# 綠色/永續化學資訊共享 2013.03.25

彰化師範大學化學系 林秋薰教授

This communication contains materials for advancing green chemistry by utilizing alternative solvents, mechanochemistry, nanocatalysis and green feedstock, either separately or together (hoping for a synergistic effect). The materials are divided into four parts: (I) green chemistry meetings (pp. 1), (II) on-line seminar (pp. 1), (III) green chemistry books (pp. 2-3) and (IV) interesting news and developments. (pp.3- 13)

## I. **Green Chemistry Meetings**: for the coming summer, 2013.

(1) The Green Chemistry & Engineering Conference, June 18-20, 2013, Rockville, MD, USA (near Washington, DC).

(2) 6th International Conference on Green and Sustainable Chemistry, August 4-7, 2013, Nottingham, United Kingdom.

(3) ICOSSE '13 - 3rd International Congress on Sustainability Science & Engineering, August 11-15, 2013, Cincinnati, Ohio, USA.

(4) Sustainable Chemistry 2013, September 3-5, 2013, New Forest, United Kingdom.

(5) Green Chemistry, Gordon Research Conference, July 27 - August 1, 2014, The Chinese University of Hong Kong, Hong Kong, China; Gordon Research Seminar, July 26-27, 2014, The Chinese University of Hong Kong, Hong Kong, China.

## II. **On-line Seminar:** speech is on March 28, 2013.

(6) ACS Webinars - Using Water to Replace Organic Solvents: Switchable Water(**此則信息由中研院化學所趙奕竫教授提供)**

## III. Green Chemistry Books:

(7) Alternative Solvents for Green Chemistry, 2nd Edition:

Authors: Francesca M Kerton and Ray Marriott; Publisher: Royal Society of Chemistry; ISBN: 9781849735957; Publication date: 31/01/2013

Conventional solvents can be hazardous in terms of toxicity, flammability and waste generation. Consequently, alternative solvents now form a substantial part of green chemistry. This book covers the latest developments in this growing field as well as some key areas that have been overlooked in previous literature. Solvents are important in many areas of chemistry so the author has adopted a general approach encompassing of a wide range of solvents. Examples are used that tie in with the 12 principles of green chemistry such as atom efficient reactions in benign solvents, processing of renewable chemicals and materials in green solvents. Accessible in style, the book is suitable for novices including research students as well as those wanting to expand their existing knowledge.

(8) Green Techniques for Organic Synthesis and Medicinal Chemistry: Editors: Wei Zhang, Berkeley W. Cue; Publisher: John Wiley & Sons, Ltd; PRINT ISBN: 9780470711514; ONLINE ISBN: 9780470711828; Publication date: 5/29/2012.

DOI: 10.1002/9780470711828

Green chemistry is a new way of looking at organic synthesis and the design of drug molecules, offering important environmental and economic advantages over traditional synthetic processes. **Pharmaceutical companies** are increasingly turning to the principles of green chemistry in an effort to reduce waste, reduce costs and develop environmentally benign processes. *Green Techniques for Organic Synthesis and Medicinal Chemistry* presents an overview of the established and emerging techniques in green organic chemistry, highlighting their applications in medicinal chemistry. The book is divided into four parts: **Introduction:** Introduces the reader to the toxicology of organic chemicals, their environmental impact, and the concept of green chemistry. **Green Catalysis**: Covers a variety of green catalytic techniques including organocatalysis, supported catalysis, biocatalysis, fluorous catalysis, and catalytic direct C-H bond activation reactions. **Green Synthetic Techniques:** Presents a series of new techniques, assessing the green chemistry aspects and limitations (i.e. cost, equipment, expertise). Techniques include reactions in alternative solvents, atom economic multicomponent reactions, microwave and ultrasonic reactions, solid-supported synthesis, fluorous and ionic liquid-based recycling techniques, and flow reactors. **Green Techniques in Pharmaceutical Industry:** Covers applications of green chemistry concepts and special techniques for medicinal chemistry, including synthesis, analysis, separation, formulation, , and drug delivery. Process and business case studies are included to illustrate the applications in the pharmaceutical industry. *Green Techniques for Organic Synthesis and Medicinal Chemistry* is an essential

resource on green chemistry technologies for academic researchers, R&D professionals and students working in organic chemistry and medicinal chemistry.

