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The Catalyst Review is designed to provide readers with a global overview of events impacting the $25 billion catalyst industry, through selected abstracts, company interviews, and original articles. There is also a special "Industry Rumors" column that gives a view of what's going on behind the scenes, too. Reader questions and comments are welcomed, to provide an additional value to subscribers. This reinforces the purpose of The Catalyst Review, which is to provide a timely line on key news and research, in an easy-to-digest format.

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Movers and Shakers
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I spent my industrial career working for and eventually leading small companies (75 to 600 people) that were developers of novel chemical processes and catalysts. When I retired at the end of 2000 and started my own consulting firm, I sought to focus my practice on helping organizations (public companies, governmental research organizations and startups) who were seeking to develop and commercialize new chemical catalysts and process technologies. This has been the cornerstone of my rather successful practice of the last 14 years.

My first exposure to a startup company came when I was approached by a venture group with the assignment of reviewing the business and research plans of a startup company that they were considering investing in. The startup company was based on a concept of a university professor who claimed to have developed a novel way of making a series of heterogeneous catalysts that could be utilized in the existing plants for a number of major chemical processes (so-called “drop-in” catalysts). The business plan, developed with the CEO of the startup company, showed rapid growth of sales of the first catalyst, followed within a year or so by commercialization of a second catalyst, and then shortly after by a third, etc. This would amount to a very large and rapidly growing projected stream of earnings. As a result, the spreadsheet of cash flows and other financials showed a very high net present value, and therefore the inventor’s company was seeking tens of millions of dollars of investment to cover expenses for the first few years.

The first catalyst proposed to be commercialized was for a process that I was very familiar with, and the early lab results of catalyst testing had yielded much higher efficiencies than any commercial catalyst on the market. Moreover, the invention, which would be applied to all of the new catalysts proposed by the inventor, involved producing a novel catalyst support, with materials never before used for these catalysts. While there were some results from small scale testing of a powdered catalyst for the first application, no data were presented to justify the improvements forecast for the other catalysts included in the business plan.

From my direct experience, the catalysts used in the first application often gave unusually good results in the laboratory, if tested as powdered catalyst at atmospheric pressure. However, when tested at elevated pressures (required for the commercial process) and with particulate catalysts, the performance was usually substantially poorer. I explained this to the venture people and the startup company, and said that since the support was so unique, and that the lab results were so good, the work should continue, but with a high priority for producing samples of particulate support and catalyst that could be tested at commercial operating conditions, including elevated pressure. I recommended that the business plan should be modified to de-emphasize the performance forecasts for the other catalyst applications, due to lack of data.

I do not know whether the business plan was modified, but after a short while the venture group decided to pass on the opportunity. However, they asked me if I would speak to another venture group, and I agreed, with their and the startup company’s approval, to discuss confidential information with the next venture group. Unfortunately, this second venture group also decided to pass.

I kept communication with the startup’s CEO, as I still felt there could be something to the professor’s novel process for producing the catalyst carrier and the catalyst. I had no contract with the startup company, but continued to answer their questions and advise them on ways to get their catalyst tested once they had produced catalyst in particulate form. Unfortunately, they pursued a number of avenues without my participation, since they did not have enough money to pay me, and to my knowledge they have never succeeded in moving to the next stage. In the midst of this, the professor passed away and I still wonder whether there was something to his invention. However, there was no way with the data they had and my specific knowledge in the area that I could in good conscience give a more positive interpretation to their sales projections and advise either venture group to invest the multimillion dollar valuation. I did urge them to consider making a very small (one hundred thousand dollar) investment to allow scale up and testing of a particulate catalyst, but I was unsuccessful in persuading either one.

Continued on page 8
Evonik Wants to Acquire Monarch Catalyst in India...

Evonik Industries AG, Essen (Germany) intends to strengthen its global catalysts business. Evonik recently signed an agreement with Monarch Catalyst Pvt. Ltd., Dombivli (India) to acquire 100% of the company’s shares. The transaction is expected to close during the first half year of 2015 after the required approvals have been received. The parties have agreed to keep the purchase price confidential. Source: Evonik, 3/11/2015.

GFBiochemicals Breakthrough Levulinic Acid Technology Ready for Commercialization...

