

Technical & Commercial Progress in the Global Catalytic Process Industries



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NMR Relaxation in Porous Catalysts: A Useful Tool to Aid Catalyst Selection and Process Optimization



Industry Perspectives: NYCS Annual Symposium Showcases Catalysis Research

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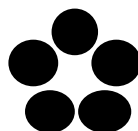
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NYCS Annual Symposium Showcases Catalysis Research

By Benjamin M. Moskowitz

The Catalysis Society of Metropolitan New York held their Annual Symposium at the Research and Development Center of the ExxonMobil Research and Engineering Company in Clinton, NJ. This year's meeting took place on March 22, 2017 and was attended by 132 participants. The technical program was comprised of one keynote address, six oral presentations, and 48 posters on display. Furthermore, 11 organizations provided generous sponsorship for the event, with seven companies exhibiting their latest products and developments for catalysis research and characterization.

The conference began with a lecture by Dr. Partha Nandi (ExxonMobil) on "O₂ Activation in Mesoporous Mixed Metal Oxides: Implications in Catalytic Aerobic Oxidation." In this lecture (**Figure 1**), it was explained how insights gained from evaluating non-precious mesoporous mixed metal oxides for the oxygen reduction reaction were used in the development of novel catalysts for the partial oxidation of organic small molecules. The following keynote address by Prof. Suljo Lincic (University of Michigan, Ann Arbor) was on the "Analysis of the Mechanism of Electrochemical Oxygen Reduction and Development of Ag- and Pt-alloy Catalysts for Low Temperature Fuel Cells." Prof. Lincic described kinetic and micro-kinetic analyses that allowed for the identification of the elementary steps and molecular descriptors governing the rate of ORR. Based on these findings, his group was able to synthesize alloys with superior ORR performance.



Dr. Partha Nandi (ExxonMobil) delivering the day's opening lecture.

After this very inspiring lecture, the attendees broke for a poster session and vendor expo, which featured mainly academic but also industrial poster presenters. This session was followed by a talk by Prof. Daniel Esposito (Columbia University) on "Membrane-coated Electrocatalysts for the Hydrogen Evolution Reaction." Prof. Esposito highlighted the remarkable durability and HER performance of electrocatalysts with oxide overlayers, an architecture with tunable transport properties. Afterwards, Prof. Thomas Schwartz (University of Maine) presented "Strategies for the Conversion of Biomass to Biobased Chemicals." Prof. Schwartz described how biological catalysts can be used to convert biomass into platform molecules suitable for upgrading by heterogeneous chemical catalysts. Furthermore, he showed an example of tuning active sites and transition states for lactic acid and triacetic acid lactone hydrogenation by control of their microenvironment.

Following lunch and another poster session, Prof. Eleni Kyriakidou (The State University of New York, Buffalo) presented "A Comparative Study of ZSM-5 and BEA Zeolites for Low Temperature Passive Adsorption." Her research focused on hydrocarbon and NO temporary storage during vehicle cold starts and subsequent release once emission control catalysts are catalytically active. Her results demonstrated the need for an ion-exchanged metal for effective performance in the presence of water. The next contribution by Dr. David Stockwell (BASF) on a "Continuous Age Distribution Method for Catalytic Cracking," described a new laboratory steam-deactivation method that reproduces the full distribution of ages found in the FCC 'equilibrium' catalyst mixture. He emphasized that with consideration for some surprising decay rates, quantitative, predictive results for catalyst replacement in the refinery can be achieved. Dr. Allen Burton (ExxonMobil) rounded out the technical program with a talk on "The Discovery, Structure Elucidation, and Characterization of Zeolite EMM-23: A Highly Unusual Zeolite." By the time Dr. Burton passed a physical model of the structure around the lecture hall, the audience appreciated the careful characterization and refinement work done to describe this new material.

At the close of the symposium, the Society awarded prizes for the best poster presentations, with Tao Chen (Stevens Institute of Technology) and Elaine Gomez (Columbia University) taking first and second place honors, respectively. Weimang Wan (Columbia University) won third place and Robyn Smith (City College of New York) and Alexandros Karaiskakis (City College of New York) tied for fourth place. Finally, Dr. Ke Xiong (Ingredient) touched on the day's highlights and thanked the organizers, sponsors, and all attendees. Altogether, the 2017 Spring Symposium featured excellent lectures and poster presentations with a wide range of catalysis topics represented. Next year marks the 60th anniversary for the Catalysis Society of Metropolitan New York. We can look forward to another stimulating program of monthly meetings and another successful annual symposium. For more information, please visit www.nycsweb.org.

About the Author

Benjamin M. Moskowitz is the Student Representative for The Catalysis Society of Metropolitan New York, a non-profit organization founded in 1958 to promote and encourage the growth and development of the science of catalysis in the New Jersey and Metro New York areas. Benjamin is currently a graduate student working towards his PhD at Lehigh University under the direction of Professor Israel E. Wachs.

China Plans Waves of New Crackers...

Details are emerging on what could be as many as 13 new crackers in China for start-up over the next few years. This raises the possibility that China might end up moving much closer to self-sufficiency in ethylene derivatives such as polyethylene (PE) than many people think. This self-sufficiency could be the result of new capacities both in China itself and via new China owned-and-operated plants in the One Belt, One Road region (OBOR). The China-led OBOR involves some 65 countries and a proposed trillions of dollars in investment in better road, rail and maritime links between these countries. Member countries, which represent around 40% of global GDP, will also be brought closer together by new free-trade deals. Eight of the new crackers will be downstream of new refineries. Some of these new refineries will be privately owned as Beijing opens up the local refinery sector to more competition. The Chinese government wants to improve the efficiency of state-owned refining giants Sinopec and PetroChina by increasing private investment in refining. The proposed crackers involve some very interesting feedstock approaches. For example, the Shenhua Ningxia project involves converting coal into naphtha. There are several routes to get to naphtha from coal including naphtha via coal pyrolysis, via hydrogenation and via gasification of coal. The global liquefied petroleum gas (LPG) market could remain oversupplied for a long time because of the US shale gas revolution. Revolution is not too strong a word because the US shale industry has transformed global gas and oil markets. One of the bright spots for the US economy is its shale technologies, and so it is a good bet that global LPG markets – that is, propane and butane – will remain oversupplied as the US exports its way to better economic growth. Ever-lower shale production costs and better logistics may allow the US to still make money, even at historically low LPG prices. This could also benefit the new crackers in China that are scheduled

to be fed entirely, or partly, by imported LPG. There is a precedent here and this is the rapid growth in China's propane dehydrogenation (PDH)-based propylene capacity. These plants are based on imported propane. Interestingly, the proposed Wanhua Petrochemical cracker, which would be located in Shandong province, might be based partly on imported ethane – perhaps from the US. This project could, to some extent, follow the model set by companies such as INEOS and Reliance Industries. Both of these companies have built their own ethane carriers to import US ethane to replace dwindling local supplies of ethane. But the Wanhua project would be different as it would be a new grassroots cracker, partly based on imported ethane. In total, the table details just over 13m tonnes/year of new ethylene capacity. At this stage it is not known what derivatives capacity will be downstream of these crackers. Source: ICIS Chemical Business, 6/30/2017, p. 24.

A First Commercial Step Towards On-site Ammonia Production...

A new company — Tsubame BHB Co., Ltd. (Tokyo, Japan) — has been established to commercialize the world's first on-site production of ammonia for supplying amino-acid synthesis, fermentation materials and fertilizers. The company — a joint venture of Ajinomoto Co., Inc., No. 1 UMI Limited Partnership (both Tokyo) and professor Hideo Hosono at the Tokyo Institute of Technology (TiTech; Yokohama) — began operations last April, and aims to implement first NH₃ production by 2021. The production process will be based on a new catalyst that was developed in the laboratories of professor Hosono. The ruthenium-loaded electride — 12CaO•7Al₂O₃ (C12A7) — was found to be an order of magnitude more efficient than conventional Ru-based catalysts for ammonia production. The development is expected to enable NH₃ production at much milder conditions than the conventional Haber-Bosch process, thereby lowering costs. Ajinomoto, a producer of amino acids (including glutamic acid) and fermentation materials, has been involved in the joint-development in order to be able to supply its NH₃ feedstock on site. The Japan Science and Technology Agency, which has funded the basic research, and TiTech have licensed patents for the new catalysts developed by Hosono's research group to the new company. Source: Chemical Engineering, 7/2/2017.

Volvo to Use Electric Motors in All Cars from 2019...

Volvo Cars announced that every model from 2019 onwards would have an electric motor, making it the first traditional carmaker to call time on vehicles powered solely by an internal combustion engine. Volvo said that it would put electrification at the core of its business. From 2019 it will only make three types of cars: pure-electric, plug-in hybrids, and so-called "mild" hybrids combining a small petrol engine with a large battery. "This announcement marks the end of the solely combustion engine-powered car," said Håkan Samuelsson, chief executive. "Volvo Cars has stated that it plans to have sold a total of 1m electrified cars by 2025." The Swedish carmaker was purchased by Chinese domestic carmaker Geely in 2010. The new owners have proven to be a catalyst in the race to electrify its models, as China is already the world leader in electric car sales and Geely is the only Chinese-owned carmaker producing vehicles for the US. Globally, the market for pure-electric cars is tiny, accounting for less than 1 per cent of sales last year, but is growing quickly. Volvo said it would launch five pure-electric cars between 2019 and 2021. Three will come from Volvo while two will come from Polestar, the high-performance unit it launched last month. By 2019 no new Volvo cars will be sold without an electric motor, as internal combustion cars are "gradually phased out", Volvo said. It also aims to make its manufacturing operations "climate-neutral" by 2025. Source: Financial Times, 7/6/2017, p. 11.

Chemical Groups Gear Up For Electric Car Revolution...