(9) Green Materials for Sustainable Water Remediationand Treatment: Editors: Anuradha Mishra and James H Clark; Publisher: Royal Society of Chemistry; ISBN: 9781849736213; Publication date: 30/03/2013

One of the most pervasive problems afflicting people throughout the world is inadequate access to clean water. Addressing these problems calls out for a tremendous amount of research to be conducted to identify robust new methods of purifying water at lower cost and with less energy, while at the same time minimizing the use of chemicals and impact on the environment. Green and sustainable water remediation is a rapidly growing field of interest to all stakeholder groups including governmental agencies, corporations, academia, environmental consultants and public interest groups. This book presents a focused set of articles covering a range of topics in the field of green materials for water remediation including the synthesis of new materials, modification of natural materials and use of clean technologies for water purification.

(10) Sustainable Preparation of Metal Nanoparticles: Methods and Preparations

Editors: Rafael Luque and Rajender S Varma; Publisher: Royal Society of Chemistry; ISBN: 978-1-84973-428-8

This timely publication bridges and presents the latest trends and updates in three hot topics of current and future society: nanomaterials, energy and environment. It provides the state-of-the-art as well as current challenges and advances in the sustainable preparation of metal nanoparticles and their applications. The book fills a critical gap in a multidisciplinary area of high economic, social and environmental importance. Currently, there are no books published that deal with these ever increasing important topics, as most books in this area focus on a particular topic (eg. nanomaterials or catalysis or energy or environment). This is the first multidisciplinary edited book covering the very basics to the more advanced, trendy developments, containing a unique blend of nano, green, renewable and bio.

## IV. Interesting News and Developments in Green Chemistry:

(11) Teaching Green: **C&E News, volume 90**, issue 40, pp. 64-65, 2012.

**A group of educators** in the U.S. has grown impatient with the slow headway in integrating the concepts of green chemistry and toxicology into the undergraduate chemistry curriculum. They are ready to ask academic institutions for pledges to accelerate that progress through an initiative called the Green Chemistry Commitment.

**The Green Chemistry Commitment's learning objectives are designed to ensure that chemistry majors have proficiency in essential green chemistry competencies.**

- **Theory:** Have a working knowledge of the 12 Principles of Green Chemistry.
- **Toxicology:** Have an understanding of the principles of toxicology, the molecular mechanisms of how chemicals affect human health and the environment, and how to access the resources to identify and assess molecular hazards.
- **Laboratory skills:** Possess the ability to recognize, assess, and design greener alternative chemical products and processes.
- **Application:** Be prepared to serve society in their professional capacities as scientists through the articulation, evaluation, and employment of methods and chemicals that are benign for human health and the environment.

(12) Petronas and LanzaTech to recycle $CO_2$ into sustainable chemicals: **C&E News**, **volume 90**, issue 35, pp. 25, 2012.

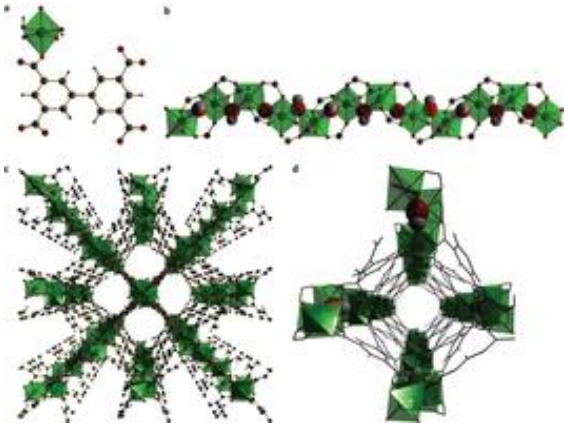
In the crowded but still-young renewable fuels and chemicals sector, one start-up firm stands out. Unlike most other companies using biology to make chemicals, LanzaTech does not rely on biomass feeds tocks. Instead, it makes its products from carbon monoxide (and from $CO_2$ by working with Petronas) found in emissions from steel mills and other industrial operations. The company's specialized microbes consume the gas and spit out ethanol and 2,3-butanediol (2,3-BDO) in a continuous process. LanzaTech intends to compete with traditional fuel and chemical companies by doing this on a large scale.


