' reactions (a) through the formation of corresponding vinyl sulfone (VS). The details on the HES and VS equilibrium and reactivity of HES with alcohol containing monomers (b) and polymers will be presented.



Keywords: Hydroxyethylsulfone; Reactive coalescing agents; Small organic compounds; volatile organic compounds (VOC).

Paper No. P-0092

CARBON FOOTPRINT ASSESSMENT TOOL FOR CO_2 VALORIZATION

Khoo Hsien Hui*, Murugappan Karthick., Paul N. Sharratt
Institute of Chemical and Engineering Sciences (ICES),

*Corresponding author: khoo_hsien_hui@ices.a-star.edu.sg

Singapore's climate policy is an important environmental agenda as demonstrated by the nation's pledge to reduce CO_2 emissions by ratifying the Paris Agreement. As such, the research of utilizing CO_2 as a resource for the synthesis of liquid fuels and other value-added chemicals have gained importance in both academia and industry. Evaluating the environmental performance of CO2 utilization options prior to commercialization is seen as a necessary step to ensure sustainable objectives are met.

From a thermodynamic standpoint, CO_2-to-chemical conversion faces the challenge of sufficient energy required to drive the reaction. Our work presents the case studies of potential CO2 conversion to: i) formic acid, ii) methanol, iii) ethylene, iv) dimethyl carbonate (DMC), and v) dimethyl ether (DME).

Paper No. P-0096

LIPID PROFILE IN LIQUIFIED DIMETHYL ETHER EXTRACTION FROM MICROALGAE *CHLORELLA VULGARIS*

Naomasa Yamamoto, Wahyudiono, Hideki Kanda*, Motonobu Goto
Department of Materials Process Engineering, Nagoya University,
Furocho, Chikusa, Nagoya 464-8603, Japan
*Corresponding author: Fax:81-52-789-3390, E-mail: kanda.hideki@material.nagoya-u.ac.jp

Microalgae contain useful several types of lipid. Liquefied dimethyl ether (DME) used as solvent, at around 0.5 - 2.5 MPa, is being proposed for lipid extraction from wet microalgae. Usual extraction media such as hexane and chloroform require high energy for heat-drying of wet microalgae and evaporation of the used solvent; on the one hand, liquefied DME can eliminate the energy-consuming processes such as drying and solvent evaporation, therefore, it is relatively energy-saving compared to usual processes.

In our previous studies [1], most of the lipids contained in several microalgae were extracted by DME; however, it has not been fully understood which type of lipids are easy to extract by DME. In this study, the composition of extracted lipids has been effectively identified, and the lipid class was evaluated.

Liquefied DME was applied as solvent to extract lipid from green microalgae *Chlorella vulgaris* using a semi-continuous system. The extraction conditions were as follows: pressure of 0.8 – 1.5 MPa, temperature of room temperature (≈ 25°C) - 60°C with DME flow rate of 1 mL/min. Organic solvents (Bligh & Dyer method [2]) was also applied to compare the yield with DME. The lipid classes in the extracts were determined using high performance liquid chromatography (HPLC) with evaporative light-scattering detector (ELSD) using gradient program, and the fatty acid compositions were analyzed by gas chromatography (GC) with flame ionization detector (FID).

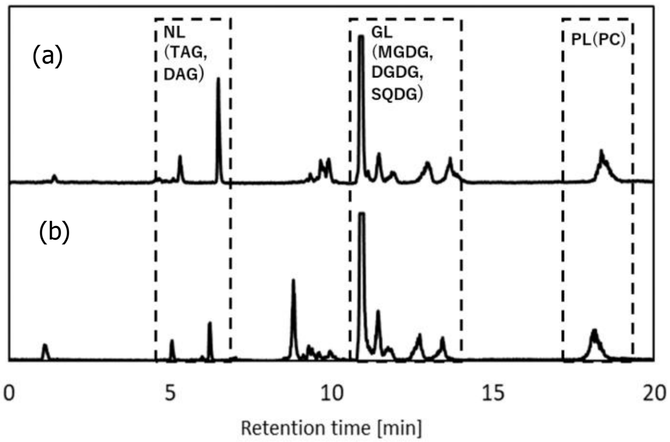


Figure 1. HPLC-ELSD lipids chromatogram of (a) BD method and (b) DME

The major lipid components, neutral lipids (NL; TAG, DAG), glycol lipids (GL; MGDG, DGDG, SQGD), and phosphor lipids (PL; PC), were detected by HPLC-ELSD (Figure 1). Quantitative estimations of the major lipids were performed by HPLC-ELSD, using a calibration curve for each lipid. The sum of the major lipids of *C. vurgaris* accounted for 0.18 g/g-dry-microalgae and 0.15 of the total lipid profiles by Bligh & Dyer method and DME extraction (40°C), respectively. As seen as Figure 1, DME could extract some lipid classes as well as organic solvent extraction.

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Paper No. P-0097

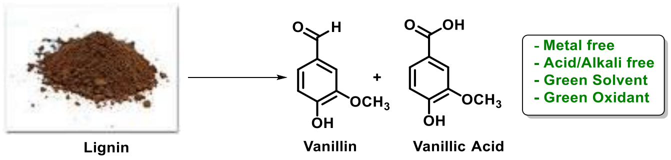
A GREENER APPROACH FOR THE DEPOLYMERIZATION OF LIGNIN TO VANILLIN AND DERIVATIVES

Yap Wei Jie, Gowrisankar Saranvanan, Balamurugan Ramalingam, Jayasree Seayad*

Organic Chemistry, 8 Biomedical grove, Singapore 138665
Institute of Chemical and Engineering Sciences
Agency for Science Technology and Research (A*STAR)
Email: jayasree_seayad@ices.astar.edu.sg

More than 35 billion tons of lignin is produced annually, and large amounts are available from the pulp and paper industries. It is projected that about 62 million tons of lignin will be produced annually as a waste product in bio-refineries by 2022. Currently, most of the lignin is used as a low-value fuel in the paper mills. More value could be extracted from the lignin if it could be converted to value added chemicals or materials. In order to be successful economically; biorefineries must also comprise integrated technologies to utilize every single stream including lignin for possible high value applications before considering the low value options.