Umicore, Johnson Matthey and BASF race to power battery-driven vehicles of future

An industrial transformation is under way. The world’s leading companies that for decades have made catalysts that cut harmful and toxic emissions in vehicle exhausts are switching focus. Their aim: to become key players in powering the electric cars of the future. The big three groups in the area — Umicore of Belgium, UK-listed Johnson Matthey and German chemicals giant BASF — are now preparing for the eventual decline of the traditional internal combustion engines that today they help to filter. So far, Umicore is ahead in the race for market share. It has a dominant position making battery materials for portable electronics, which has helped its shares more than double in price over the past 18 months. But the other two groups are chasing hard — and keen to catch up in the hope of providing materials for the lithium-ion batteries that are vital for the electric car industry to properly take off. Although sales for catalytic converters are holding up, markets are preparing for the demise of diesel engines and growth in electric cars with platinum prices falling sharply over the past year. The big three car catalyst groups hope to capture the growth in demand for components used in rechargeable lithium-ion cells manufactured by the likes of Samsung and LG, and are planning to expand production of cathode materials, critical in increasing the amount of power a battery can deliver. Some investors and analysts think Umicore will be the overall winner from the technological disruption of the car market as they have the lead in so-called nickel manganese cobalt batteries (NMC), which are likely to become the standard for electric vehicles as they allow motorists to drive for longer on a single charge. This explains the outperformance of the group’s share price against its rivals over the past year-and-a-half. Source: Financial Times, 7/10/2017.



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Shell Acquires Exclusive Development and Licensing Rights for SBI Bioenergy Drop-In Biofuels Technology...

Shell and SBI Bioenergy Inc. have reached an agreement granting Shell exclusive development and licensing rights for SBI's patented continuous catalytic process that can convert a wide range of waste oils, greases and sustainable vegetable oils into renewable diesel, gasoline, and jet fuel at various proportions. Under the agreement, Shell and SBI will work together to demonstrate the potential of the technology and, if successful, scale up for commercial application. Compared to conventional reactor systems, SBI's Process Intensification and Continuous Flow-Through Reaction (PICFTR) reactor enables a smaller physical footprint and the ability to quickly scale-up with much lower risk. SBI's proprietary catalysts, called "Continuous Green Catalysts" (CGC), are inexpensive, have a long active life, and are easy to rejuvenate. The PICFTR reactor is used in two stages to initially convert triglycerides and fatty acids into biodiesel and then into renewable fuels. During this process, a stream of pure glycerin is separated prior to the second stage and is protected from reducing to low-value fuel propane. High quality biodiesel and pure glycerin are produced from triglycerides present in natural oils and fats by reacting with methanol and a proprietary CGC (catalyst 1) held in a PICFTR reactor in one single step. The process consumes no chemicals or water at any stage and produces no waste. This process can use 100% free fatty acids and mixtures with triglycerides in almost any ratio. The biodiesel is then fed into a second-stage PICFTR reactor, holding another proprietary CGC (catalyst 2). Without adding hydrogen or other consumable chemicals, the biodiesel is stripped of its oxygen contents and long hydrocarbons molecules are generated. The hydrocarbon stream is then distilled and fractionated continuously and automatically into the various types of renewable fuels. Source: Green Car Congress, 6/29/2017.

IndianOil and LanzaTech to Construct First Refinery Offgas-to-Bioethanol Production Facility...

Indian Oil Corporation Limited (IndianOil) and LanzaTech signed a Statement of Intent to construct the world's first refinery off gas-to-bioethanol production facility in India. The basic engineering for the 40-million liter per year (10.6 million gallons US/year) demonstration facility will begin later this year for installation at IndianOil's Panipat Refinery in Hayrana, India, at an estimated cost of US \$55 million. It will be integrated into the existing site infrastructure and will be LanzaTech's first project capturing refinery off-gases. LanzaTech's first commercial facility converting waste emissions from steel production to ethanol will come online in China in late 2017. LanzaTech has developed a gas fermentation process based on biological catalysts to make fuels and chemicals from a range of waste gases instead of sugars and yeast. Currently, the large volume of waste gas produced at industrial facilities such as refineries cannot be stored or transported; instead, it is combusted to make power locally and emitted as carbon dioxide (CO₂). LanzaTech's technology allows refineries to divert waste gases from the grid, supporting the transition to fully renewable power while recycling this carbon into liquid fuels and petrochemicals. The potential impact of using off-gases from the refining sector in India is considerable. India would be able to produce 40-50 KMTA of ethanol per refinery while saving about 1 million tonnes of CO₂ per annum. Source: GreenCar Congress, 7/11/2017.

Glut Kills Appetite for Keystone...

Keystone XL is facing a new challenge: The oil producers and refiners the pipeline was originally meant to serve aren't interested in it anymore. Delayed for nearly a decade by protests and regulatory roadblocks, Keystone XL got the green light from President Donald Trump in March. But the pipeline's operator, TransCanada Corp. is struggling to line up customers to ship crude from Canada to the U.S. Gulf Coast, say people familiar with the matter. TransCanada has spent \$3 billion to date on Keystone XL, much of it on steel pipe, land rights and lobbying. The lack of interest has put the pipeline's fate in jeopardy. The company, based in Calgary, Alberta, has said it wants enough customers to fill 90% of Keystone's capacity before it proceeds. It started to aggressively court potential customers earlier this year as it seeks to meet that target, according to people familiar with the situation. TransCanada expects the pipeline, which would carry up to 830,000 barrels of oil a day, to cost \$8 billion, compared with its initial estimate of \$7 billion. The company took a \$2 billion write-down related to the pipeline last year. A TransCanada spokesman said the company is making progress with customers and anticipates it will firm up support in coming months. The company has said construction could begin next year and finish as early as 2020. Keystone XL still requires final approval from Nebraska and faces the prospect of additional protests from a reinvigorated antipipeline movement in the U.S. following the fight over the Dakota Access Pipeline. TransCanada is betting the demand that spurred the project still exists. Analysts project that over the long term the Gulf Coast's demand for Canadian crude will rise as oil imports from Venezuela and Mexico fall. Source: The Wall Street Journal, 6/30/2017.

Aramco, Dow JV Starts Propylene Glycol Plant...

Sadara Chemical Co, a \$20 BIL joint venture (JV) between Saudi Aramco and US firm Dow Chemical, has started production at its propylene glycol plant, moving closer to full operation of the JV's petrochemicals complex. The Sadara complex, comprising 26 integrated facilities in Jubail, eastern Saudi Arabia, is the world's largest petrochemical facility to be built in a single phase. All facilities are scheduled to be commissioned by the end of this year. Sadara started its mixed-feed cracker last year. It is the first company in any member state of the six-country Gulf Cooperation Council to crack naphtha and ethane. It has the capacity to produce more than 3 MMtpy of products. Source: Hydrocarbon Processing, 7/10/2017.

Chevron Lummus Global Announces Four New Technology Licenses in China...

Chevron Lummus Global (CLG) announced it has been awarded the license, engineering design and catalyst supply for a grassroots integrated refining and petrochemical project in China. The new complex will use CLG's ISOCRACKING®, ISOTREATING®, and delayed coking technologies feeding kerosene, diesel, vacuum gasoil, and residuum feedstocks to produce finished products. The high-quality, heavy naphtha produced by the complex will be used in a downstream plant employing BP Paraxylene OPEX advantaged crystallization technology, which is exclusively licensed by CB&I. Source: Digital Refining, 6/26/2017.

Brazilian Ethanol Producer Sees Boost from Plant Waste...

Raízen Energia, Brazil's largest producer of sugar cane ethanol, is planning to scale up production at a new "second-generation" biofuel plant, in a move that will sharply increase the productivity of one of the country's most important industries. The company says that it will increase production more than fivefold within two years, making the new technology competitive with traditional ethanol and harnessing potentially millions of tonnes of plant material that currently goes to waste. While a number of countries are commercializing cellulose from plants for use as ethanol, Brazilian sugar cane waste, known as bagasse, is seen as one of the most promising sources because of its plentiful supply and the large existing infrastructure for processing conventional ethanol. "Second generation technology allows you to extract more value from what you have," said João Alberto Fernández de Abreu, chief executive officer of Raízen Energia, part of a joint venture between Brazil's largest sugar producer, Cosan, and oil major Royal Dutch Shell. "You produce more ethanol in the same area. It is using feedstock that is today being wasted."

The Raízen plant, in Piracicaba in São Paulo state, produced 7m litres of next-generation ethanol last year and is on course to double this in 2017. Mr Abreu said it would produce 40m by 2018. That is tiny compared to the around 30bn litres of conventional ethanol produced annually in Brazil, but would be enough to make the second-generation product cost competitive and could prove the technology is ready to be rolled out more widely. While first generation plants convert the sucrose extracted from sugar cane into ethanol, second generation technology uses enzymes to break down the waste from the traditional sugar cane crushing process and convert it to sugars that can be fermented into biofuel. Raízen has 24 traditional first generation ethanol plants and Mr Abreu said these could be married with seven or eight large-scale second generation plants to realize the full potential of the new technology. This configuration would increase Raízen's current production of more than 2bn litres by about 1bn litres of ethanol, or 50%, he said. In addition to working on second generation ethanol, Raízen was exploring other ways to use sugar cane and its byproducts, including methane to power its fleet of harvesters and trucks and biochemicals to compete with petrochemicals. Source: Financial Times, 7/2/2017, p. 15.

Umicore to Acquire Haldor Topsoe's Heavy Duty Diesel and Stationary Catalyst Businesses...

Umicore announced that it has reached an agreement to acquire the heavy duty diesel and stationary catalyst businesses of Haldor Topsoe for an enterprise value of DKK 900 million (approx. EUR 120 million) plus an earn-out. Through this acquisition Umicore will gain access to an extended customer base, particularly in Europe and China, a broader product portfolio for heavy-duty diesel applications, as well as additional IP and technology in the field of emission control catalysis. It also provides Umicore with an entry into the stationary emission control segment. It is anticipated that the acquisition will be earnings accretive from 2018 and is expected to be finalized around year-end. Source: Umicore, 6/20/2017.

Toagosei First to Commercialize Process Making Acrylic Acid from Propane...