**(13)** Selectivity and direct visualization of carbon dioxide and sulfur dioxide in a decorated porous host: **Nature Chemistry**, 2012, **4**, 887–894.

DOI:10.1038/nchem.1457

Understanding the mechanism by which porous solids trap harmful gases such as $CO_2$ and $SO_2$ is essential for the design of new materials for their selective removal. Materials functionalized with amine groups dominate this field, largely because of

their potential to form carbamates through $H_2N(\delta^-)\cdots C(\delta^+)O_2$ interactions, thereby trapping $CO_2$ covalently. However, the use of these materials is energy-intensive, with significant environmental impact. Here, we report a non-amine-containing porous solid (NOTT-300) in which hydroxyl groups within pores bind $CO_2$ and $SO_2$ selectively. *In situ* powder X-ray diffraction and inelastic neutron scattering studies, combined with modelling, reveal that hydroxyl groups bind $CO_2$ and $SO_2$ through the formation of $O{=}C(S){=}O(\delta^-)\cdots H(\delta^+)–O$ hydrogen bonds, which are reinforced by weak supramolecular interactions with C–H atoms on the aromatic rings of the framework. This offers the potential for the application of new 'easy-on/easy-off' capture systems for $CO_2$ and $SO_2$ that carry fewer economic and environmental penalties.



The structure of NOTT-300.

(14) Solvent Choices and Sustainable Chemistry - Editorial: **ChemSusChem,** 2012, **5**, 2291-2292. **(此則信息由台大化學系劉廣定教授提供)**

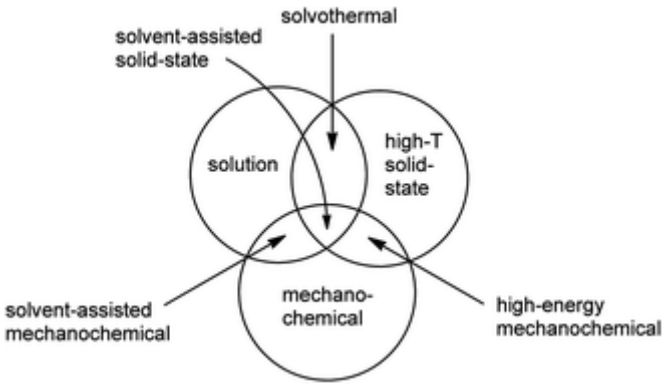
DOI: 10.1002/cssc.201200873

**No easy solutions:** Choosing a solvent for a certain reaction is not easy, and involves sustainability on many levels. The choice can be motivated by wanting to reduce or avoid wastes, reduce resource use, lower risks to humans and the environment, lessen energy use, or other ways of avoiding liabilities and costs. *ChemSusChem* wishes to promote thoughtful discussions on solvent use, and outlines in this Editorial basic guidelines for authors and referees.

(15) Solvent-assisted mechanochemistry: **Chem. Commun.**, 2013, **49**, 334-348. **(此則信息由台大化學系劉廣定教授提供)**

DOI: 10.1039/C2CC35694E

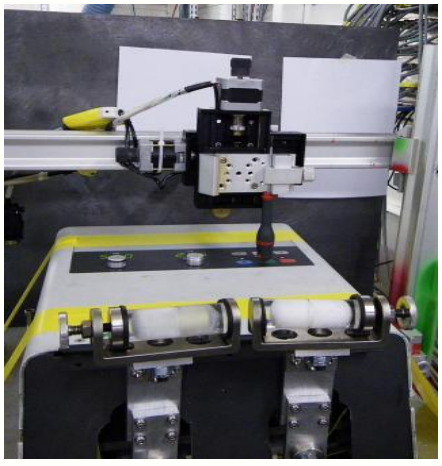
A review of solvent-assisted **mechanochemistry** covering its range of applicability, theories of mechanism, and summarizing its advantages and limitations.