The most prevalent approach to valorize lignin is depolymerization into monomeric phenolic derivatives by C-O and C-C cleavage under reductive or oxidative conditions. Majority of these methods operate under harsh conditions such as super and subcritical conditions, although recent reports show the possibility of milder depolymerization conditions. However, selective depolymerization of lignin to value added chemicals is still very challenging and limited. In this poster a metal, alkali and acid free oxidative depolymerization of lignin to value added chemicals such as vanillin and vanillic acid will be presented.



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Paper No. P-0099

ENHANCED CATALYTIC ACTIVITY OF PTFE/ZEOLITE FOR PROPANE DEHYDROGENATION

Ryosuke Ushiki, Hiroyoshi Hoshino, Masahiko Matsukata*
Department of Applied Chemistry, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan 2Advanced Research Institute for Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan.

Propylene is one of the most important base chemicals in petrochemical industry. The demand for propylene is growing in recent years. Along with the spread of ethane crackers, catalytic propane dehydrogenation (PDH) have been received a great attention in recent years as a new propylene source.

While it is known that Pt and Sn loaded Al_2O_3 has high PDH activity are widely studied [1,2], in this presentation, we will report the PDH activity and durability on the five types of Pt and/or Fe loaded zeolites.

PtFe/zeolites were prepared by a liquid phase ion exchange method, using $Pt(NH_3)_4(NO_3)_2$ aq., and $FeCl_3$ aq. The amounts of loading were targeted as 0.4 wt% for Pt and 2.0 wt% for Fe, respectively. Catalytic activity tests were carried out at 773K using a fixed bed flow reactor with 50 mg of catalyst. WHSV was set to be 4.32 h^{-1}. Catalyst was pretreated at 773K in flowing H_2. The reaction gas composition was set to be Ar/C_3H_8 = 42/2 (STP). Pt supported zeolite was observed with STEM-EDX.

We found that Pt and Fe co-loading on several zeolites, *BEA, MOR, EMT, LTL, and FAU exhibited high dehydrogenation activities for propane than Pt-loaded zeolite.

Figure 1 shows their catalytic activities. All types of Pt/Zeolites exhibited low activity and poor durability for PDH. Propylene is obtained by Pt/zeolite at initial time, and then they rapidly decreased. Compared with these results, PtFe/zeolite exhibited high PDH activity. In the case of using PtFe/FAU, the propylene yield was 41.1 % in the early stage of reaction and 35.4 % even after 120 min.

Figure 2 shows typical STEM-EDX images of Pt/FAU and PtFe/FAU. The bright area means the presence of Pt particles. There was no observation of aggregated Pt in PtFe/FAU. Hence, we judged that Pt was highly dispersed on PtFe/FAU. We considered that the high dispersion of platinum by Fe addition is responsible for the enhancement of PDH activity.

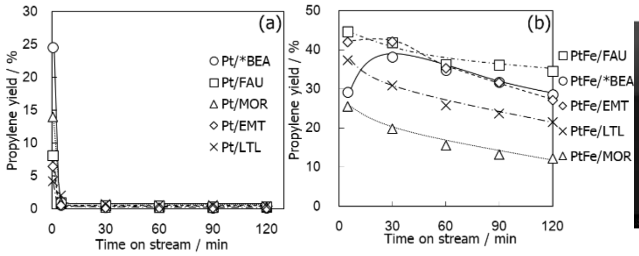

Fig. 1 Propylene yield in propane dehydrogenation over (a)Pt/zeolite and (b)PtFe/zeolite.

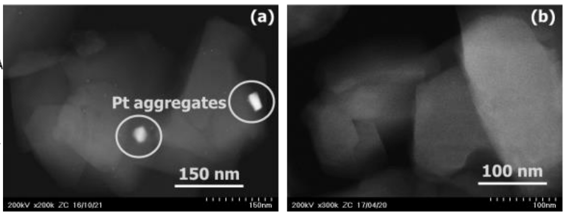

Fig. 2 Typical STEM-EDX images of (a)Pt/FAU and (b)PtFe/FAU.

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Paper No. P-0100

SELECTIVE WATER TRANSPORT OF WATER/ACETIC ACID MIXTURE THROUGH SAPO-34 MEMBRANE USING VAPOR PERMEATION METHOD

Ataher Ahmed[1], Matsukata Masahiko[1.2]

[1]Department of Applied Chemistry, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan; [2]Advanced Research Institute for Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan.

Acetic acid is one of the most important intermediates in chemical and food industries. Dehydration of acetic acid requires a large amount of energy since the relative volatility of water to acetic acid is close to unity. We employed the vapor permeation (VP) separation technique, a membrane-based separation process using vapor mixtures as feed, to study separation behavior and transport mechanism of water-acetic acid (AcOH) mixtures through SAPO-34 membranes.

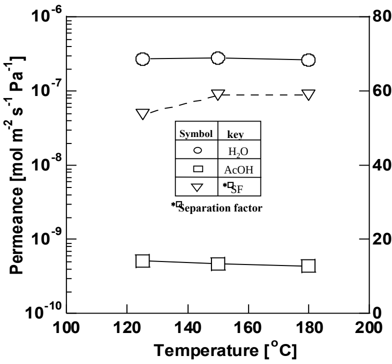

Fig. 1: Effect of temperature dependency through SAPO-34 membrane results for 50/50 kPa of mixed H_2O/AcOH through SAPO-34 membrane by vapor permeation.

In this study, SAPO-34, CHA-type zeolite, membranes were formed on porous α-Al_2O_3 tube and its dehydration properties was evaluated with various concentrations of water and acetic acid to gain insights into their permeation and separation mechanisms. Furthermore, the adsorption experiments were carried out using these single-component and binary mixtures to measure their adsorbed amounts on the SAPO-34 membrane.

Micropores of SAPO-34 (0.38 nm) can allow water (kinetic diameter: 0.28 nm) permeation and block acetic acid (kinetic diameter: 0.43 nm) permeation. The separation of water from water/AcOH mixture through SAPO-34 membrane is expected to be based on molecular sieving effect.

Fig. 1 shows temperature dependency of permeances for a water/AcOH separation mixture of 50/50 (wt/wt). The water permeance was almost independent of temperatures, whereas the AcOH permeance slightly decreased and exhibited the separation factor as high as ca. 600 at 180 ^{0}C.