Toagosei Co. Ltd. has success in its sights with a new process for directly manufacturing acrylic acid from propane on an industrial scale. The most common process for manufacturing acrylic acid is a multi-step method in which propylene obtained from naphtha cracking is oxidized in the first-stage using a catalyst. The resulting acrolein is then oxidized into acrylic acid using a different catalyst. However, naphtha cracking is a high-temperature process that generates considerable CO₂. While there is a technique that uses propylene obtained from the dehydrogenation of propane, the manufacturing process is complex. In contrast, Toagosei succeeded in synthesizing acrylic acid in a one-step reaction using a single type of catalyst. Toagosei developed a catalyst manufacturing technology that increases activity by controlling the redox reaction using an industrially available metal raw material. This enabled the firm to develop a new three-in-one catalyst for use in dehydrogenation and two-step oxidation. In developing the process technology, Toagosei designed a mid-sized demonstration facility using reaction tubes of the same size as those in a commercial-scale unit. A yield of 65% was achieved in a one-pass flow reaction. Toagosei is on track to increase yield to a maximum of 75% or so by circulating unreacted propane in the reaction off-gas back into the reaction process. This will bring it within sight of the yield achieved with naphtha-derived propylene in the multi-step process. Toagosei also succeeded in curbing the deterioration of the catalyst over time by selectively modifying the catalyst crystal surface. The mid-sized demonstration facility has been in continuous operation for just under a year, raising expectations that performance can be maintained in the long term. The commercial process is likely to be widely used, as existing reaction vessels and refining equipment can be repurposed. Source: Japan Chemical Daily, 6/20/2017.

University of Minnesota Seeking to License New Process to Produce Isoprene from Biomass at High Yield...

Researchers from the University of Minnesota, with colleagues at the University of Massachusetts Amherst, have developed a new high-yield process—a hybrid of fermentation followed by thermochemical catalysis—to produce renewable isoprene from biomass. In the process, fermentation of sugars produces itaconic acid, which undergoes catalytic hydrogenation to produce 3-methyltetrahydrofuran (MTHF). The MTHF then undergoes catalytic dehydracyclization to isoprene. This catalytic process dehydrates MTHF to isoprene via several combinations of temperatures, pressures, and space velocities (reactant volumetric flow rate per volume of catalyst) and achieves selectivity of MTHF to isoprene. The University of Minnesota has applied for a patent on the renewable rubber technology and plans to license the technology to companies interested in commercializing the technology. The first step of the new process is microbial fermentation of sugars, such as glucose, derived from biomass to the intermediate itaconic acid. In the second step, itaconic acid is reacted with hydrogen to MTHF. This step was optimized when the research team identified a unique metal-metal combination that served as a highly efficient catalyst. The process technology breakthrough came in the third step to dehydrate methyl-THF to isoprene. Using a catalyst recently discovered at the University of Minnesota called P-SPP (Phosphorus Self-Pillared Pentasil), the team was able to demonstrate a catalytic efficiency as high as 90% with most of the catalytic product being isoprene. By combining all three steps into a process, isoprene can be renewably sourced from biomass. The performance of the new P-containing zeolite catalysts such as P-SPPP was surprising. This new class of solid acid catalysts exhibits dramatically improved catalytic efficiency and is the reason renewable isoprene is possible. Source: Green Car Congress, 7/2/2017.

Tropylium Cation Now Serves as an Organocatalyst...

The tropylium ion is a curious seven-membered aromatic ring ($C_7H_7^+$) used in organic synthesis and as a ligand for metal complexes. Chemists led by T. Vinh Nguyen of the University of New South Wales Sydney have shown for the first time that tropylium salts can act as organic Lewis acid catalysts. Carbonyl compounds used in multistep reactions are often temporarily functionalized via acetalization reactions to mask their reactivity. This protection step typically relies on a metal salt Lewis acid catalyst. But residual metal can pose problems in purifying pharmaceutical products, leading to excessive use of solvents and generating waste. Organocatalysts that avoid metals are often a greener option. Building on their prior research on tropylium chemistry, Nguyen and coworkers reasoned that the carbocation with one positive charge delocalized over the conjugated seven-membered ring could serve as a “soft Lewis catalyst” for protective acetalizations of aldehydes with alcohols and esters. The team also tested the method in a flow reactor system to save time and facilitate catalyst recycling, further reducing the environmental impact of the reaction. “This is one of the most interesting papers I have read in a long time,” says James H. Davis Jr. of the University of South Alabama, who studies ionic liquids and molecular salts. “I find the simplicity of the catalyst and its broad, metal-free scope of activity especially exciting.” Source: Chemical & Engineering News, 7/3/2017, p.9.

Taking the Heat Off Distillation...

The American Chemical Society (ACS) and the American Institute of Chemical Engineers (AIChE) are leading a new alternative separation initiative, called AltSep, to advance low-energy separation technologies. AltSep is coordinated by the Chemical Manufacturers Roundtable, an industry group established by the ACS Green Chemistry Institute (GCI) and led by Robert J. Giraud of Chemours and Amit Sehgal of Solvay. AltSep aims to address common problems and identify needs in separation science and technology and then translate promising ideas into implementable, cost-effective, and low-business-risk technologies. Giraud and Sehgal want chemical companies to face these challenges together, before their new products go head-to-head in the marketplace. GCI roundtable members began exploring the idea for AltSep in 2013, Giraud explains. At first, the group gathered company insights on what it would take to replace distillation when a manufacturer is considering refurbishing an existing plant, adding a new unit, or building a complete facility from scratch. One of AltSep’s starting points was taking a look at the types of chemical separations that could yield the greatest sustainability benefits from cuts in energy use. To help get things started, the AltSep team received a \$500,000 competitive planning grant from the National Institute of Standards & Technology’s (NIST) Advanced Manufacturing Technology Consortia program. The roundtable members have been using the grant to hammer out the details for an innovation road map, slated to be completed by the end of this year, for achieving their vision of a chemical process industry that operates with more energy-efficient separation processes. To satisfy one of the first needs in developing AltSep’s road map, the Chemical Manufacturers Roundtable partnered with chemical informatics specialists Vincent K. Shen, Nathan A. Mahynski, and their colleagues at NIST’s Material Measurement Laboratory to obtain a \$300,000 Department of Energy (DOE) High Performance Computing for Manufacturing grant. The funding is providing computing time at Lawrence Berkeley National Laboratory (LBNL) in conjunction with big data architect Debbie Bard to better understand the properties needed in porous materials to achieve energy-efficient separations of multicomponent fluids. The yearlong study, just now getting under way, will systematically explore parameters, including pore geometry and intra- and intermolecular fluid dynamics, that describe molecular-material interactions. Source: Chemical & Engineering News, 6/19/2017, p.19.



NMR Relaxation in Porous Catalysts: A Useful Tool to Aid Catalyst Selection and Process Optimization

By Carmine D'Agostino, PhD

Introduction

Liquid-phase catalysis is a crucial technology in industry, particularly for the production of high-value products, such as fine and specialty chemicals, drugs, and pharmaceuticals. A considerable amount of these products are manufactured by exploiting homogeneous catalytic processes; mostly due to the higher and tuneable activity and selectivity achieved in such processes, and to a better understanding of the structure-activity relationship. This technology has, however, some drawbacks: for example, a central issue often reported is that of catalyst separation and recycling, which may involve laborious and energy intensive processes and in some cases may be very challenging to achieve. Homogeneous catalyst regeneration can also be challenging, especially due to low stability and ease of decomposition below 100 °C (Cole-Hamilton and Tooze 2006).

In recent years, there have been increasing attempts to develop processes using liquid-phase heterogeneous catalysis for the production of a variety of specialty and fine chemicals, through various reactions such as hydrogenation, oxidation, and condensation reactions. For example, selective hydrogenation of α,β unsaturated carbonyls, such as cinnamaldehyde, is an important route for the production of unsaturated alcohols, which are widely used as aroma chemicals in fragrances and food. Oxidations using molecular oxygen over solid catalysts are also valuable routes for a more sustainable production of fine chemicals, by avoiding the use of hazardous oxidizing agents such as nitric acid and potassium permanganate.

The advantages of heterogeneous catalysts are reflected in their ease of recycling, separation, and regeneration, and high thermal stability; however, several drawbacks arise due to usually poor activity and selectivity and the lack of understanding of surface phenomena occurring over the catalyst surface. In studying heterogeneous catalysts there is usually a trade-off between the choice of simple, ideal systems that can be studied almost at atomistic level, and the choice of more complex systems, which are, however, difficult to study in great detail. Density Functional Theory (DFT) and other approaches such as ultra-high-vacuum single-crystal experiments can be used to have a detailed understanding of the surface science underlying catalytic processes (Delbecq and Sautet 2002; Liao et al. 2013; Liu et al. 2004). However, in most cases these techniques work with materials and reaction conditions that are substantially different from operating conditions of industrial reactors. Indeed, the real world is always more complicated and “dirtier” than the ideal picture; the same applies to catalysts. Catalytic reactors usually operate at atmospheric or much higher pressures and temperatures. In addition, industrial catalysts are far more complex than ‘ideal’ single-crystal surfaces; for example, their structure and surface composition may be rather different and often not well-defined. Other experimental, robust techniques are necessary to deal in a more pragmatic way with such materials while simultaneously being able to explore the fundamentals.

Despite the wide applications of heterogeneous catalysis, there is still a lack of understanding of the surface science underlying it. Various experimental tools are available to gain insights into such surface phenomena. For example, infrared spectroscopy (IR) is a valid tool to characterize acidity of many solid catalysts, including zeolites (Lercher et al. 1999). Other techniques such as temperature-programmed oxidation, reduction or desorption can reveal important information on the oxidation state of the surface, its composition and its ability to retain adsorbed molecules (Choudhary and Karkamkar 2003).

In very recent years, Nuclear Magnetic Resonance (NMR) relaxation methods have arisen as complementary, non-invasive tools to understand and quantify the effect of catalytic surfaces on molecular dynamics (Mitchell et al. 2013) and adsorption in liquid-phase heterogeneous catalytic systems. The technique has several advantages, including: 1) rapid acquisition times (e.g., down to few minutes as opposed to several hours of temperature-programmed desorption experiments); 2) exploitation of the chemical specificity of NMR; 3) ability to probe simultaneous species inside catalyst pores; and 4) the ability of the technique to separate molecular species based on their relaxation time characteristics.