Biobased chemicals company GFBiochemicals is starting commercialization of its levulinic acid thanks to its proprietary breakthrough technology. Commercial-scale production will start in Summer 2015 in Caserta, Italy plant. GFBiochemicals’ process technology has been developed and tested at demo-scale since 2008. The Caserta plant will scale-up to 8,000 MT/yr by 2017. Source: GFBiochemicals, 3/1/2015.

Neste Oil and Preem Enter into Patent License Agreement...

Neste Oil Corporation and Preem AB have entered into a Patent License Agreement whereby Preem has licensed Neste Oil intellectual property rights for renewable fuels production for use at Preem Gothenburg refinery. Source: Neste Oil, 3/10/2015.

SPOTLIGHT: New Feeds and Growth Markets Buoy Refinery Catalysts...

Although refiners are grappling with a dramatic decline in oil prices, catalyst suppliers to the sector say global GDP and fuels growth in 2015 will keep the category growing. Products that help refiners maximize the value of product slates and handle challenging feedstocks will continue to provide opportunities to grow the business. While $50 oil is dragging down refiners’ profits and capital expenditure forecasts, their catalyst suppliers have an upside. “Technology development, innovation, addressing future market needs—doing [these] proactively is generally what separates the leaders from the laggards,” says John Murphy, president of The Catalyst Group Resources (TCGR). Al Beninati, president/catalyst technologies at W.R. Grace says that when customers see shifts in their business, they expect catalyst suppliers to find solutions. “A prime example is the current expansion of our portfolio of FCC catalysts within the Achieve catalyst series. This new platform offers a slate of tailor-made technical solutions at multiple price points to help refiners maximize operating flexibility. In commercial application, the economic benefit of achieve catalysts has been averaging... $0.40-0.95/bbl, which will drive significant improvement to the refiner’s bottom line. For refiners processing resid in their FCC, we have launched Midas Gold FCC catalyst, which has demonstrated an economic uplift on the order of $1.00/bbl in commercial application.” According to Detlef Ruff, senior v.p./process catalysts and technologies at BASF, a number of feedstock trends are impacting demand. These include the continued need for next-generation, high-conversion catalysts; tight oil, particularly in North America, where light, sweet crudes that require high-activity catalysts tailored for processing highly reactive feeds continue to rise; heavier crudes to refineries globally, including feeds that require metals passivation in order to mitigate the impact of contaminant metals, such as vanadium and nickel; growing demand for petrochemical feedstocks, such as propylene, in the product slate and its impact on new refinery construction in Mideast and China; and incremental demand for diesel over gasoline, particularly in Western Europe and, increasingly, the North American market. Ruff says refiners worldwide are looking for ways to maximize the value from their operations, and catalyst innovation is a key enabler. One recent product innovation from BASF—dubbed boron-based technology (BBT)—allows refiners to maximize value from resid operations as an improved nickel-tolerant catalyst. Products from the BBT platform are being tested with customers to overcome FCC unit constraints, such as gas compressor limits or the capability to add crude feedstocks with higher metals. Feedback has been encouraging, and BASF is fine-tuning the first products for a broader market entry in the third quarter, Ruff says. Source: Chemical Week online, 3/13/2015.
Sinopec Maoming Completes Butadiene Off-gas Hydrogenation Facility...

Sinopec Group reported that it completed construction of the 40,000 t/a butadiene off-gas hydrogenation facility at its Maoming branch in Guangdong province. This facility is designed to recover off-gas and heavy C4 cuts from the two existing butadiene manufacturing lines, and alkyne, dienes and mono-olefins in the after-etherification reaction of C4 mixtures from the MTBE facility, and then process them into butane, which can be used as cracking feedstock to replace naphtha. Construction on the facility was started on September 24, 2013. Startup was scheduled for February 2015. Source: China Chemical Reporter, 3/6/2015, p. 10.

CLG Expands Technology Portfolio to Include Full Range of Bottom-of-the-Barrel Conversion Technologies...