Fig. 2 shows that partial pressure dependency in the feed, the water permeance was independent of the concentration of acetic acid in the feed for both unary and binary systems, and vice-versa. Aqueous mixtures can be separated over SAPO-34 membranes because of molecular sieving.

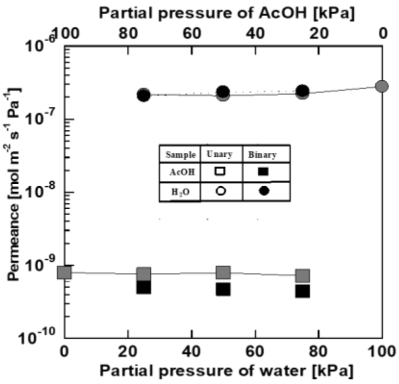

Fig. 2: Effect of partial pressure dependence on SAPO-34 membrane in the feed of VP at 150 ^{0}C.

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Paper No. P-0102

GEM-DIALKYL EFFECTS IN Pd-DIPHOSPHINE COORDINATION CHEMISTRY

Dillon W. P. Tay; Nobbs, J. D.; van Meurs, M.; Britovsek, G. J. P.*

Department of Chemistry, Imperial College London, United Kingdom
Institute for Chemical and Engineering Sciences (ICES), A*STAR, Singapore
Email: g.britovsek@imperial.ac.uk

The *gem*-dialkyl effect, first proposed by Thorpe and Ingold in 1915,[1] postulates that mutual repulsion arising from *gem*-dialkyl substitution on a carbon chain forces bond angle compression, promoting cyclisation and stabilising small ring structures. In the context of ligands, a similar effect can be generated by *gem*-dialkylating the central carbon of propylene-bridged diphosphines (Figure 1). This effect has been observed to improve the stability of chelate complexes,[2] influence regioselectivity in Ru-catalysed allylation[3] and alter the ligand bite angle.

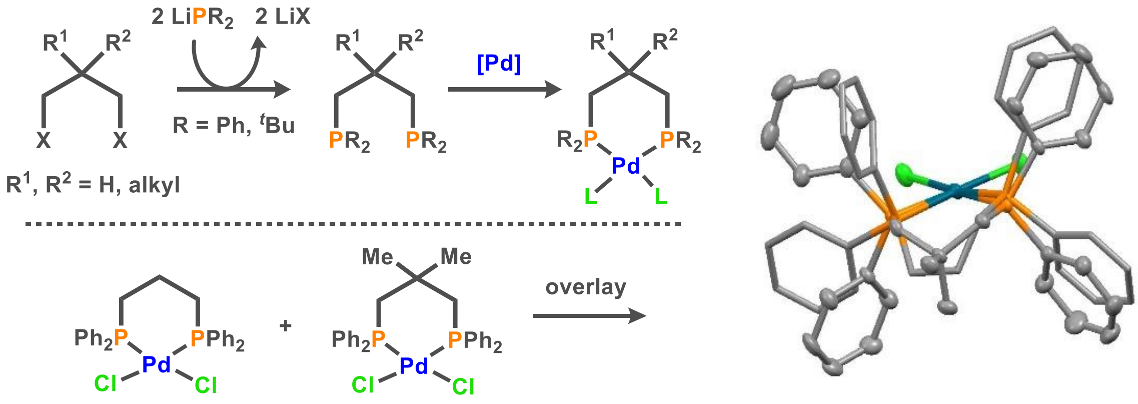

Figure 1 – Synthesis of Pd complexes and an overlay of crystal structures

A series of novel diphosphine ligands with *geminal* di-hydrogen, di-methyl and higher alkyl groups has been synthesised. The structures of their $PdCl_2$ complexes have been compared and their performance in Pd-catalysed carbonylations studied.

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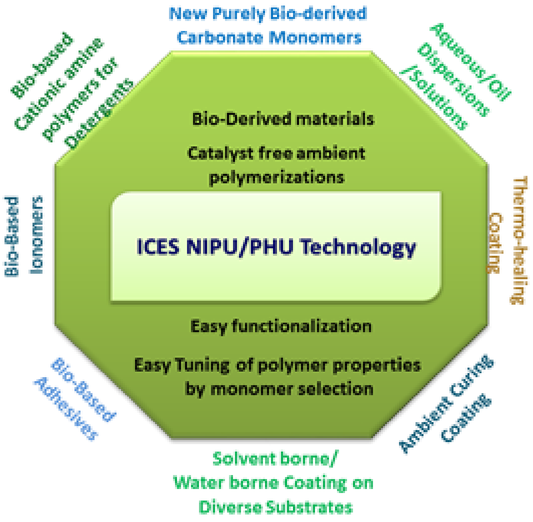
Paper No. P-0103

BIO-BASED FUNCTIONAL NON-ISOCYANATE POLYURETHANES (NIPUs) FOR SPECIALTY APPLICATIONS

Ping Sen Choong,[1] Ning Xi Chong,[2] Kwok Wai Eric Tam,[2] Abdul Majeed Seayad,*[2] Jayasree Seayad*[2] and Satyasankar Jana*[1]
[1]Polymer Engineering and Characterization, [2]Organic Chemistry
Institute of Chemical and Engineering Sciences
Agency for Science, Technology and Research (A*STAR).
Email: abdul_seayad@ices.a-star.edu.sg; jayasree_seayad@ices.astar.edu.sg; satyasankar_jana@ices.a-star.edu.sg

Polyurethanes (PU) are one of the most versatile polymers having a wide range of applications such as rigid and flexible foams, coatings, adhesives, and textiles. Traditional polyurethanes (PUs) are derived from highly toxic, carcinogenic and moisture instable isocyanates which are in turn made using highly toxic phosgene,[1] rendering the production of PUs potentially hazardous. This demands rigorous safety precautions causing inconvenience and high production costs. Recently, more stringent regulations in the manufacturing and new applications of PUs are being instigated in view of consumer safety and environmental protection. Therefore, there is a growing interest for alternative routes to PUs such as non-isocyanate polyurethanes (NIPUs) or polyhydroxyurethanes (PHUs) via polyaddition reaction between diamines and bis-cyclic carbonates, which completely eliminates the use of phosgene and isocyanates.[2] The demand for bio-based monomers is rapidly rising due to the depletion of fossil resources and increased awareness for environmental sustainability. The main challenge is to expand the range of bio-based monomers that allows polymers to have more versatile chemical structures and to achieve target properties for various applications. In this presentation, we will highlight our efforts on developing functional NIPUs especially utilizing bio-derived diamines and bis-cyclic carbonates and their potential applications.[3]