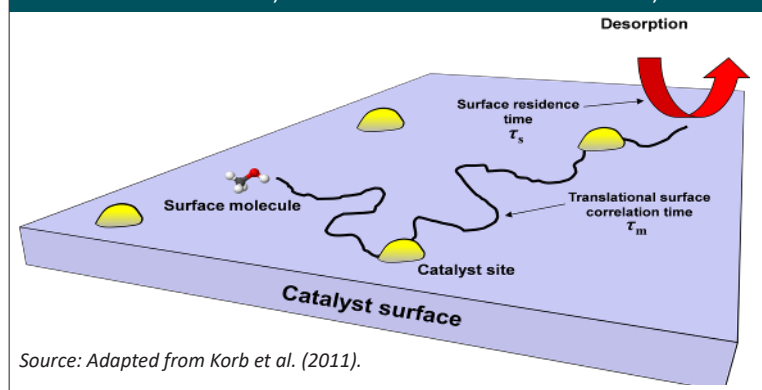
In terms of hardware needed for NMR measurements, superconductive magnets are rather expensive to buy and operate and are not always available in industrial facilities. The good news is that nowadays, for many applications, the rapid development in NMR hardware has led to portable, bench-top NMR instruments, which are more affordable and easy to fit in industrial and manufacturing facilities. Let's now briefly discuss the main principles underlying NMR relaxation of liquids in porous catalysts.

NMR Relaxation of Liquids in Porous Catalysts

NMR relaxation exploits the measurement of NMR relaxation times of fluids; notably, the spin-lattice, or T_1 , and transverse spin, or T_2 , relaxation times. These relaxation times are caused by local fluctuations in magnetic fields on the molecular scale and can be considered as a fingerprint of molecular dynamics. In addition, they are very sensitive to the environment surrounding molecular species. For example, when liquids are confined within the pores of a catalyst, their relaxation times may change dramatically due to the influence of the catalyst surface on rotational and translation dynamics of molecules. This concept can easily be visualized in **Figure 1**, where the layer of molecules inside the pores and closer to the surface exhibits a different dynamics compared to the same molecules in the center of the catalyst pore, which behave more like bulk liquid.

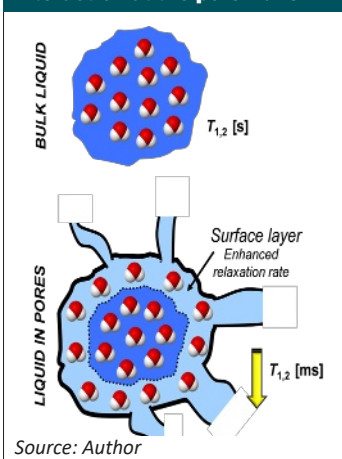
This happens because molecules close to the surface will experience the effect of the pore walls, including presence of acid sites, surface hydroxyl groups, and other catalytically active sites such as transition metal nanoparticles deposited on solid supports. As a result, the relaxation rates, $1/T_1$ and $1/T_2$ are enhanced, with a consequent drop of T_1 and T_2 values. It is important to note that the T_1 and T_2 NMR relaxation times depend on some typical ‘correlation’ times of molecule over the surface layer—notably, the surface residence time and the surface diffusion correlation time between different sites—and are affected by changes in rotational and translation dynamics at the surface to different extents (Korb 2011). A simplified picture of this process is shown in **Figure 2**.

Figure 2. NMR relaxation times of molecules over a solid surface depend on surface diffusion time, m as well as surface residence time, s .



Source: Adapted from Korb et al. (2011).

Figure 1. Solid surfaces in porous catalysts affect the molecular dynamics of fluids due to adsorbate-adsorbent interaction at the pore walls.



Source: Author

In particular, molecules adsorbed onto solid surfaces exhibit modified rotational dynamics and slower translational diffusion; as a result the T_1/T_2 increases (Mitchell et al. 2013). In simple words, a higher T_1/T_2 ratio usually indicates a higher strength of surface interaction between the fluid and the solid surface.

Using this technique it is actually possible to explore a variety of phenomena including: 1) determination of pore size distribution (Li et al. 2015); 2) changes in molecular dynamics at the surface (Godefroy et al. 2001); 3) probing strength of interaction adsorbate-adsorbent (Weber et al. 2009); and 4) evolution of reactive species during reaction (Buljubasich et al. 2010).

Early applications of NMR relaxation on catalytic systems were shown to be able to quantify strength of liquid-surface interactions of reactants, 2-butanone, and solvents, water and 2-propanol, in Ru/SiO₂ and Pd/Al₂O₃ industrial catalysts used for the hydrogenation of 2-butanone (Weber et al. 2009). For the Ru/SiO₂ catalyst, water was seen to have a stronger interaction with the surface compared to 2-propanol or 2-butanone, the latter species having a similar relative strength of surface interaction. In Pd/Al₂O₃, water was seen to have a much stronger surface interaction compared to 2-propanol and especially 2-butanone, the latter showing the weakest interaction. The relative strengths of surface interaction were deduced directly from the average ratio of relaxation times, T_1/T_2 . The authors concluded that, based on the observation that in Pd/Al₂O₃ the solvents have much stronger surface interaction than 2-butanone, then 2-butanone would have reduced access to adsorption sites on the catalyst surface as compared to the surface composition in Ru/SiO₂, where all the liquids had more comparable strengths of interaction. No direct comparison with reaction data was attempted in this early study. Research into this field has therefore moved towards a more direct application to reactions of interest, including those of industrial and commercial relevance, focused on solvent and catalyst selection.

Solvent Selection

Solvents in catalytic reactions are often necessary to make soluble reactive species as well as improve heat and mass transfer; however, it is important to understand that the solvent will also affect catalyst performances and reaction rate and this is due to several reasons, such as changes in solvation properties and competitive adsorption with reactants over the catalyst surface. Solvent effects in heterogeneous catalysis have been widely reported in the literature and are often a matter of debate (Bertero et al. 2011; Takagi et al. 1999). An ideal solvent should be able to dissolve reactive species without being adsorbed onto the catalyst surface or at least its adsorption strength should be much lower than that of the reactant. Indeed, one way in which solvents may inhibit catalytic

reactions is by blocking active sites, hence preventing reactant molecules to access such sites. For example, non-polar solvents such as hydrocarbons, are expected to exhibit relatively weak interactions with solid surfaces compared to polar species such as alcohols, acids, and molecules containing functional groups that are able to interact with surface sites, such as hydroxyl groups, Lewis bases, and carboxylic groups (Lanin et al. 2008). NMR relaxation measurements, being able to non-invasively probe the affinity between fluids and solid surfaces, can therefore be used to quantify strength of interaction of solvents and reactants in catalytic processes. Such measurements have been used to study the solvent effects on the oxidation of various chemical reactions of interest from a “greener” chemistry perspective, such as the aerobic oxidation of polyols over solid catalysts.

Polyols, such as propylene glycol, glycerol, and sugars, are bio-renewable resources which can be used as raw materials for the production of many value-added chemicals, such as acrolein, alcohols, lactic acid, hydroxyacetone, and many other important intermediates used in the chemical industry. In the past decades, efforts have been focusing on liquid-phase catalytic reactions of these feedstocks over heterogeneous catalysts in order to improve process sustainability. The high viscosity of these chemical species always requires the use of solvents to make soluble and enhance mass transfer properties. Water and methanol have been the most widely used solvents; water is perhaps the most benign, environmentally friendly solvent, whereas methanol has attracted interest because it is the main impurity present in crude glycerol, which is an important platform chemical and also the main by-product of the transesterification of fats and oils for bio-diesel production. Therefore, it becomes important to understand what the role of these solvents is in these chemical reactions. In a study on oxidation of 1,3-propanediol and its methyl substituted homologues over Au/TiO₂ catalyst in methanol solvent, it was found that the addition of water has a detrimental effect on catalyst activity (D’Agostino et al. 2013). Some key results are depicted in **Figure 3**.

NMR T_1/T_2 relaxation studies revealed that the addition of water has a detrimental effect on the adsorption strength of reactants, which is thought to decrease the catalyst activity, suggesting that water is likely to inhibit catalyst activity by reducing the access of the reactants to the catalytically active sites. Similar findings were observed in a different study on 1,4-butanediol oxidation (D’Agostino et al. 2012a).

Catalyst Selection

The examples discussed above highlight the usefulness of the technique in selecting solvents for a given catalyst. However, the method can also be used to aid catalyst selection. For example, in a recent work, the technique was used to quantify competitive adsorption in the liquid-phase catalytic oxidation of 1,4-butanediol to γ -butyrolactone in methanol over various heterogeneous catalysts (D’Agostino et al. 2016b). It was found that the catalysts with the lowest activities were those showing the highest degree of solvent inhibition as suggested by NMR measurements, which was quantified using a parameter, β , which compares the T_1/T_2 ratio of the reactant over that of the solvent for various porous catalysts, as shown in **Figure 4**.

The technique can therefore be used as a screening tool to guide catalyst development and selection for a particular chemical process. The relevance and exploitation of these methods in industry can be further strengthened by the development of portable, low-field NMR instruments. Krzyżak and Habina (2016), for example, have recently used low-field ¹H NMR to characterize mesoporous silica MCM-41 and SBA-15 filled with different amounts of water. In particular, T_1 and T_2 measurements were carried out to measure pore size distribution as well as

Figure 3. Catalytic conversion (squares) and strength of surface interaction, measured as T_1/T_2 (columns), in the liquid-phase oxidation of 1,3-propanediol and its methyl substituted homologues in methanol and methanol/water solvents.

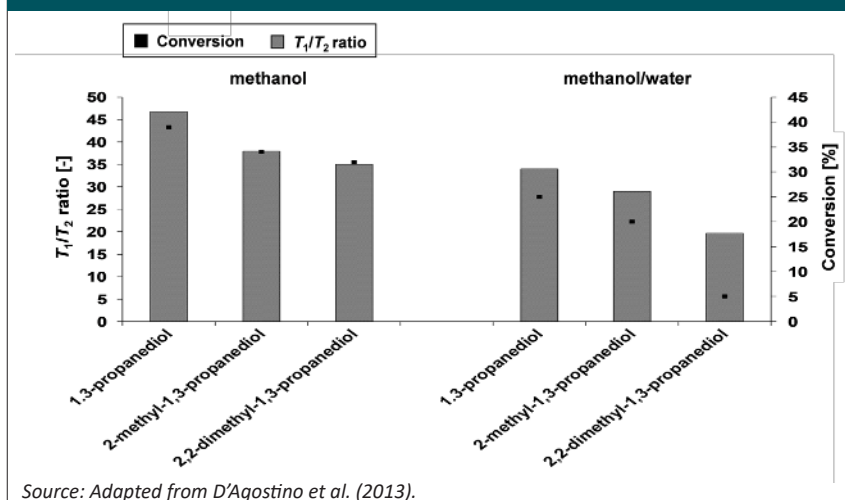
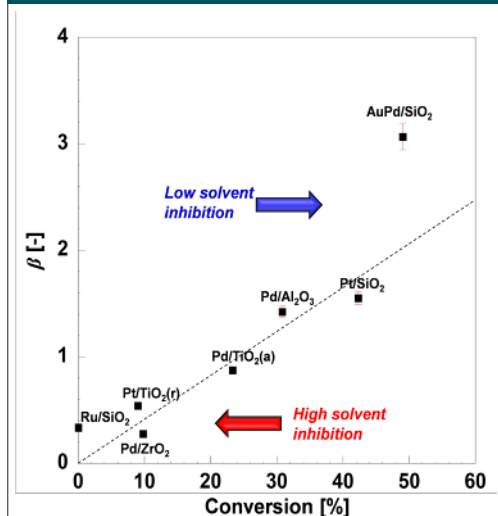


Figure 4. Competitive adsorption parameter, $\beta = (T_1/T_2)_{\text{reactant}} / (T_1/T_2)_{\text{solvent}}$, for different porous catalysts used for the liquid-phase oxidation of 1,4-butanediol. Low values of β indicate higher degree of solvent inhibition. Adapted from D’Agostino et al. (2016b).