Chevron Lummus Global (CLG), a joint venture between Chevron and CB&I, announced an expansion of their technology portfolio to include Chevron’s slurry residue hydrocracking technology and CB&I’s coking business. The extension of the business became effective January 1, 2015. Chevron has contributed Vacuum Resid Slurry Hydrocracking (VRSH™) to the portfolio, a patented slurry catalyst technology for high conversion of heavy feedstocks to transportation fuels. Building on Chevron’s long history of residue hydroprocessing, it is based on CLG’s well-demonstrated LC-FINING™ platform and will be marketed as CLG Residue Slurry Hydrocracking (CRSH™). CB&I has added its delayed and needle coking business, which is in use by numerous licensees worldwide. Source: CLG, 3/3/2015.

U.S. Shale Industry Shows Remarkable Resilience...

U.S. independents are telling their investors that they can maintain production roughly level, even while running fewer rigs. EOG Resources, for example, plans a 40% capital spending cut this year but expects just a 3% drop in production. Hess is cutting spending by 14% but expects production growth of about 12%. Achieving the outcomes projected by U.S. shale producers for this year would represent one of the most remarkable productivity performances ever achieved. The number of rigs drilling for gas fell from 1,606 in the summer of 2008 to just 268 last week. Yet U.S. gas production has continued to rise. EIA data show remarkable improvements in productivity, with production per rig from new wells rising in the past year by 24% in the Eagle Ford, 29% in the Bakken and 30% in the Permian basin. Last October, the median break-even oil price needed for shale projects was estimated at $57 per barrel. Falling costs mean this year that number will be significantly lower. If crude prices do start to pick up again, many analysts and executives think U.S. shale producers may be able to step up activity again and resume production growth even with oil below $75. Although U.S. shale is a higher-cost source of oil than some of the great fields of the Middle East, it may well turn out to be more resilient than Saudi Arabia and other OPEC members would like. Source: Financial Times, 3/16/2015, p. 17.

Albemarle and ASOS to Collaborate on Fluid Catalytic Cracking (FCC) Catalyst Facility in the Middle East...

Albemarle Corporation announced that it has entered into discussions with its Middle Eastern partner Ali & Sons Oilfield Supplies & Services Co. (ASOS) to construct a manufacturing facility for FCC catalysts and additives in Abu Dhabi, United Arab Emirates. Abu Dhabi represents the ideal site for the proposed facility because it would allow Albemarle to meet rapidly growing regional demand for refinery catalyst solutions and would provide an unmatched security of supply for existing customers in the Middle East. The facility would manufacture Albemarle’s value-added AFX® catalysts, which promote increased propylene yield from resid feedstocks. this announcement follows Albemarle’s successful delivery of catalysts for the startup of the FCC unit in Takreer’s newly expanded Ruwais refinery. Source: Albemarle, 3/12/2015.

Petrochemicals’ Oil Shock...

The oil price decline hasn’t quelled the U.S. petrochemical industry’s shale revolution; it has merely slowed the charge. Oil prices are now about half of what they were at their peak, providing some relief to foreign competitors. Natural gas prices have fallen too but not by as much. Last summer, oil was four times as expensive as natural gas on an energy content basis. Now, it is three times as much—still a robust advantage for U.S. chemical producers to enjoy. In addition to cheaper natural gas, other factors are mitigating the oil price decline to the benefit of U.S. chemical producers. The price of ethane, the main ethylene feedstock, has dipped below that of natural gas on an energy content basis. On top of that, shale has led to a glut of propane and butane too, making them at times even cheaper to run through chemical plants than ethane. Mauro Gregorio, Dow Chemical’s president of feedstocks and energy, says his company monitors feedstock prices on a weekly basis and can adjust its production just as fast. Naushad Jamani, senior vice president of olefins and feedstocks for Nova Chemicals, is not worried about oil. He says prices would have to drop to $30 per barrel for oil and natural gas to reach parity. “Natural gas liquids will continue to remain the preferred feedstock for North America,” he says. Source: Chemical & Engineering News, 3/9/2015, p. 27.
Energy Group, Total, Makes Investment & Initiates Joint Development Agreement with Renmatix...