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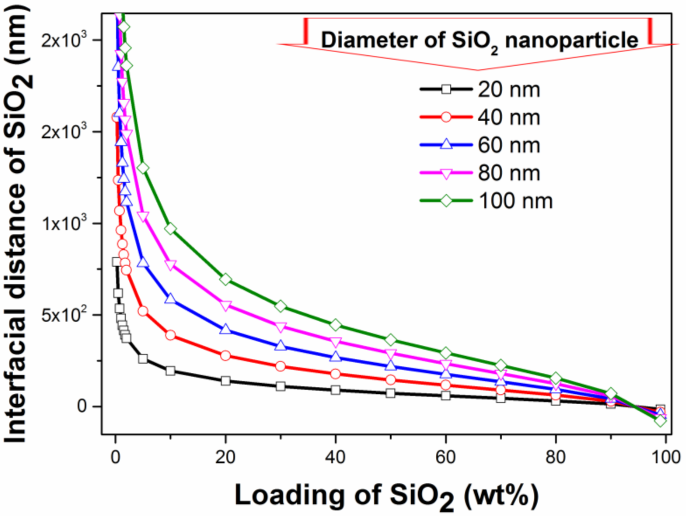
Paper No. P-0105

COMPOSITE MATERIALS USING GREEN CHEMISTRY PRINCIPLES

Ritwik Panigrahi, Alexander M. van Herk, Praveen Thoniyot*
Polymer Engineering and Characterization, Institute of Chemical and Engineering Sciences (ICES), Agency for Science, Technology and Research (A*STAR), 1 Pesek Road, Jurong Island, Singapore 627833
*E-mail: thoniyotp@ices.a-star.edu.sg

Preparation of polymer-inorganic materials nanocomposites through environmental-friendly methods have been under lime light in materials research. In contrast to the reported methods using volatile solvent based approaches,[1] present work deals with green technology for preparation of polymer/Inorganic nanoparticle composite (INp) using water as solvent. The objective is our work is to minimize the use of volatile organic compound (VOC) through simple method to develop composite materials having competitive performance to embed in the principles of Green Chemistry. In our approach we prepared composites by simple solution mixing method and both homopolymers as well as polymer latex particles were used as matrix material. It is observed that glass transition temperature of polyvinyl alcohol and copolymer latex were enhanced by SiO_2 loading. The current strategy mainly finds its application in the present trends of SOC free odorless paint formulation where INp are loaded ~50% or even more with respect to the polymer binder.



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Paper No. P-0109

BIOCATALYTIC PRODUCTION OF RHAMNOLIPID BIOSURFACTANTS

Margarete Nawrath[1,2], Christoph Ottenheim[2], Wolfgang Zimmermann[1], Jin Chuan Wu[2*]

[1] Microbiology and Bioprocess Engineering, Institute of Biochemistry, Leipzig University,
04103 Leipzig, Germany

[2] Institute of Chemical and Engineering Sciences, Agency for Sciences, Technology and
Research (A*STAR), 1 Pesek Road, Jurong Island, Singapore 627833, Singapore

Microbially derived surfactants, so-called biosurfactants, have gained increased attention in the past few decades as they are considered an environmentally friendly alternative to their chemically synthesized, non-biodegradable counterparts. While for some biosurfactants, such as sophorolipids, economically feasible bioprocess technologies have been established, the industrial production of rhamnolipids still remains challenging.

Rhamnolipids are naturally produced by the opportunistic pathogen *Pseudomonas aeruginosa* under quorum sensing regulation, a highly complex bacterial intercellular communication system, limiting rhamnolipid production. In *P. aeruginosa*, quorum sensing also plays a vital role in pathogenicity mediated by various adhesins, toxins, proteases and pigments which modulate or disrupt host cell pathways. The emerging threat of antibiotic-resistance in *P. aeruginosa*, illustrated in a recent publication of the World Health Organisation (WHO), makes this strain even less attractive for industrial use.

The aim of our study was to uncouple the rhamnolipid production from the complex regulation system responsible for low titres, and to use a safe production host. Here, we present the isolation of a promising non-pathogenic strain of the genus *Pantoea*, a genetically versatile bacterium. We also demonstrate its successful functional heterologous expression of the rhamnolipid operon rhlAB, derived from a natural producer, *P. aeruginosa*, resulting in the biosynthesis of mono-rhamnolipids. The production was confirmed by an oil displacement test, surface tension measurements and finally by MALDI-TOF mass spectrometry.

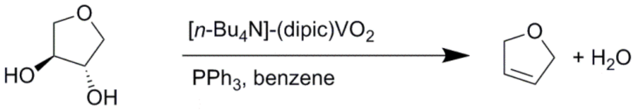
Paper No. P-0110

DEOXYDEHYDRATION OF CYCLIC *TRANS*-DIOL SUBSTRATES USING VANADIUM-BASED CATALYSIS : A DENSITY FUNCTIONAL THEORY STUDY

Ebru Aksanoglu,[a] Irfan Alibay,[b] Kok Ping Chan,[c] Charles W. Johannes,[c] Yee Hwee Lim,[c]
Richard A. Bryce*,[a]

[a] Division of Pharmacy and Optometry, School of Health Sciences, Manchester Academic Health Sciences Centre, University of Manchester, Oxford Road, M13 9PL, UK.
[b] Structural Bioinformatics and Computational Biochemistry, Department of Biochemistry, University of Oxford, South Parks Road, Oxford, OX1 3QU, UK.
[c] Organic Chemistry, Institute of Chemical and Engineering Sciences, 8 Biomedical Grove, #07-01/02, Singapore 138665.