(16) A better way to make chemicals? Technique for observing synthesis could boost green chemistry.

http://www.mcgill.ca/medicine/channels/news/better-way-make-chemicals-219243

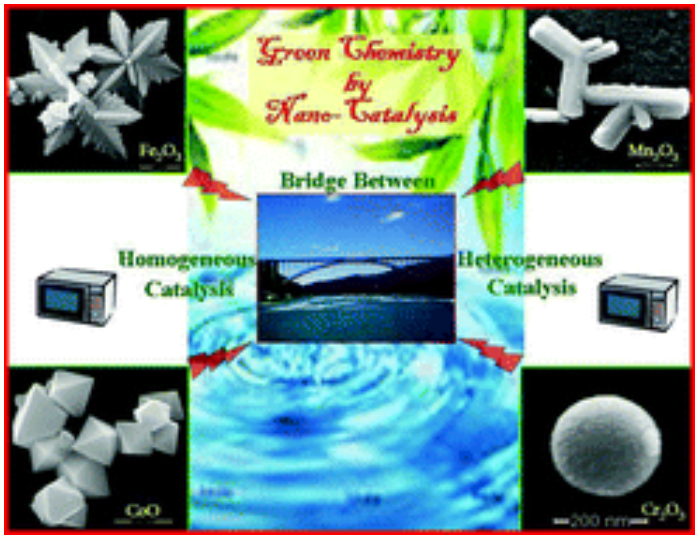
Bulk solvents, widely used in the chemical industry, pose a serious threat to human health and the environment. As a result, there is growing interest in avoiding their use by relying on **"mechanochemistry"** – an energy-efficient alternative that uses high-frequency milling to drive reactions. Because milling involves the intense impact of steel balls in rapidly moving jars, however, the underlying chemistry is difficult to observe.



(17) Green chemistry by nano-catalysis: ***Green Chem.***, 2010, **12**, 743-754.

DOI: 10.1039/B921171C

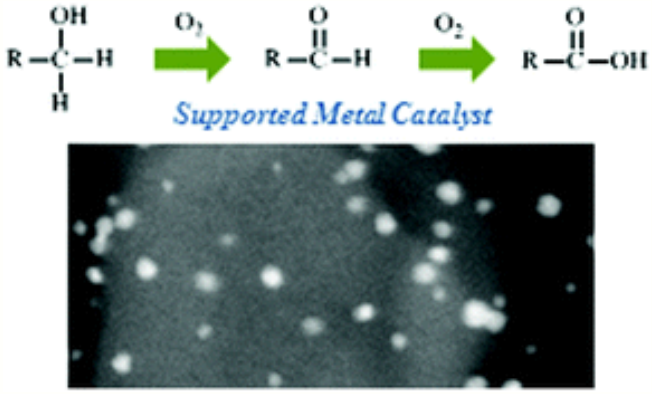
Nano-materials have emerged as sustainable and high surface area heterogeneous catalysts which mimic the homogeneous catalysts. This review focuses on the role of nano-catalysts in green chemistry development including the strategy of using **microwave** heating with **nano-catalysis** in benign **aqueous media** which offers an extraordinary **synergistic effect** with greater potential than these three components in isolation.




(18) Selective oxidation of alcohols and aldehydes over supported metal nanoparticles - Critical Review: ***Green Chem.***, 2013,**15**, 17-45.