Renmatix announced an investment by the New Energies Division of Total, and the signature of a joint development agreement (JDA) between Total and Renmatix. Under the agreement, Renmatix and Total will utilize Renmatix’s proprietary Plantrose™ process with specific feedstocks to extract sugar for use in production of biobased products of interest to Total. In concert with the investment and R&D projects, Total also joins the Renmatix Board of Directors. Existing Renmatix investors, including BASF and Kleiner Perkins Caufield & Byers, join Total in the initial tranche of this Series D fundraise. The patented Plantrose process uses supercritical water to reduce costs in conversion of biomass to cellulosic sugars, the critical intermediary for second generation biofuels and biochemicals. With faster reactions and no associated consumable-expenses, Renmatix’s supercritical hydrolysis economically enables a multitude of renewable process technologies to address the market needs for ‘high volume, low cost, broadly sourced’ cellulosic sugars that persists today. “Having a global oil and gas major like Total join our ranks signals the important role cellulosic sugars play in enabling growth of the bioeconomy, and the transformative impact of Plantrose technology. Our licensing business model allows us to work with the pace-setters of the chemical, forestry, and fuels industries – namely BASF, UPM, and now Total,” said Renmatix CEO, Mike Hamilton. Source: Renmatix, 3/3/2015.

SIBUR Partnering with Norway’s Norner to Develop New Polyolefin Grades/Focus on High Value-Added Products...

Building on their existing collaboration, which dates back to 2012, Russian petrochemical giant SIBUR and Norway’s independent industrial polymer institute Norner have teamed up to develop new polyolefin grades and broaden the former’s product portfolio. As part of the project, Norner will support Sibur in streamlining interaction between its business functions, including sales and marketing, development, technical support, strategic marketing as well as SIBUR’s Technologies Centre, with the aim of developing new products and establishing new segments in the polyolefin market. Over the course of the past few months, the two companies have already laid the groundwork for the collaboration, establishing cross-functional teams, mapping market opportunities with SIBUR’s capabilities, holding meetings and interviews with major brand owners and converters and working on devising a strategy. The next steps involve the creation of value-added product development projects, drawing up launch plans, training the commercial team as well as market introduction and benefit tracking. Source: Plasteurope.com, 3/11/2015.

Rosneft’s Acquisition of Sanors Creates Major Petchems Player In Russia...

Russia’s energy major Rosneft (Moscow) says it has completed acquiring the Novokuibyshevsk Petrochemical Co. (Sanors; Novokuibyshevsk, Russia). The purchase of the Sanors group of companies is in line with Rosneft long-term development strategy, which aims to integrate Rosneft’s oil and gas production and refining assets with the existing Sanors petrochemical production facilities. The synergy of the integration will help strengthen Rosneft’s development of the petrochemical business, the company says. This transaction will allow Rosneft to develop its own line of import substitution as well as meeting growing domestic demand for key polymers and other chemical products on the Russian market. Source: Chemical Week online, 3/16/2015.

Rennovia and Johnson Matthey to Co-Develop Commercial Catalysts for Biobased Adipic Acid Process...

Rennovia Inc. and Johnson Matthey announced that they have entered into a joint development agreement (JDA) for the co-development and manufacture of catalysts to be used in the scale-up and commercialization of Rennovia’s process for the production of bio-based glucaric acid and adipic acid. This agreement, for the co-development and manufacture of catalysts, builds upon the existing collaboration, announced in March 2014, under which Rennovia and Johnson Matthey Davy Technologies are working together on the engineering and construction of a mini-plant to optimize and scale the process, which will enable commercial production of these products. The focus of the joint development effort announced will be to develop and supply catalysts for the mini-plant and future commercial plants. Source: Rennovia, 2/27/2015.
Yale Researchers Discover New Catalysts to Generate Renewable Fuels...

For the last seven years, Yale PhD student, Staff Sheehan, has been working on splitting water. Now, a paper just published in Nature Communications reveals how one of the methods he and his team have uncovered for this process—using a specific iridium species as a water oxidation catalyst—could aid in the development of renewable fuels. The process which Sheehan is investigating is known as artificial photosynthesis—storing energy from the sun as plants do, but more efficiently. The iridium-based catalyst represents one of two novel methods Sheehan and other Yale researchers have discovered for splitting water in artificial photosynthesis—the other utilizes cobalt. Both have been patented through the Yale Office of Cooperative Research. Sheehan is developing these technologies as a commercial venture through the Yale Entrepreneurial Institute (YEI) under the name Catalytic Innovations. While use in generating renewable fuels remains a long-term goal for Catalytic Innovations, Sheehan says a near-term market opportunity is using their catalysts for metal refining, which takes advantage of the iridium-based catalyst’s stability in strong acids. These catalysts can also be used to remediate chemical waste and have military fuel cell applications. The team is successfully raising research and development funds. “What we’ve discovered is a new architecture for catalysts that is highly efficient and very stable for the eventual development of renewable fuels,” Sheehan says. Source: Yale University, 3/11/2015.