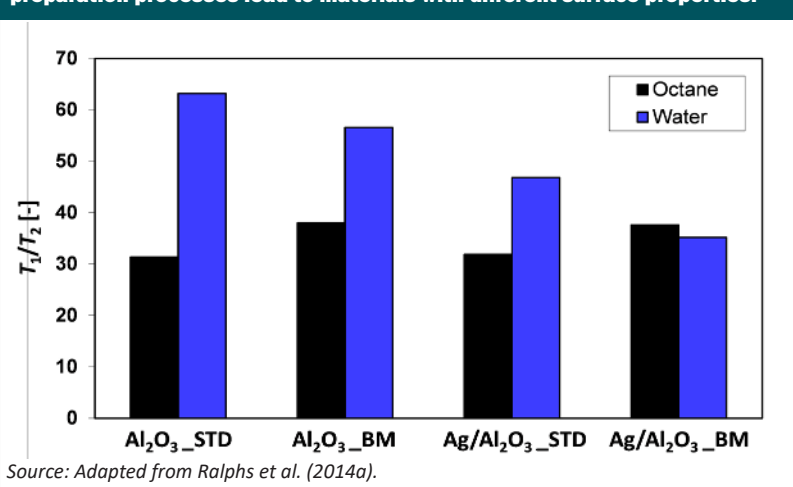
concentration of –OH surface groups. The affinity of the two porous materials towards water was also quantified. These parameters are very important in order to understand reactivity and affinity of different materials towards different solvents and other chemical species.

Other applications of this protocol have been used in understanding catalytic performances of catalysts that find application in automotive engine exhausts, in particular those used for the selective catalytic reduction (SCR) of NO_x in the presence of reducing agents such as hydrocarbons, alcohols, and ammonia. The aim of these catalysts is to convert noxious NO_x in N_2 . Some major issues in the development of new SCR catalysts, such as those based on silver on alumina, $\text{Ag}/\text{Al}_2\text{O}_3$, are those related to poisoning and deactivation of active sites by water, which is always present in engine exhaust streams. Water is thought to compete with reactive species and inhibit the catalyst activity. A recent work has exploited the ability of NMR relaxation measurements to probe adsorbate-adsorbent surface affinity relative to water of a series of reducing agents used for the SCR reduction of NO_x over $\text{Ag}/\text{Al}_2\text{O}_3$ (D'Agostino et al. 2016a). The results showed a correlation between reducing agent with higher affinity for the catalyst surface and catalyst activity. In particular, reducing agents such as alcohols, which give improved catalytic performance, were seen to have a higher affinity towards the surface relative to water, compared to hydrocarbons, the latter giving lower conversion. The results confirmed hypothesis previously speculated in the literature, suggesting that the lower ability of hydrocarbons to compete with the water by-product over the surface may be responsible for the poorer catalytic performance.

In another study, the focus was on trying to figure out the effect of mechano-chemical treatments of solid catalysts on activity in SCR reactions. A recent work showed that through a solvent-free, ball milling process, it was possible to obtain a $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst with significantly higher activity for NO_x reduction with *n*-octane, compared to a standard $\text{Ag}/\text{Al}_2\text{O}_3$ prepared by wet impregnation (Ralphs et al. 2014b). No significant differences were observed between the two catalysts and the reasons for the improved activity of the ball milled $\text{Ag}/\text{Al}_2\text{O}_3$ remained unclear for a while. However, a recent study used NMR T_1/T_2 measurements to probe the affinity of these two catalysts towards the *n*-octane reactant and water by-product (Ralphs et al. 2014a).

The results, shown in **Figure 5**, clearly showed that the ball milling process is altering surface properties of the $\text{Ag}/\text{Al}_2\text{O}_3$, making the catalyst more affine towards *n*-octane, which is thought to increase the surface concentration of intermediate reaction species and improve the catalyst performances.

Figure 5. T_1/T_2 of water and *n*-octane in Al_2O_3 and $\text{Ag}/\text{Al}_2\text{O}_3$ samples prepared with standard wet impregnation (STD) and by ball milling (BM). The two preparation processes lead to materials with different surface properties.



Conclusions and Outlook

It is clear that the NMR techniques highlighted above have a great potential for further exploitation in industrial catalytic processes, especially considering the latest NMR hardware developments of compact, bench-top NMR instruments that can be easily fit into R&D labs. Together with NMR diffusion techniques, the so called Pulsed-Field Gradient (PFG) NMR method (D'Agostino et al. 2012b; Kortunov et al. 2005), it becomes possible to have access to a wealth of information on the physico-chemical phenomena occurring inside catalyst pores, particularly on adsorption and diffusion (which are of fundamental importance in order to understand catalyst behavior) important issues in the scale-up of chemical processes and the key parameters to take into account when designing a catalyst for a specific process. It should be stressed that although measurements of relaxation times can nowadays be routinely done, caution is required when measuring, processing, analysing and interpreting the data. The theory of NMR relaxation is rather complex, particularly for fluids in porous materials, such as is the case for liquid-phase catalytic reactions. It is therefore important to have scientific researchers with solid knowledge of the physics behind this phenomenon in order to make a proper analysis of the results. In this regard, it is important that industrialists and scientists come together with a common goal in creating powerful synergies. It is indeed often the case that new methods are often initially encountered with scepticism, whereby traditional characterization tools are often preferred to new experimental methodologies. However, it is important to stress that NMR relaxation methods are here proposed not as a substitute of other characterization tools, such as gas adsorption porosimetry, calorimetry, and other tools for studying catalysts, but rather as an added-value tool that can reveal new insights in phenomena that are difficult to probe with other methods.

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About the Author



Carmine D'Agostino received a BEng and MEng in Chemical Engineering from the Università di Napoli "Federico II", Italy. After working for a few years in the Oil & Gas sector, he undertook a PhD in Chemical Engineering at the University of Cambridge, UK. He is currently a lecturer and a research fellow at Cambridge, where he works on development of new methodologies to characterise the behaviour of fluids in catalytic materials using NMR and other spectroscopic methods. He also works closely with the industry in order to promote technology transfer from and to academia.



New TCGR Multi-Client Study to Assess Direct Oil-to-Chemicals Production via Advanced Process Configurations...

"Oil-to-Chemicals: Technological Approaches and Advanced Process Configurations"

It is clear that among the leading positions/approaches developed to date, notably by ExxonMobil and Saudi Aramco, the full breadth of the potential need may not be addressed because each user will require a unique solution. Therefore it would be useful to evaluate the olefins and/or aromatic needs of chemical plants in reverse order, back towards the intake of crude oil using different existing and new technologies that may prove more economical at smaller scale, than the massive CAPEX schemes currently being proposed by licensors, as solutions. Beyond these leading activities, numerous independent technology developers like UOP/Honeywell, Axens, CB&I and other majors like SABIC are working towards combinations of technologies which can achieve a similar objective.

TCGR's proposed assessment will take an end-market based approach with the objective of documenting the available technologies, plus those in development (including the needed combinations) to maximize the return on conversion based on product slate (chemicals/ petrochemicals and specialty/intermediates).

Key questions to be addressed include how chemical companies can target this technology opportunity - from an olefins and aromatics/ BTX chemical plant feedstock point of view - but enhance the olefins and/or BTX yields even higher through retrofit catalysts and known process technology incremental revamps? What is needed is to document recent catalyst and process advances relevant to olefins and BTX chemical products that avoid the upfront investment in catalytic distillation units (CDUs) and vacuum distillation units (VDUs) and other parts of the refinery while maximizing BTX and olefin yields (primarily C3+ and C4+) beyond typical refinery economics and normal/known process configurations that have historically been optimized for fuels production.

The scope will consider the following:

- Modified steam crackers; catalytic steam cracking
- Resid FCC: Multiple riser systems, R2R, Milos (Shell), HSFCC (Axens)
- H-Oil and slurry HC (IFP); LC Fining (Lummus/CB&I)
- Ebullated bed – EST (Eni)
- Deep catalytic cracking (DCC)
- Others (to be determined via "charter" subscriber input)
- Gasoil/steam cracking, gasoil/HSFCC
- Hydrocracker/FCC; Flexicoking/FCC; FCC/Reforming
- Hydroconversion upgrader (GHU, Genoil)
- Pyrolysis catalytic cracking (PCC)
- Aromax (CP Chem), Cyclar (UOP/Honeywell), etc.

Additional information, including the complete study proposal, the preliminary Table of Contents and the Order Form, is available at: http://www.catalystgrp.com/multiclient_studies/oil-chemicals-technological-approaches-advanced-process-configurations/ or by contacting John J. Murphy at +1.215.628.4447 or John.J.Murphy@catalystgrp.com

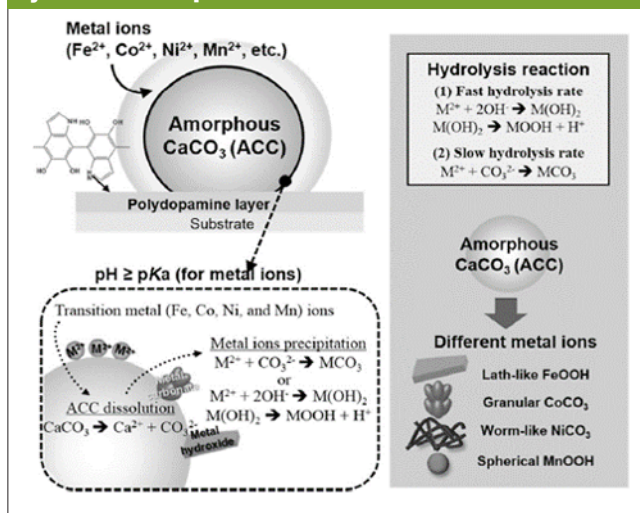
The Catalyst Group Resources (TCGR), a member of The Catalyst Group, is dedicated to monitoring and analyzing technical and commercial developments in catalysis as they apply to the global refining, petrochemical, fine/specialty chemical, pharmaceutical, polymer/elastomer and environmental industries.