DOI: 10.1039/C2GC36441G

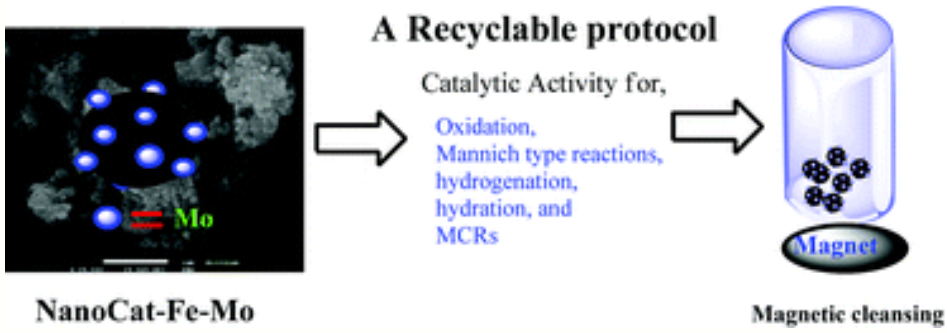
Oxidation is a key reaction in organic synthesis and will likely play a significant role in the development of value-added chemicals from biomass. The application of heterogeneous catalysis and molecular oxygen to oxidation reactions offers a green alternative to traditional, toxic chemical oxidants. However, making comparisons of catalyst performance (reaction rate, product selectivity) between reports in the literature is difficult because of inconsistencies in the ways results are reported. Herein, we examine the literature on supported metal catalysts for the oxidation of molecules of interest in biomass conversion (primary alcohols, polyols, 5-hydroxymethylfurfural, and various sugars). Reaction rates are calculated and compared in a consistent manner and recommendations for avoiding common pitfalls in kinetic investigations are made.




(19) Catalytic applications of a versatile magnetically separable Fe–Mo (Nanocat-Fe–Mo) nanocatalyst: ***Green Chem.***, 2013,**15**, 682-689

DOI: 10.1039/C3GC36844K

A novel nano-$Fe_3O_4$–$MoO_3$ (Nanocat-Fe–Mo) catalyst was prepared *via* simple wet impregnation and characterized by several techniques. The synthesized Nanocat-Fe–Mo was found to be a highly active and efficient catalyst in the oxidation of benzyl alcohol and a series of examples of important organic reactions including A3 couplings, hydrogenations and hydrations. The Nanocat-Fe–Mo could be reused and recycled up to 7 times without any significant yield loss.

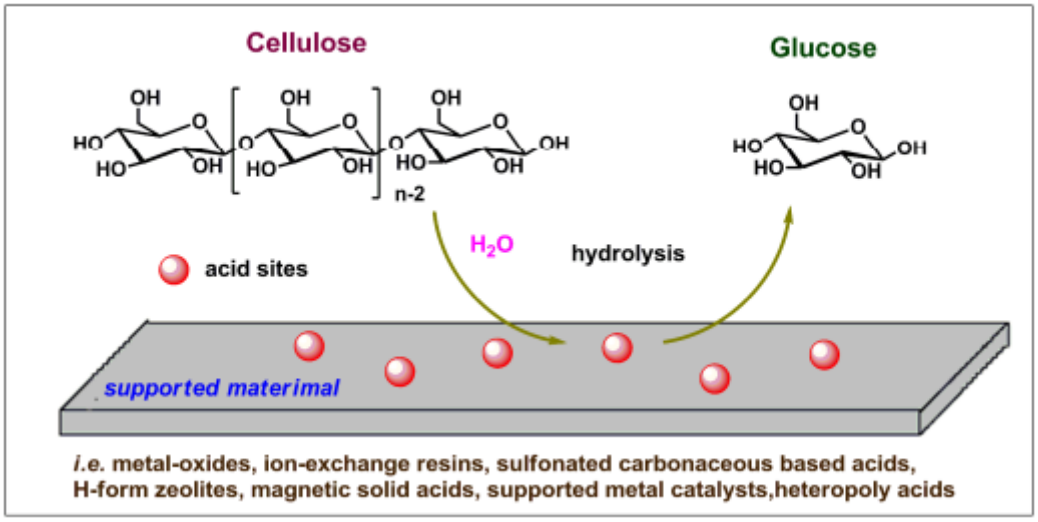



(20) Hydrolysis of cellulose to glucose by solid acid catalysts - Tutorial Review: ***Green Chem.***, 2013, Accepted Manuscript.