Another Offspring from Catalyst Union...

Combining organic catalysis and photoredox catalysis continues to bear fruit for chemists. Princeton University’s David W. C. MacMillan and James D. Cuthbertson report that using an iridium photocatalyst and a thiol organocatalyst together allows them to add aryl groups directly to allylic sp³ C–H bonds. MacMillan’s group has previously used the catalyst combo to asymmetrically alkylate aldehydes, enantioselectively α-trifluoromethylate aldehydes, and β-arylate aldehydes and ketones. The new reaction gives chemists an easy way to tack electron-deficient aromatic nitriles onto olefins, which could come in handy for making many types of molecules. The reaction works by linking two catalytic cycles. The photoredox catalyst turns the aromatic nitrile into a persistent radical by transferring an electron. At the same time, the thiol organocatalyst abstracts an allylic hydrogen atom from the olefin to create a radical. The two radicals then meet up to form the product. Source: Chemical & Engineering News, 3/9/2015, p. 35.

Zeoite Membranes for Xylenes Separation...

Current technologies to separate xylene isomers are very well established and commercialized. Their high energy intensity is inherent, regardless of several efforts to optimize. Their requirement for multiple distillations, excessive heating/cooling cycles, and a lot of rotating equipment is what makes the operating cost high. On the other hand, membrane processes in general offer a lower energy intensive solution and are more economically and environmentally attractive. Their compact sizes and independence of expensive sorbents are additional advantages. The performance of a suitable membrane process that can offer these advantages will rely primarily on finding the right membrane material. For xylenes separation, nanocomposite zeolite membranes have proven their superiority over film-like membranes. The separation factor exhibited by nanocomposite membrane is orders of magnitude higher than for film-like membranes. In fact, nanocomposite membranes show the highest recorded separation factors, ranging from 3500 to 4000 at xylene pressures around 30 kPa. Nanocomposite membranes also require significantly less time to stabilize the process and attain steady results compared to film-like membranes. Nanocomposite MFI zeolite membranes, although still new and undergoing continuous improvement, clearly show superior performance compared to conventional separation methods (selective adsorption and crystallization) and other membrane processes. Regarding the area of combined isomerization and separation, recent experiments have demonstrated much higher production and yield. The equilibrium composition limitation imposed on conventional fixed bed reactors (FBRs) can be overcome, reaching p-xylene yields beyond equilibrium. An increase in p-xylene yield in catalytic membrane reactors (CMRs) as high as 26% compared to FBR was achieved at 643°K. ExxonMobil was granted a patent for a xylenses isomerization process using a zeolite CMR. Finally, zeolite membrane defects and scalability are issues that have been plaguing the technology for decades. The recent introduction of nanocomposite zeolite membranes has contributed significantly to a reduction in defects. Furthermore, an recent advancement made by Professor Michael Tsapatsis eliminated cracks created at the boundary of grain zeolite crystals during synthesis of the membrane. The treatment developed, called rapid thermal processing (RTP), showed significant improvement in the number of defects in calcinated zeolite membranes. Focusing on reduction of defects and scalability issues could pave the way for zeolite membrane in industrial applications, revolutionizing the petrochemical industry. Source: Petroleum Technology Quarterly, Q1/2015, p. 111.
A novel bitumen upgrading process that decreases the amount of diluent required for pipeline transportation and reduces overall operating costs has been proven in a 100-b/d demonstration plant in Pennsylvania. Superior Upgrading Technologies’ (SUT) Hammer Technology (HT) relies on the combination of fluid hammer effect, hydrodynamic cavitation, and extreme shear to create macroscopic fluid flows. These set molecules on a collision course with kinetic energies large enough to break bitumen’s molecular hydrocarbon bonds at nearly ambient temperature and pressure (cold cracking) in lieu of the more energy-intensive processes associated with conventional delayed coking or catalytic cracking technology. Developed after 2 years of research, SUT HT provides bitumen upgrading that, in addition to its capability for deployment at wellheads, can be aggregated into a larger installation of 100-100,000 b/d at a construction cost of less than $2,000 bbl and an operating cost of less than $1-2/bbl. Comparative economic analysis with a conventional upgrading system and an installation utilizing the new process showed an SUT HT system will pay for itself in 1-2 years. To validate the HT process, SUT constructed a 100-b/d demonstration plant in Bellefonte, Pa. and tested it on bitumen and atmospheric residue, which have similar viscosities. The results indicate it takes about 15 min to process 55 gal (1.3 bbl) of material, and a total 25 kw-hr of power was consumed. This gives the performance of about 100 b/d and the energy use of 70 MJ/bbl, which translates into about $1/bbl assuming the $0.06/kw-hr power cost. Field-testing is next for SUT HT. Only field-testing on 100-1,000 b/d of bitumen can help build a case for commercial application of the technology as well as reveal any potential problems. Source: Oil & Gas Journal, 2/2015, p. 66.