With the rapid depletion of fossil fuel resources and increasing demand for transportation fuels and platform chemicals, the search for a sustainable alternative is of pressing importance.[1] Carbohydrates constitute the largest form of biomass and therefore possess potential as a renewable source. Carbohydrates differ from petrochemical-derived hydrocarbons in the large number of hydroxyl groups they possess.[2] To be incorporated into the chemical industry, it is desirable for their oxygen content to be lowered. Deoxydehydration (DODH) reactions are able to do this by converting vicinal diols into desirable, easily chemically-manipulated olefin products:[3]



Rhenium-based catalysts have proven to be the most efficient and highest yielding with a broad substrate scope. Experimental and computational work show that cis-cyclic diols are able to undergo DODH reactions to provide high olefin yields whereas trans-cyclic diols are unable to, or in some cases can but provide poor olefin yields. Vanadium-based catalysts such as [n-Bu_4N]-(dipic)VO_2, have been evaluated for use in DODH reactions and show potential as an inexpensive yet efficient alternative to rhenium[5]. However there is no research previously carried out on the V-catalysed DODH of biomass-like cis- and trans-cyclic diols. Therefore, we apply DFT calculations to characterise the V-catalysed reaction energetics for DODH of cyclic trans-diol substrates and compare with their cis analogues.

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Paper No. P-0114

IMPROVED SYNTHESIS OF GLUCOSINOLATES

Yi Wee Lim, Michelle J.H. Ong, Russell J. Hewitt*

Institute of Chemical and Engineering Sciences, Agency for Science Technology and Research (A*STAR), Singapore

Glucosinolates are a naturally-occurring series of thioglycosides, found in a variety of plants in the brassicaceae family, including broccoli, mustard, wasabi etc. As the precursors to the broad-spectrum antimicrobial isothiocyanates, glucosinolates have been extensively studied in the scientific literature. However, their availability has always been limited whether they are obtained through plant extracts, or synthesis. Herein we report an improved "green" synthesis of glucosinolates, in which typical scalability concerns have been addressed. We have successfully eliminated the use of chromatographic purification and undesirable solvents including ethers, chlorinated solvents and polar aprotics. This has allowed us to prepare glucosinolates in 10–25 gram scale using common discovery lab equipment (up to 0.5 L), and dramatically reducing the projected cost of materials with this optimised methodology.

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Paper No. P-0115

PREPARATION OF POLYMERIC JANUS NANOPARTICLES BY EMULSION POLYMERISATION USING CROSS-LINKED CORE-SHELL PARTICLES AS SEEDS

Hai Liu,[1] Anqi Chen*[1]; Wenguang Zhao[2] and Alexander van Herk*[2]

[1]Organic Chemistry, [2]Polymer Engineering & Characterization, Institute of Chemical and
Engineering Sciences, Agency for Science, Technology and Research (A*STAR)
E-mail: alexander_herk@ices.a-star.edu.sg; chen_anqi@ices.a-star.edu.sg

Janus particles, named after the two-faced Roman God Janus, are an emerging class of particles possessing anisotropic morphology, chemical functionality and properties. Owing to their unusual structure, properties and potential application in many fields, such as surfactants, sensors, drug-delivery, bioimaging, displays, coatings, probes etc, the synthesis of Janus particle has attracted much attention in recent years.[1-3] Among several methods for the synthesis of polymer based Janus particles, seeded emulsion polymerisation is the most convenient, scalable, cost-effective and environmentally friendly method as the process is carried out in water.

The chosen approach is to use core-shell polymer particles in a seeded emulsion polymerization. In such an approach, primary cross-linked seed particles, prepared by emulsion polymerisation, are polymerized with a suitable monomer having desirable polarity and reactivity to form a core-shell structure. The core-shell particles are then swollen with a second monomer dispersed in water, resulting in an elastic stress incurred on the polymer network. Upon heating, the stress is released by contraction of the swollen network, leading to expulsion of monomer droplet(s) localised on the particle's surface. The droplet then serves as a seed for polymerisation of the second monomer, leading to the formation of a Janus type structure (Figure 1).[4] In this presentation, we will report the synthesis of two Janus nanoparticle systems based on this concept.

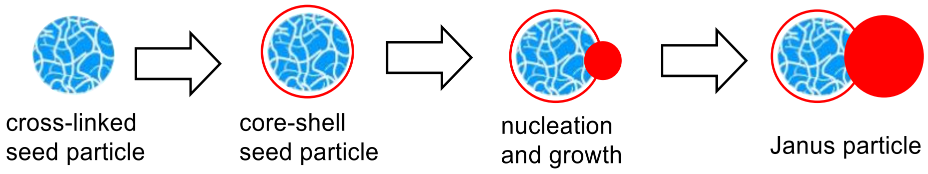

Figure 1. Synthesis of polymer Janus nanoparticles using core-shell particles as seeds.

This work is supported by Agency for Science, Technology and Research (A*STAR) (grant No. SERC1528000049).

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Paper No. P-0124

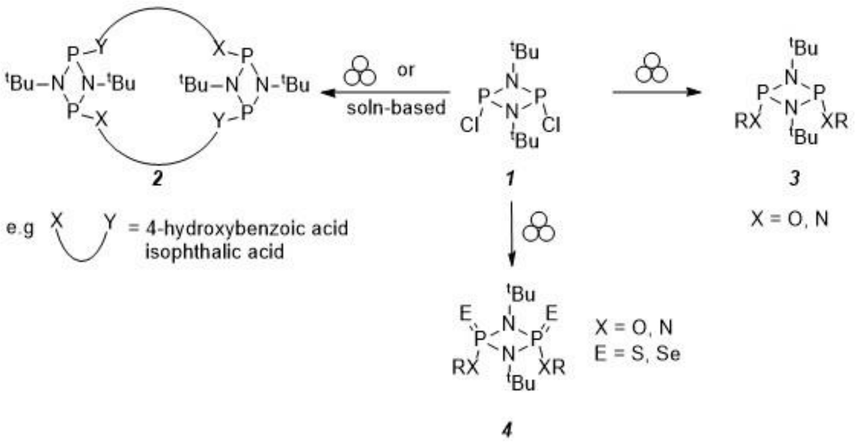
MECHANOCHEMICAL SYNTHESES OF CYCLODIPHOSPHAZANE-BASED FRAMEWORKS

Ying Sim, Felipe García*

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical
Sciences Nanyang Technological University, Singapore 637371, SINGAPORE
Email: Fgarcia@ntu.edu.sg

In pnictogen-nitrogen ring systems, cyclodiphosph(III)azanes, [XP(μ-N^{t}Bu)]$_2$, can be considered as the most extensively research family particularly the dichlorocyclodiphosphazane derivatives (***1***). Cyclodiphosphazanes have been employed in various areas such as ligands in coordination chemistry, catalysis and biological arenas.[1-4] Compound ***1*** has been widely used to synthesize acyclic and cyclic derivatives (***2***-***4***). Despite the vast examples of compounds ***2*** and ***3***, the sensitivities of the compounds towards air and moisture have limited their potential applications. Hence, oxidations were performed on the phosphorus(III) species to yield phosphorus(V) derivatives such as ***4***.