**DOI:** 10.1039/C3GC40136G

As the main component of lignocelluloses, cellulose is a biopolymer consisted of many glucose units through β-1, 4 glycosidic bonds. Breakage of the β-1, 4 glycosidic

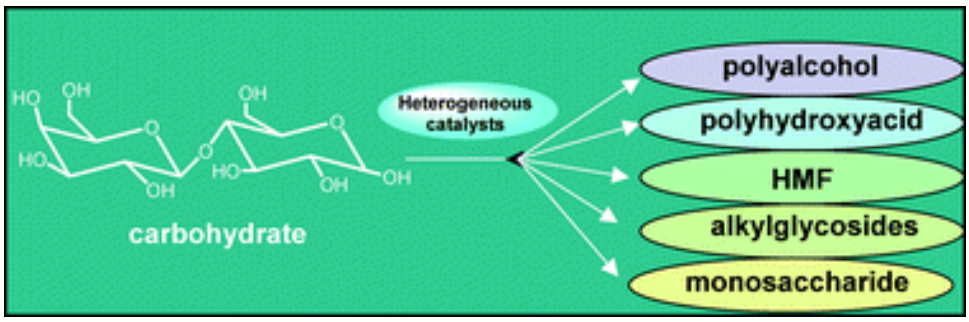
bonds by acids leads to the hydrolysis of cellulose polymers, resulting in the sugar molecule glucose or oligosaccharides. Mineral acids, such as HCl, H2SO4, have been used in the hydrolysis of cellulose. However, they suffer from the problems of product separation, reactor corrosion, catalyst recycle and the treatment of waste effluents. The use of heterogeneous solid acids can solve some of the mentioned problems through the ease of product separation and good catalyst recyclability. The review summarized the recent advances on the hydrolysis of cellulose by different types of solid acids, such as sulfonated carbonaceous based acids, polymer based acids and magnetic solid acids. The acid strength, acid sites density, adsorption of the substance and micro pores of the solid material are all key factors for the effective hydrolysis processes. Methods used to promote reaction efficiency such as the pretreatment of cellulose to reduce its crystallinity and the use of ionic liquid or microwave irradiation to improve the reaction rate have also been discussed.




(21) Converting carbohydrates to bulk chemicals and fine chemicals over heterogeneous catalysts: ***Green Chem.***, 2011,**13**, 520-540.

DOI: 10.1039/C0GC00639D

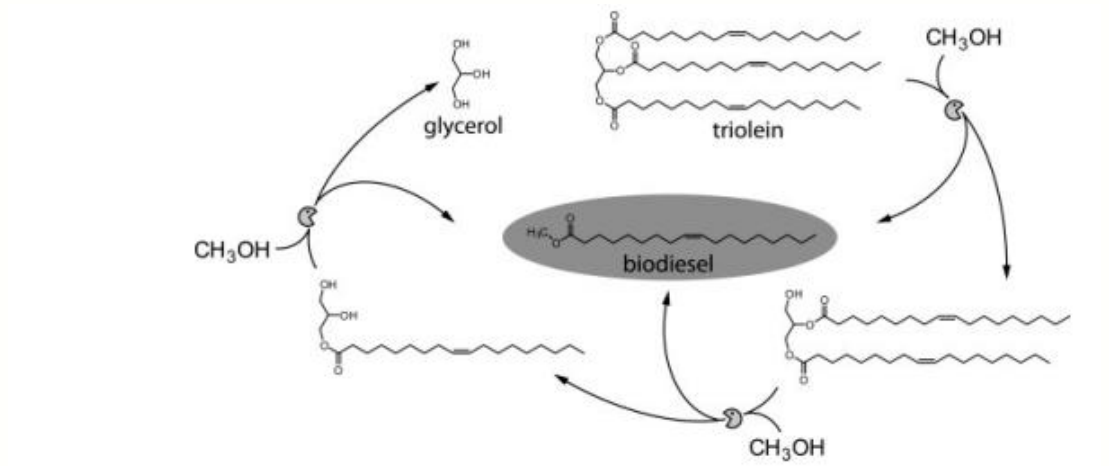
In this Critical Review, we discuss how carbohydrates can be transformed into a variety of chemicals through heterogeneous catalysis. We focus particularly on oxidation, reduction and dehydration of hexoses, as well as one-pot reactions of di- and polysaccharides. Most of the reactions involve heterogeneous catalysts, although some interesting homogeneously catalyzed processes are also included.