Iron’s abundance and low cost make it an attractive substitute for costly cobalt catalysts used for mediating Fischer-Tropsch (FT) synthesis. That industrial-scale carbon coupling process converts mixtures of CO and hydrogen to liquid fuels and other valuable organic products. But iron catalysts deactivate quickly during FT synthesis. The metal nanoparticles agglomerate, undergo phase changes, and accumulate a carbon buildup, all of which render iron catalysts inactive. Those problems can be avoided by preparing the catalyst from an iron-based metal-organic framework (MOF) compound, according to a research team headed by Jorge Gascon of Delft University of Technology, in the Netherlands. The team, which includes researchers at Dow Chemical, treated a commercially available MOF (Basolite F300) with furfuryl alcohol to tune the ratio of iron to carbon, then pyrolyzed the crystalline material, which contains a network of pores and channels. Analysis shows that the procedure yields catalytically active, confined iron carbide particles that outperform standard reference catalysts. The new catalysts resist sintering, degradation of the carbide phase, and other forms of deactivation, the team reports. Source: Chemical & Engineering News, 3/16/2015, p. 27.

University of Tokyo researchers have developed a novel selective catalyst that allows the creation of several basic chemicals from biomass instead of petroleum. This discovery may lead to the use of plant biomass as a basic feedstock for the chemical industry. The new catalyst developed by Prof. Kyoko Nozaki’s research group at the Graduate School of Engineering enables selective cleaving (hydrogenolysis) of carbon-oxygen (C-O) single bonds in phenols and aryl methyl ethers, two of the main components of lignin. Producing these building blocks from lignin requires the selective hydrogenolysis of C-O bonds in phenols and aryl ethers, but their aromatic rings are also susceptible to hydrogenation. Using their new catalyst, the research group accomplished selective C-O bond hydrogenolysis without also cleaving the aromatic rings for the first time ever. Prof. Nozaki’s research group employed hydroxycyclopentadienyl iridium complexes as catalysts under hydrogen (dihydrogen) at atmospheric pressure. Using these new catalysts, arenols (phenol derivatives) were successfully deoxygenated to afford the corresponding arenes. In addition, aryl methyl ethers were converted selectively to arenols after demethylation with dihydrogen using the same catalysts. Source: University of Tokyo, 2/23/2015.

This depicts the mechanism of selective hydrogenation of the carbon-oxygen bond by concerted action of the ligand and the metal. CREDIT © 2015 Kyoko Nozaki
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what is precious to you?
A second startup company I have been involved with was also started by a professor who had a new material that he proposed to use as a catalyst that could be a “drop in” catalyst for a plant producing a major petrochemical. Again, the client was a venture group, and I was subcontractor to another consultant. The professor maintained that this catalyst could allow the desired reaction to exceed the equilibrium-limited conversion per pass, due to its unique chemical nature. We were skeptical, and again, experimentation was in by batch tests in small vials, with powdered catalyst. Work was at the professor’s university with a post-doc, so costs were low.