Nature-Inspired Synthesis of Nanostructured Electrocatalysts through Mineralization of Calcium Carbonate...

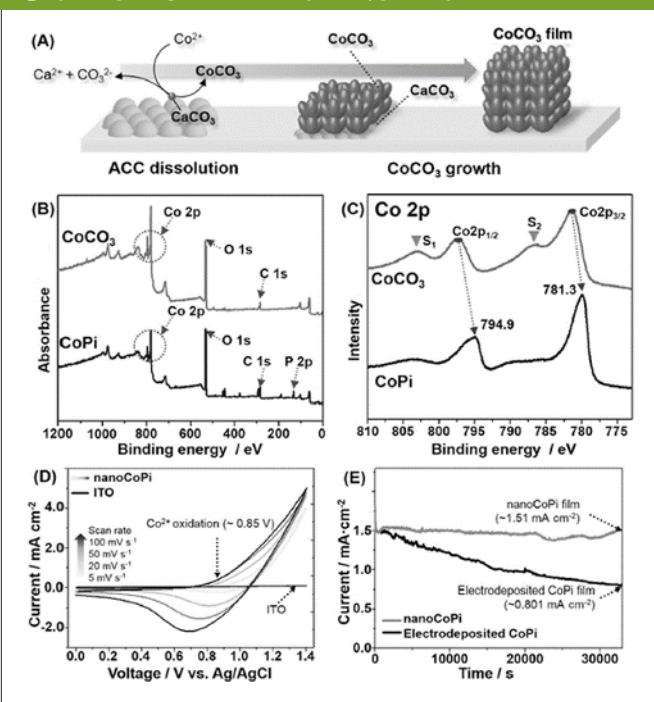
Metal-oxide minerals (MOMs) contain various functions for diverse applications in sustainable environment research, such as electrocatalysis and energy storage. Recently, calcium carbonate has been found to serve as a facile template for the synthesis of nanomaterials. Herein, the authors report the development of a new amorphous calcium carbonate (ACC) film which can function as a versatile template for the synthesis of nanostructured MOMs such as FeOOH, CoCO₃, NiCO₃, and MnOOH. These MOM films were obtained by incubating catechol rich polydopamine (PDA)-induced ACC films in solutions of metal ions (e.g., FeCl₂, CoCl₂, NiCl₂, and MnCl₂) at room temperature. The PDA-induced ACC was found to function as a sacrificial material for the synthesis of MOMs by solid-state transition. Thus, when a PDA-induced ACC film was immersed in a slightly acidic metal (e.g., Fe²⁺, Co²⁺, Ni²⁺, and Mn²⁺) chloride solution (pH<5), individual ACC granules decomposed into Ca²⁺ and CO₃²⁻ ions with concurrent precipitation of MOMs (e.g., hydroxides and carbonates) on the substrate (**Figure 1**) of nanostructured electrocatalysts via bio-mimetic CaCO₃ mineralization.

Figure 1. Transition of amorphous CaCO₃ to MOMs (e.g., carbonates and hydroxides). Under metal ion-containing solution, the PDA-induced ACC takes up metal ions (e.g., Fe²⁺, Co²⁺, Ni²⁺, and Mn²⁺) as a substitutional cation for Ca²⁺, and ACC dissolves into Ca²⁺ and CO₃²⁻ while forming MOMs. The composition and structure of the synthesized metal carbonates/hydroxides are influenced by the hydrolysis rates, which vary with the degree of hydration enthalpies for each metal ion.



This PDA-induced ACC templating for the synthesis of nanostructured MOMs was found to take place through a very simple and environmentally friendly procedure in an aqueous solution at room temperature without any additives. The authors theorized that such films might facilitate increased performance as an electrocatalyst because of enhanced mass transportation and larger surface area.

Figure 2. (A) Schematic representation of the synthetic process for the nanostructured CoCO₃ film (nanoCoPi) using ACC as a sacrificial template. (B) Surface-composition analysis of the CoCO₃ film and the CoPi film with the XPS survey showing Co 2p, O 1s, and C 1s signals. The peak corresponding to the P element exists only in the CoPi film. (C) High-resolution XPS spectra of Co 2p for the CoCO₃ film and the nanoCoPi film exhibiting the shift of Co 2p_{3/2} and Co 2p_{1/2} peaks toward lower binding energy and the change of two shoulder peaks of Co 2p shown in CoCO₃. (D) CV curves for the nanoCoPi film on ITO glass in 0.1M sodium phosphate buffer (pH 7.0) with different scan rates. (E) Long-term stability test for water electrolysis conducted with the nanoCoPi film and the CoPi film prepared by conventional electrodeposition under an applied voltage of 1.15 V (vs. Ag/AgCl) in a phosphate buffer (0.1 M, pH 7.0).



To test this hypothesis, they conducted electrochemical experiments with ACC-templated MOM films employing the electrocatalytic water oxidation reaction (WOR) **Figure 2**. They first prepared a cobalt phosphate (CoPi) electrocatalyst film by incubating the CoCO₃ film (**Figure 2A**) in a phosphate buffer under an applied potential of 0.95 V (vs. Ag/AgCl). They then prepared a CoPi electrocatalyst by using a conventional electrodeposition method which yielded a dense CoPi film. The electrodeposited CoPi displayed a lower electrochemical WOR activity compared to the CaCO₃-templated cobalt phosphate (nano-CoPi) film. The latter exhibited high stability as a water-oxidation electrocatalyst with a current density of 1.5 mAcm⁻². It is believed that the nanostructure of nano-CoPi, consisting of individual nanoparticles (70 nm) and numerous internal pores facilitates an additional charge-transfer pathway from the electrode to individual active sites of the catalyst. Source: Ko JW, Son EJ, and Park CB. (2017). ChemSusChem, online preview, DOI: 10.1002/cssc.201700616.

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Ultrathin Nitrogen-Doped Carbon Coated with CoP for Efficient Hydrogen Evolution...

Efforts to identify less costly but equally efficient water splitting catalysts than those commonly employed (Pt- and Ru/Ir-based noble metal materials) have tended to focus on transition-metal carbides, nitrides, chalcogenides, oxides, alloys, and phosphides. In addition, transition metal phosphides (TMPs) have shown promising performance for the hydrogen evolution reaction (HER), no doubt due to their hydrogenase-like catalytic mechanism. Herein, the authors report a facile two-step process to prepare CoP nanoparticles encapsulated in an ultrathin nitrogen-doped porous carbon shell (CoP@NC) with ZIF-9 as the precursor and making use of metal-organic framework (MOF) (**Figure 1**). The as-synthesized CoP@NC was found to serve as an excellent catalyst for the HER in both acidic and alkaline media, with excellent electrocatalytic activity and long-term durability. HER activities of these Co-based catalysts in acidic media were evaluated in a three-electrode system, using 20% Pt/C as a reference (**Figure 2**). The Tafel slope fitted from the polarization curve by the Tafel equation is an inherent property of the electrocatalyst.

Figure 1. (a) Schematic illustration of the synthetic process of CoP@NC. TEM images of (b) Co@NC and (d) CoP@NC. HRTEM images of (c and inset) Co@NC and (e and inset) CoP@NC.

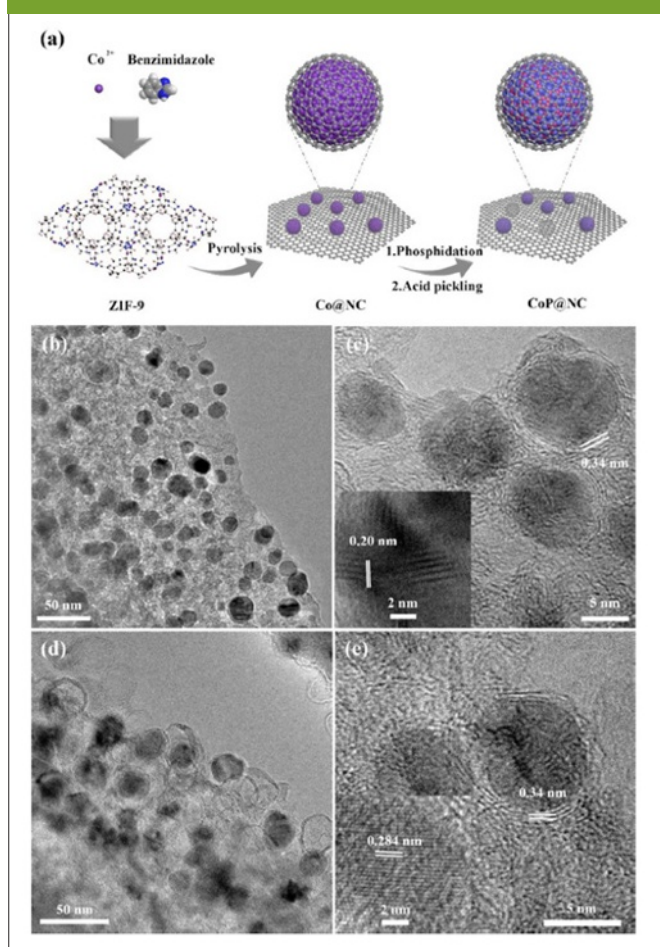
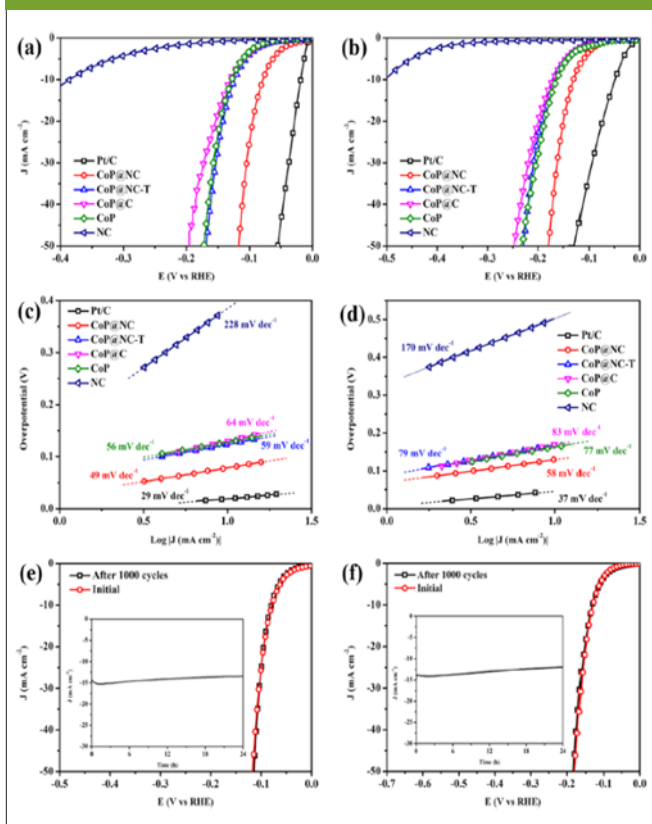