(22) Ionic liquids and deep eutectic solvents for biodiesel synthesis: a review: **J Chem Technol Biotechnol**, 2013, **88**, 3-12.

DOI: 10.1002/jctb.3935

During the past decade, **ionic liquids (ILs)** have gained tremendous attention in nearly every branch of the chemical and physical sciences as designer (task-driven) and budding 'green' solvent alternatives to conventional volatile organics. In particular, with a more in-depth understanding of their physicochemical properties, the active exploration of ILs as alternative solvents and/or catalysts in the chemical or enzymatic (biocatalytic) production of biodiesel has gained momentum. Most excitingly, very recent developments in the science of **deep eutectic solvents (DESs)** have initiated potentially more cost-effective approaches to biodiesel synthesis. At this stage, there is sufficient research completed to provide an important opportunity to stand back and assess the progress in the field, critically examining the strengths and limitations for IL and DES technology in biodiesel synthesis. No such comprehensive evaluation exists. This work, therefore, seeks to bridge this gap by systematically reviewing the reported methods for biodiesel production which make use of ILs, either as (co)solvent components or catalysts, highlighting existing problems and limitations, with an emphasis placed on the future research required to bypass the hurdles to employing ILs in commercial biodiesel production.

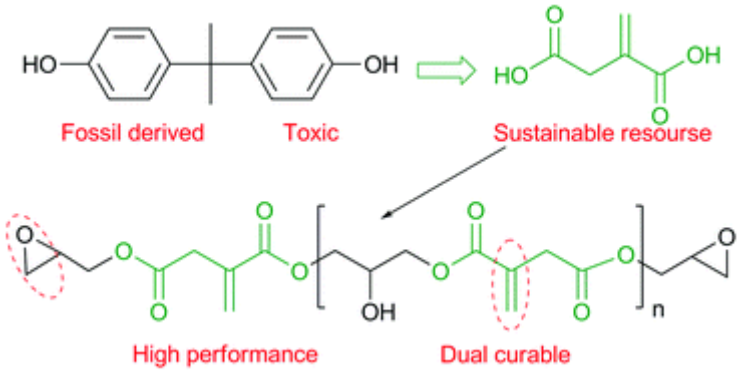



**Scheme 1.** Schematic illustration of the chemo- or bio-catalyzed synthesis of biodiesel by methanolysis of triolein (glyceryl trioleate).

(23) Bio-based epoxy resin from itaconic acid and its thermosets cured with anhydride and comonomers: ***Green Chem.***, 2013, **15**, 245-254.