Herein, we report on the work carried out on compound ***1*** using 'greener' synthetic method *i.e.* mechanochemical milling. Compounds ***2***-***4*** can be successfully obtained and isolated by milling for a duration of 3.5 – 10.0 hours at 30 Hz.[5,6] The syntheses of ***4*** were conducted in an orthogonal one-pot one-step manner, shortening the reaction time required as compared to the solution-based method.



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Paper No. P-0127

CORANNULENE MEETS N-HETEROCYCLIC CARBENES

Ezzah M Muzammil, Felipe Garcia*, Mihaiela C. Stuparu*

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University (Singapore)

Corannulene is a maverick in the realm polycyclic aromatic hydrocarbons with its unusual properties; bowl structure, bowl-inversion capability and electron-accepting nature to name a few.[1,2] While corannulene chemistry is still relatively fresh, *N*-heterocyclic carbene (NHC) chemistry is a well-studied field rich in its catalytic applications. We aim to amalgamate these two areas by designing corannulene-based N-heterocyclic carbenes to study the behavior of the corannulene moiety in the carbene, the carbene itself and its catalytic possibilities as metal-ligand complexes. We have successfully synthesized a trio of preceding imidazolium salts and Ag-NHC complexes with corannulene-based substituents using solution-phase and 'greener' mechanochemical means.

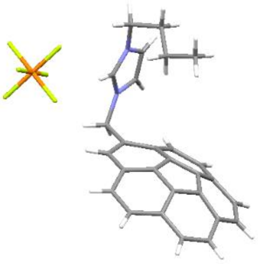

Figure 1. X-ray structure of a corannulene-incorporated imidazolium salt.

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Paper No. P-0128

Pd-CATALYZED ENANTIOSELECTIVE [6+4] CYCLOADDITION OF VINYL OXETANES TO ACCESS TEN-MEMBERED HETEROCYCLES

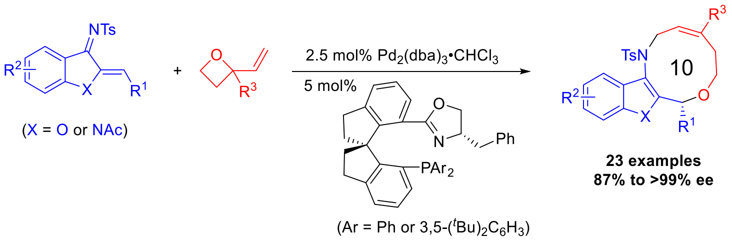
Ya-Nong Wang, Yu Zhao*

National University of Singapore, SINGAPORE

Medium-sized rings are found in a variety of biologically active natural products[1] and their synthesis has attracted much attention in organic chemistry community. The efficient synthesis of them, however, has been a long-standing challenge in organic chemistry. The unfavourable entropic effect for cyclization as well as the strains associated with these cyclic compounds represent key hurdles to overcome.

We have developed the first enantioselective [6+4] cycloaddition of vinyl oxetanes with azadienes to prepare benzofuran- or indole-fused ten-membered heterocycles.[2] By using a commercially available chiral Pd-SIPHOX catalyst, a wide range of azadienes and vinyl oxetanes bearing various substituents can undergo cycloaddition to afford ten-membered heterocycles in excellent yield (66-99%) and enantioselectivity (mostly > 95% ee). A unique Lewis-acid induced fragmentation of these ten-membered cyclic compounds was also discovered.

Highly enantioselective formal [6 + 4] cycloaddition via Pd-catalysis



✓ First enantioselective cycloaddition of vinyl oxetanes

✓ Excellent ee (mostly >95%) for a range of ten-membered heterocycles

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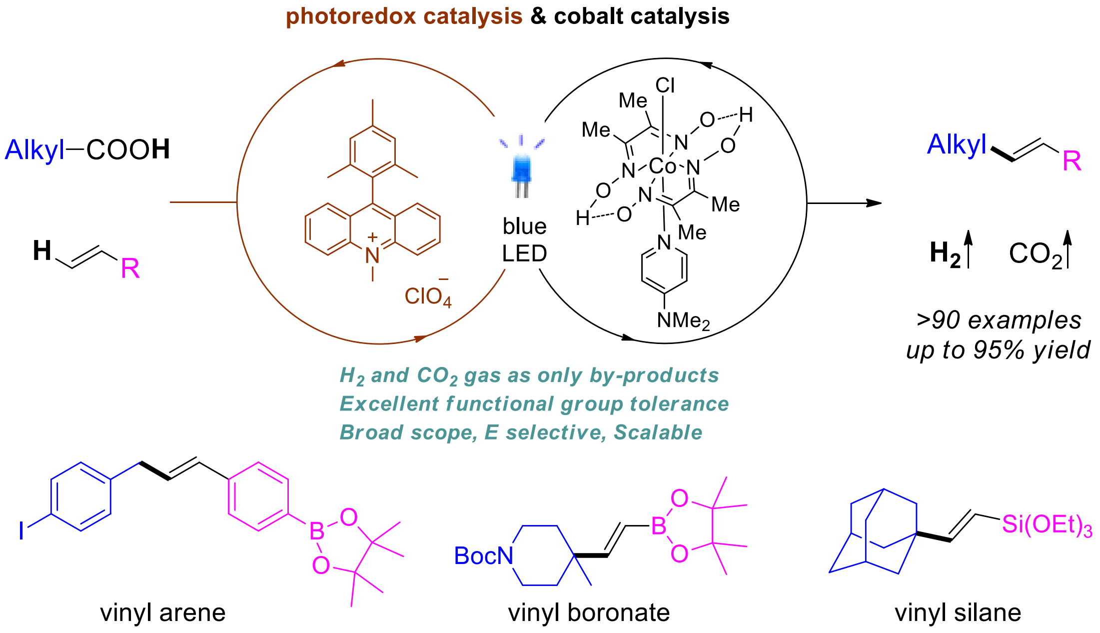
Paper No. P-0131