Figure 2. HER polarization curves in 0.5 M H₂SO₄ (a) and 1.0 M KOH (b) and the Tafel slopes in 0.5 M H₂SO₄ (c) and 1.0 M KOH (d) of CoP@NC, CoP@NC-T, CoP@C, CoP, NC, and Pt/C, with a scan rate of 5 mV s⁻¹. HER polarization curves of CoP@NC before and after 1000 CV cycles from 0.05 to -0.20 V in 0.5 M H₂SO₄ (e) and 1.0 M KOH (f). Chronoamperometry i-t curve of CoP@NC at an overpotential of 100 mV in 0.5 M H₂SO₄ (inset of e) and 150 mV in 1.0 M KOH (inset of f).



As can be seen, the Tafel slope of CoP@NC is lower than those of CoP@NC-T, CoP@C, CoP, and NC (228 mV dec⁻¹), indicating that the HER on the CoP@NC probably follows the Volmer–Heyrovsky mechanism. Furthermore, under the large overpotential, the Tafel slope of CoP@NC is lower than that of Pt/C indicating the superior HER performance of CoP@NC under large electric current conditions. In addition, CoP@NC also exhibits a remarkable electrocatalytic performance in alkaline media. As shown in **Figure 2b**, only a small overpotential of 129 mV is needed to afford a current density of 10 mA cm⁻² for CoP@NC, which is superior to those of CoP@NC-T, CoP@C, CoP, and NC- and lower than those of most of the reported TMP-based catalysts.

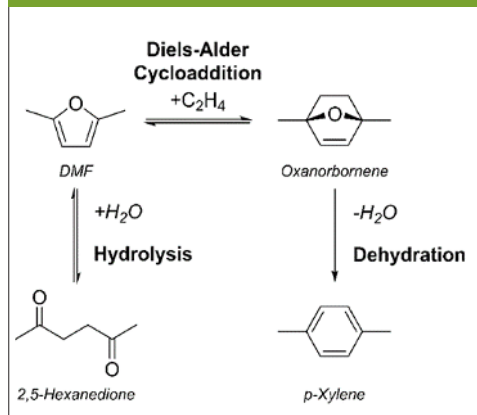
EXPERIMENTAL

The authors believe that the *N*-doped graphitic carbon layers coated on CoP NPs play a fundamental role in boosting the HER performance. DFT theoretical calculations, as well as the experimental data demonstrate that the synergistic effect between CoP cores and *N*-doped graphitic carbon layer shells lead to an outstanding electrocatalytic HER activity, and the direct active sites are located on the carbon atoms adjacent to the N dopants in carbon shells. Source: Yang F, Chen Y, Cheng G, et al. (2017). ACS Catal., 7: 3824-3831.

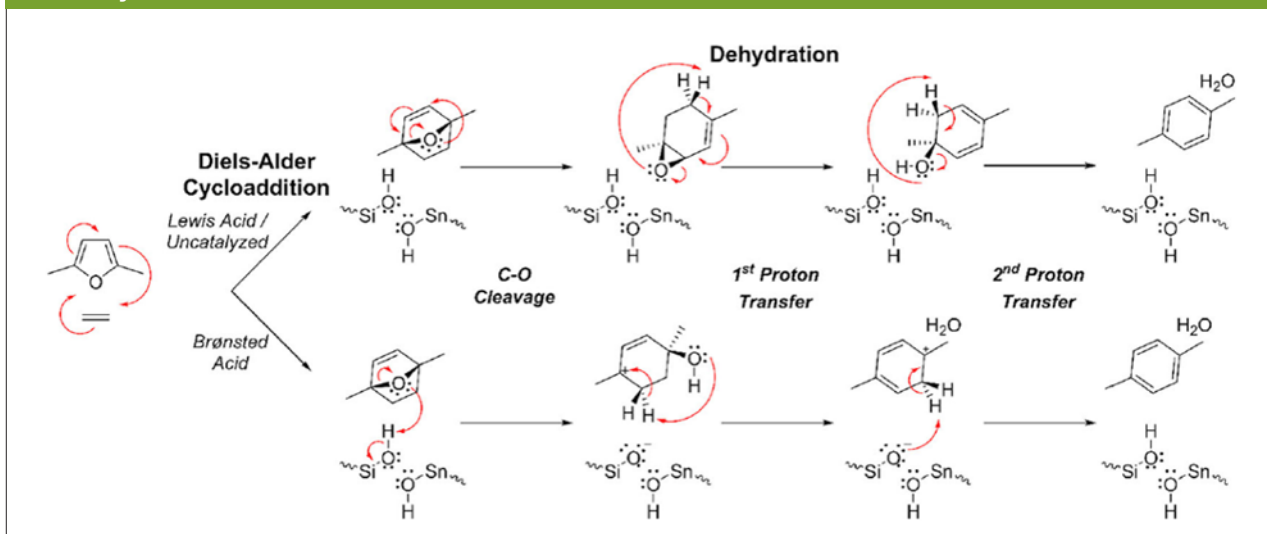
Tandem Diels–Alder Reaction of Dimethylfuran and Ethylene and Dehydration to *para*-Xylene Catalyzed by Zeotypic Lewis Acids...

Development of alternative routes for the production of aromatics from renewables is the subject of ongoing interest. One possible pathway under consideration involves the dehydrative aromatization of the Diels–Alder (DA) product between bio-derived furans with an appropriate dienophile. This process involves a tandem scheme in which the oxanorbornene derivative obtained from the DA cycloaddition is catalytically dehydrated to an aromatic (**Scheme 1**). Although Lewis acids can catalyze the dehydration of the Diels–Alder cycloadduct, the tandem scheme precludes decoupling of the two steps needed to infer whether these same catalysts can catalyze the Diels–Alder step. Herein, the authors present two sets of test results; the first involving electronic structure calculations (based on a mechanically embedded three-layer (QM/QM/MM) ONIOM cluster) model and the second derived from microkinetic modeling constructed and parameterized based on the free energy profiles obtained from the electronic structure calculations. Based on these studies the authors propose a mechanism for the formation of *p*-xylene and water from DMF and ethylene (**Scheme 2**), in which the oxanorbornene intermediate formed by Diels–Alder cycloaddition subsequently undergoes dehydration in three steps to form *p*-xylene.

Scheme 1. Diels–Alder aromatization of 2,5-dimethylfuran (DMF) and ethylene to *p*-xylene and hydrolysis of DMF to 2,5-hexanedione.



Scheme 2. Reaction mechanism for the Diels–Alder cycloaddition of DMF and ethylene, and subsequent three-step dehydration to water and *p*-xylene. Top mechanism: uncatalyzed or Lewis acid catalysis; bottom mechanism: Brønsted acid catalysis.



These calculations show that the open sites are catalytically more active than the closed ones and, although there is the potential for Brønsted acidity within the zeolites with open sites (from the formation of silanol groups), the calculations predict higher activity by the Lewis acidic metal centers, especially for Zr-BEA. This finding is significant for two reasons. First, the fact that Lewis acids can catalyze dehydration reactions opens the possibility of a wider range of catalysts, beyond Brønsted acids, capable of catalyzing the dehydrative aromatization of Diels–Alder products between functionalized furans and olefins. Second, it shows that the silanol groups of the open sites can affect Brønsted acid catalysis, and are solely responsible for the hydrolysis of furans. Thus, elimination of undesired side reactions that require Brønsted acid catalysis, including side reactions that can cause catalyst coking, might demand the design of catalysts that do not possess silanol groups. Source: Patet RE, Fan W, Vlachos DG, et al. (2017). ChemCatChem, online preview, DOI: 10.1002/cctc.201601584.

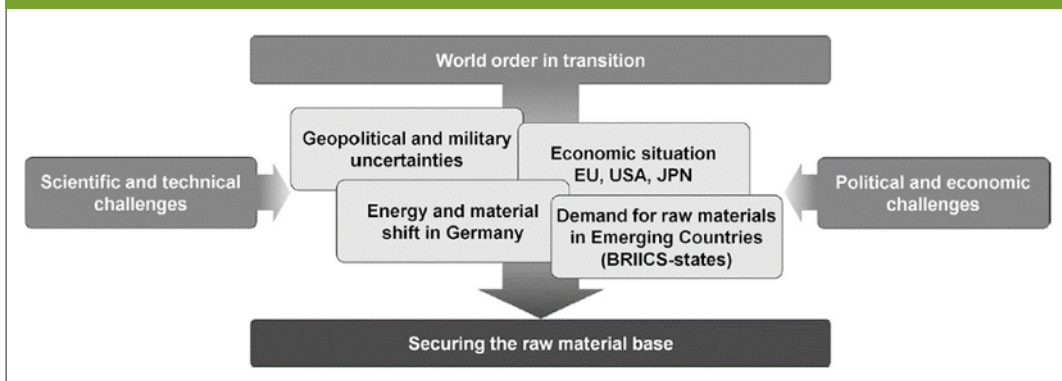
Valuable Metals-Recovery Processes, Current Trends, and Recycling Strategies...