DOI: 10.1039/C2GC36715G

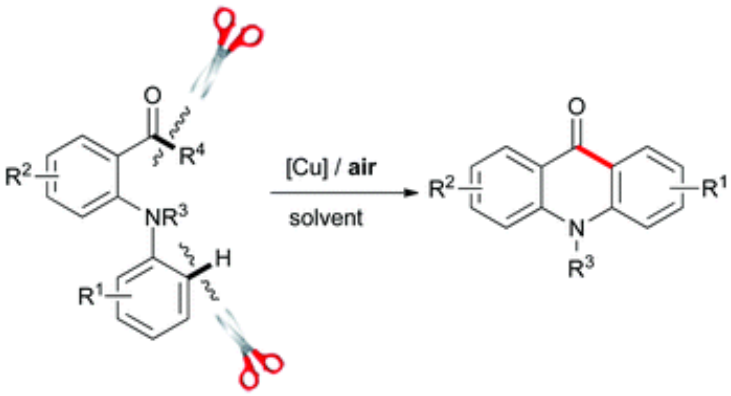
A novel itaconic acid (IA) based epoxy resin with curable double bonds (EIA) was synthesized by the esterification reaction between IA and epichlorohydrin (ECH). Its chemical structure was confirmed in detail by FT-IR, $^{1}$H-NMR and ESI-ION TRAP MS before being cured by methyl hexahydrophthalic anhydride (MHHPA). In order to manipulate the properties of the cured resin, divinyl benzene (DVB) and acrylated epoxidized soybean oil (AESO) were employed here to act as comonomers. The results demonstrated that EIA showed a higher epoxy value of 0.625 and higher curing reactivity toward MHHPA compared with the commonly used diglycidyl ether of bisphenol A (DGEBA). The glass transition temperature, tensile strength, flexural strength and modulus of the cured EIA without comonomers were 130.4 °C, 87.5 MPa, 152.4 MPa and 3400 MPa, respectively, which were comparable or better than those of DGEBA cured by the same curing agent. After being copolymerized with DVB or AESO, the properties of the cured EIA could be regulated further. The results indicated that EIA has great potential to replace the petroleum-based thermosetting resin, such as DGEBA.




(24) Copper-catalyzed C–C bond cleavage and intramolecular cyclization: an approach toward acridones: ***Green Chem.***, 2013,**15**, 76-80

DOI: 10.1039/C2GC36502B

A copper-catalyzed approach for the synthesis of acridones *via* C–C bond cleavage and intramolecular cyclization using air as the oxidant under neutral conditions is described. This transformation offers an alternative method to prepare medicinally important acridones and a new strategy for C–C bond cleavage.




(25) Selective Separation of Water, Methanol, and Ethanol by a Porous Coordination Polymer Built with a Flexible Tetrahedral Ligand: **JACS**, 2012, **134**, 13145-13147.

A novel porous coordination polymer, CuI I(mtpm)Cl2 [mtpm = tetrakis(m-pyridyloxy methylene)methane], has been synthesized, and its crystal structure has been determined. Its adsorption isotherms for water, methanol, and ethanol are totally different from each other. It adsorbs water at low humidity and shows gate-open behavior for methanol, but it does not adsorb ethanol. **This compound has the capacity to separate both methanol and water from bioethanol,** which is a mixture of water, methanol, and ethanol.

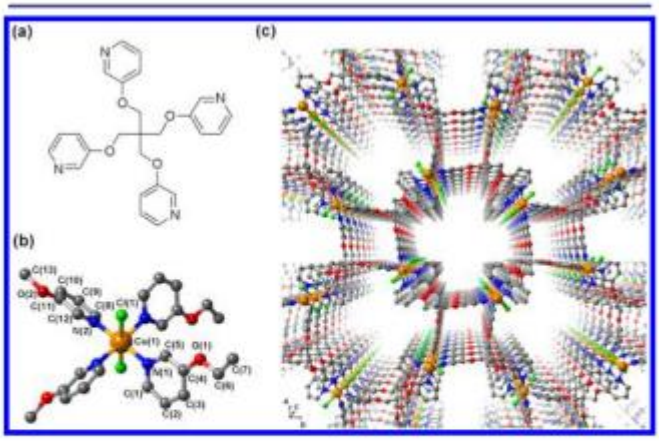



**Figure 1.** (a) Structure of mtpm. (b) Coordination geometry of copper ions with the labeling scheme of the building unit, $Cu(mtpm)Cl_2$. (c) View of **1** along the *c* axis. The colors red, blue, gray, green, and orange correspond to oxygen, nitrogen, carbon, chlorine, and copper atoms, respectively.

(26) Gas storage in renewable bioclathrates: ***Energy Environ. Sci.***, 2013, **6**, 105-107.

DOI: 10.1039/C2EE23565J

Methane and carbon dioxide can be stored in 'bioclathrate' form—that is, as a clathrate supported in a biological structure—by using plants or fungi to greatly accelerate clathrate formation kinetics, thus avoiding the use of energy-intensive mixing technologies or petrochemically derived materials.