PHOTO-INDUCED DECARBOXYLATIVE HECK-TYPE COUPLING OF UNACTIVATED ALIPHATIC ACIDS AND TERMINAL ALKENES IN THE ABSENCE OF SACRIFICIAL HYDROGEN ACCEPTORS

Hui Cao,† Heming Jiang,‡ Hongyu Feng,† Jeric Mun Chung Kwan,† Xiaogang Liu,† and Jie Wu*,†

†Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Republic of Singapore
‡Lab of Computational Chemistry & Drug Design, Key Laboratory of Chemical Genomics, Peking University Shenzhen Graduate School, Shenzhen, 518055, China

1,2-Disubstituted alkenes such as vinyl arenes, vinyl silanes, and vinyl boronates are among the most versatile building blocks that can be found in every sector of chemical science. We herein report a noble-metal-free method of accessing such olefins through a photo-induced decarboxylative Heck-type coupling using alkyl carboxylic acids, one of the most ubiquitous building blocks, as the feedstocks. This transformation was achieved in the absence of external oxidants through the synergistic combination of an organo photoredox catalyst and a cobaloxime catalyst, with H_2 and CO_2 as the only by-products. Both control experiments and DFT calculations supported a radical-based mechanism which eventually led to the development of a three-component selective coupling of aliphatic carboxylic acids, acrylates and vinyl arenes. More than 90 olefins across a wide range of functionalities were effectively synthesized with this simple protocol.



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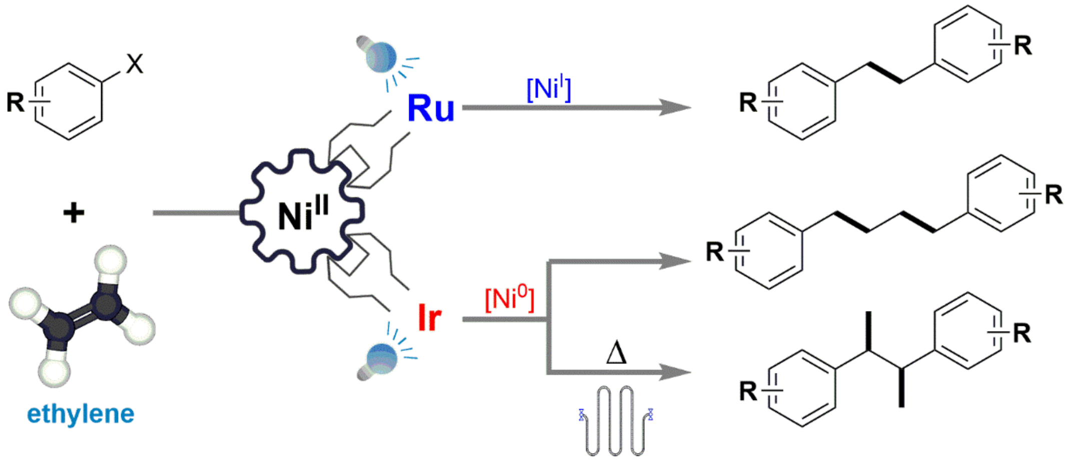
Paper No. P-0132

PHOTOREDOX CATALYSIS MODULATED NICKEL-CATALYZED DIVERGENT DIFUNCTIONALIZATION OF ETHYLENE

Li Jiesheng[1], Luo Yixin[2], Cheo Han Wen[1], Lan Yu[2,]*, Wu jie[1,]*

[1]Department of chemistry, National University of Singapore, 3 Science Drive 3, Republic of Singapore 117543
[2]School of chemistry and chemical engineering, Chongqing University, Chongqing, P. R. China 400044

Divergent synthesis represents a powerful strategy to directly access different molecular scaffolds originating from the same starting materials. The access to different end-products via transition-metal catalysis is conventionally achieved by ligand control. We herein demonstrate the use of ethylene feedstock and commercially available aryl halides to accomplish the divergent synthesis of 1,2-diarylethanes, 1,4-diarylbutanes, or 2,3-diarylbutanes in a highly selective fashion through the synergistic combination of nickel and photoredox catalysis. Mechanistic studies suggest that the observed selectivity was due to different active states of Ni(I) and Ni(0) modulated by Ru- and Ir-based photoredox catalysts respectively. The ability to access different organometallic oxidation states via photoredox catalysis promises to inspire new perspectives for synergistic transition-metal-catalyzed divergent synthesis.



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Paper No. P-0133

Ultrafast electrochemical expansion of black phosphorus towards high-yield synthesis of few-layer phosphorene

Cheng Chen[1]and Jiong Lu[1,2]*

[1]Department of Chemistry, National University of Singapore, Singapore

[2] Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore, Singapore

To bridge the gap between laboratory research and applications, it is vital to develop scalable methods to produce large quantities of high-quality and solution-processable few-layer phosphorene (FLBP). In this project, we successfully develop a novel electrochemical exfoliation approach for the large-scale production of black phosphorus thin films. Remarkable progress has been made by using the electrochemical method for the exfoliation of graphite into thin-layer graphene without oxidization. This approach will be further modified for the exfoliation of black phosphorus into phosphorene as well as other 2D materials. Our method relies on the intercalation of black phosphorus using organic ions tetrabutylammonium and organic solvent DMSO. These organic ions can be driven by electrical voltage and diffuse into the interlayer space of black phosphorus. This electrochemical reaction leads to the expansion of black phosphorus and formation of black phosphorus intercalated compounds. Large-sized black phosphorus and thin fakes can be obtained after the dispersion of expanded BP in the organic solvent. Different organic solvents and different alkane ammonium salts are explored to optimize the results. We noticed that electrolyzing bulk black phosphorus in DMSO and ammonium ions gives the best results of large-sized thin layer black phosphorus after sonication dispersion in DMSO.