Because of globalization, industrialized countries find themselves actively competing with the so-called “emerging countries” for both raw materials and markets. Because of increasing economic uncertainty, nations find themselves caught between political-economic challenges on the one hand and technical-scientific ones on the other (Figure 1). Numerous developments have arisen from process optimizations, recycling, and substitution, and have culminated in holistic approaches. Although there has been significant progress in the last few years, particularly in the field of recycling and recovery, many of these have not progressed from the laboratory scale, and others have proved to be too expensive.

In 2014, the European Commission published the most recent list of critical elements of relevance to the European economy: antimony, beryllium, cobalt, gallium, germanium, indium, lithium, magnesium, niobium, platinum group metals, rare earth elements, and tin. Herein, the authors

present a comprehensive, well-balanced, and differentiated review of which technical areas of application are affected by which raw material supply, as well as how these metals are currently recovered from primary and secondary raw materials. Each metal or elemental group is assessed from the perspectives of economic significance, raw materials, extraction technologies, and recycling processes, often in significant detail as exemplified by the recovery and refining of platinum group metals shown in Figure 2.

Figure 1. Securing raw materials in response to political-economical and scientific and technical challenges.



The authors believe that although chemistry holds the promise to address many of the issues covered in this study, it has yet to achieve its full potential for the following reasons. First, metal recovery from primary resources (mining) is still a dominating factor. Secondly, although secondary raw materials (recycling) have gained huge significance over the last five years, low commodity prices deter industry from investing in optimizing metal recovery. Also, traditional metallurgical processes based on well-established routes are often the only way to remain competitive under current conditions.

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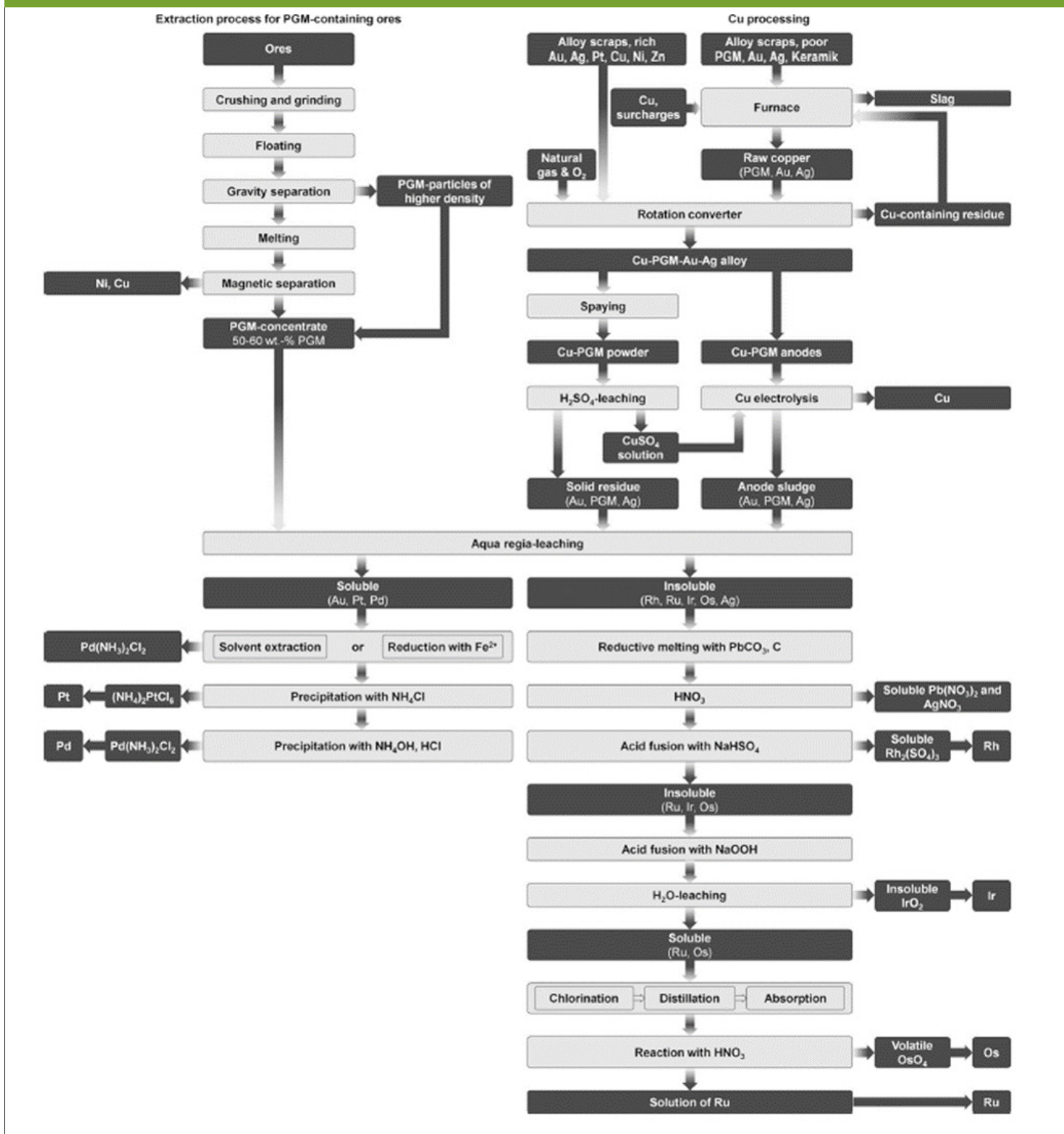
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Figure 2. Recovery and refining of ores containing platinum group metals and secondary raw materials originating from Cu production.



Nevertheless, it is becoming clear that chemistry and, in particular, the substance and material knowledge of chemists, will markedly contribute to further development of this sector particularly regarding optimizing production processes relative to integrated processes. The authors believe that future processing of raw materials will aim at not only one target metal, but all of the raw materials present which will require similar chemical compositions of primary and secondary raw materials to allow for joint processing. Source: Fröhlich P, Lorenz T, Martin G, et al. (2017). *Angew. Chem. Int. Ed.*, 56: 2544–2580.

Joyanta Choudhury, PhD**Associate Professor, Department of Chemistry, IISER Bhopal, India**

Professor Choudhury received his BSc and MSc from the University of Burdwan (India) and then joined the group of Professor Sujit Roy at IIT Kharagpur (India) to pursue his doctoral studies. He completed his PhD in 2006 working on the development of well-defined Ir-Sn heterobimetallic complexes for electrophilic aromatic C-H functionalization reactions. Dr. Choudhury then moved to The Scripps Research Institute, Florida (USA) for postdoctoral work with Professor Roy A. Periana in the field of transition-metal catalyzed C-H activation reactions. In 2008, he received the prestigious Marie Curie International Incoming Fellowship from the European Union

and went to the Weizmann Institute of Science (Israel) for a second postdoctoral posting with Professor Milko E. van der Boom, conducting research on coordination-driven molecular assemblies on solid surfaces. In April of 2011, he returned to India and joined the Department of Chemistry, IISER Bhopal, India first as an Assistant Professor-becoming an Associate Professor earlier this year. His research interests include: (a) small molecule activation and functionalization including CO₂, H₂, alkanes, arenes, and H₂O to address renewable energy and fuel related problems; (b) smart stimuli-responsive switchable catalyst design and its application in tandem and network catalysis; and (c) surface-anchored functional molecular assemblies to develop technologically useful materials. Dr. Choudhury can be reached at joyanta@iiserb.ac.in and his research group webpage <http://jcomchem.wixsite.com/osml>.

The Catalyst Review asked Dr. Choudhury to discuss the newest/most promising catalyst development efforts currently underway in his laboratory.

Catalysts for Sustainable Energy Supply: The ever increasing energy consumption of the modern society has necessitated humankind to think and innovate new ways to produce alternative/renewable energy sources. 'Methanol economy' and 'hydrogen economy' have been proposed as potential solutions for the energy problem which must be solved within the next century. Chemical hydrogen storage (CHS) within CO₂ or other suitable unsaturated small organic molecules through catalytic hydrogenation and as-required delivery of hydrogen through a reverse catalytic dehydrogenation process is an interesting concept in this context. However, a highly efficient, practical, industry-friendly, and relatively economical catalyst is the primary requirement in this prospective technology. One major research project in our lab is focused on this issue. Recently, we have developed a class of novel 'molecular-switch'-based robust catalyst system (using ruthenium/iridium metal, and NHC-benzimidazole hybrid ligand) which performs both 'hydrogenation of imines' and 'dehydrogenative reaction of amines' efficiently in a reversible manner controlled by acid/base alternate inputs. Most importantly, this catalyst system not only operates at ambient atmospheric pressures, but also is fully reversible, decomposition-proof over many cycles, efficient, and applicable under realistic operating conditions. Thus, it seems to be a highly promising system for us to develop a practical 'reversible chemical hydrogen storage and delivery' platform built on small liquid organic molecules (the so-called liquid organic hydrogen carrier, LOHC technology), and on CO₂ (CO₂-HCOOH and/or CO₂-CH₃OH systems) as well. Currently, we are looking at the technical aspects and technological prospects of this novel system to ultimately upgrade it to a larger scale and wider applicability.

Catalysts for Fine Chemicals and Organic Materials: Designing homogeneous and single-site heterogeneous direct C-H functionalization catalysts has been a global research interest for many years. Several fundamental breakthroughs signify the importance and demand of this catalytic process which includes C-H oxidation/oxygenation or other derivatization leading to commodity chemicals, fine chemicals, or pharmaceuticals. During the last five years, our group has been working to devise homogeneous as well as single-site well-defined heterogeneous catalysts to carry out these processes in a more efficient way. In this context, recently we developed robust, efficient, and highly-selective aromatic and non-aromatic C-H functionalization catalysts by integrating the metals (mainly ruthenium, iridium, rhodium, and palladium) within a strong donor NHC ligand backbone to avoid decomposition/degradation problem generally encountered during these oxidative transformations. Thus, via stabilizing the high oxidation state(s) of the catalytic metal centers during the catalytic cycles, we could achieve high catalytic efficiency in simple transformations such as arylalkanes to their carbonyl derivatives, alkenes/alkynes to the corresponding aldehydes/ketones, arenes to their halo/acetoxo derivatives, and aromatic heterocycles to highly conjugated and annulated compounds which are potential organic emitting materials.

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