We have reported an ultrafast cathodic expansion (in minutes) of bulk black phosphorus in the non-aqueous electrolyte of tetraalkylammonium salts that allows the high-yield synthesis of nonoxidative few-layer BP flakes with high crystallinity in ambient conditions. The yield of FLBP (> 80%) obtained from bulk BP electrode is significantly higher than that produced by liquid-phase exfoliation methods. The FLBP via our method shows extraordinary crystal quality and electronic properties. In addition, the fully expanded BP can be further dispersed in a wide range of solvents. The BP thin flakes dispersed in high-boiling solvents exhibit a high air-stability, facilitating the development of long-term stable electronic and optoelectronic devices. The concentrated BP inks can also be obtained using low-boiling point solvents, which make them suitable for use in large-area inkjet printing technology to produce uniform BP thin films for printable optoelectronic devices. Therefore, the high-quality and solution processable FLBP obtained here holds great promise for use in a wide range of applications ranging from hybrid compositions, wearable sensors to printable electronic and photonics devices.

Word count: 427

CONTACT/PRESENTING AUTHOR

* Jiong Lu, tel: +65-81984182; E-mail: chmluj@nus.edu.sg

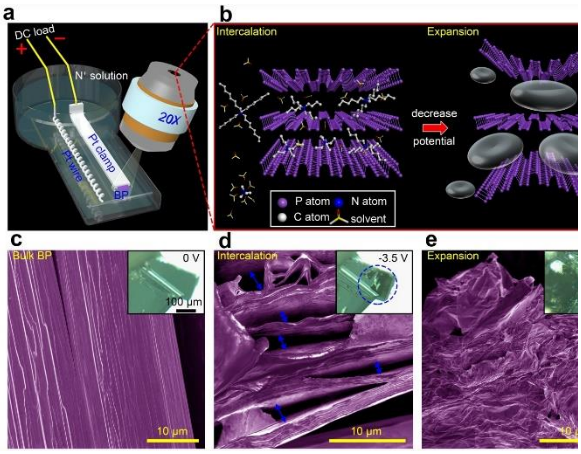

Figure 1. Schematic illustration of micro-electrochemical cell mounted beneath optical microscopy and Illustration of the intercalation and expansion of BP cathode in organic DMSO electrolyte consisting of TAA salts.

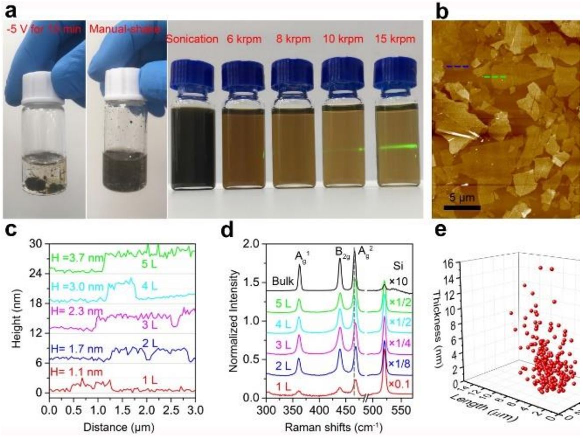

Figure 2. Basic characterization of as-exfoliated FLBP. (a) Photographs of (left) bulk BP in DMSO after electrochemical charging at -5 V for 10 min, (center) dispersion of expanded BP via manual-shaking; (right) FLBP dispersions centrifuged at different speeds exhibit the Tyndall effect. (b) A representative AFM image of FLBP flakes deposited onto a SiO2/Si substrate via drop-casting and (c) AFM height profile and (d) Raman spectra of the exfoliated BP flakes with different thickness ranging from one to five layers. (e) The statistic information of the size (length and width) and thickness distribution of exfoliated FLBP flakes.

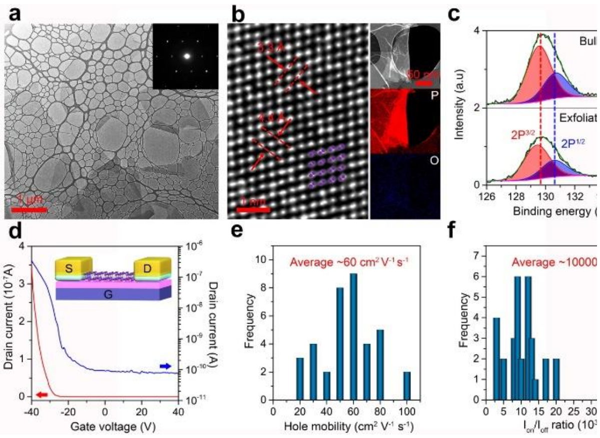

Figure 3. Structural characterization and charge transport measurement of the exfoliated FLBP and FET devices. (a)(b) TEM image of FLBP flakes with the corresponding SAED and TEM-EELS imaging (c) P 2p core level XPS spectra of bulk BP and the exfoliated FLBP. (d) A charge transport curve for a FLBP FET device. A schematic illustration of as-fabricated device is included in the inset of (d). (e)-(f) Histograms of the hole-mobility and on/off ratio for the FLBP FET devices.

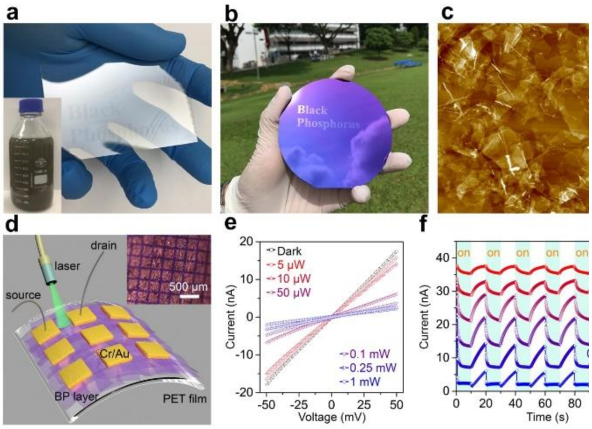

Figure 4. The inkjet printing of as-exfoliated FLBP flakes. (a)-(b) Inkjet printing of FLBP to form the patterns on a (a) PET and a (b) SiO2/Si wafer (c) AFM imaging of printed BP thin films on a SiO2/Si substrate. (d) Schematic illustration and optical microscopic image (inset) of the large-area photodetector consisting of FLBP thin films deposited on a PET substrate. (e) I-V characteristics and the corresponding (f) photoresponse of large-area FLBP optical devices under a global irradiation of 532 nm laser with different power.

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