The startup company had a number of advisors who were retirees from very large chemical companies. They prepared the usual very optimistic spreadsheets, promising many plants using the new catalyst with high valuations. Our team proposed larger-scale testing with once-through gas flow, not trusting the lab data. When this was accomplished, the results refuted the unrealistic expectations of the professor and the venture group withdrew.

The five lessons that the startups should have learned, included:

1) Avoid “pie in the sky” business plans
In both startups described, the business plans were very optimistic, showing rapid penetration of existing catalyst markets with inadequate testing to back up the catalyst performances. This may have been because the sources of potential investment in both cases were venture groups, who were looking for rapid growth. Seeking funding from angel investors or companies in the businesses being targeted might have been a better choice for a smaller round of initial financing.

2) Get the right consultants early, with experience in going from lab to commercial scale
In the case of the first start up described above, I believe I was a good choice for consultant, but my client should have been the CEO of the startup company, and not the venture group seeking advice. I know I could have guided the CEO towards the right sources of potential investment funds for the first catalyst.

In the case of the second startup, the CEO (not the professor himself) was following the advice of the large-company consultants, and not managing his cash flow, so that when the venture group decided to pass on the opportunity, the startup quickly ran out of money.

3) Scale-up to appropriate test conditions quickly to avoid wasting cash; and 4) Ensure enough cash to get to the point where proof of concept is achieved
These two are related. The first requires relying on the right consultant who can advise on the critical path of experimentation, and the second requires the consultant to be knowledgeable and credible as an advisor to the CEO, rather than just the technical team.

5) Partner early with potential users of the innovation
It is important to bring potential investors into the process early, so that they may understand the risks and the potential rewards of funding critical experimentation aimed at proving concepts. Again, the right consultant should be able to lead the startup team in this regard.

About the Author
Dr. Joseph Porcelli’s professional career spans more than 40 years, with such firms as Scientific Design Company, Inc., ChemSystems, Inc., and Halcon SD Group, Inc. He has been intimately involved in every aspect of chemical process innovation, including: evaluation of process concepts, carrying out and supervising process, catalyst research and development, and leading efforts to commission new plants, processes, and catalysts. Much of his career has been spent as a chief executive in the international chemical arena, wherein he has gained knowledge and experience in all company operating functions. He has negotiated the sale and purchase of packages of technologies and businesses and has conceived of and executed international technology alliances. In 2001, Dr. Porcelli established JVP International, Inc. as a vehicle to offer the international chemical industry his technical expertise and management experience.
Olefin Paraffin Separation
Using Ionic Liquids

By Peter Goodrich, PhD

Introduction
Today one of the most imperative challenges for industry is to find alternatives that improve the efficiency of processes to make more sustainable use of energy. The processes involving olefin/paraffin separations performed using cryogenic distillation normally require vast amounts of energy and, therefore, an improvement in these processes is vital for improving the energy balance. Hence, researchers are looking for potential alternative technologies to replace the energy and cost-intensive processes (Li et al. 2015).

The potential technology requires high selectivity and must be economical in energy and cost compared with conventional approaches. Currently, there are a number of commercial membranes primarily used for the separation of air, hydrogen/hydrocarbons and water/hydrocarbon (Ravinchi et al. 2009). Two main areas of research have been explored. In the development of novel polymer materials, membrane technology offers prospective increase between permeability and selectivity for gas separation through interactions between reactive carriers of membrane materials and the target gas. Facilitated transport membrane (FTMS) technology in the separation of olefins from paraffins has been a topical area of research. Therein, the performance of the membranes and its current application related to the polymer, solvent and carrier structure has been reviewed (Azhin et al. 2008). Transition metals such as copper and silver have long been known to form electron donor/acceptor complexes with olefins. Several chemical systems using these transition metals as the selective separating agent have been studied and reviewed (Safarik and Eldridge 1998).

A number of disadvantages are still associated with chemical absorption related to selective olefin/paraffin separation. These include stability of the transition metal, solvent losses and maximum operating temperature. This has opened the door for alternative technologies.

Ionic Liquid Technology
Based on their unique properties—such as low vapor pressure, good thermal stability and large liquidus range—ionic liquids (ILs) have also been used as alternative solvents for gas and liquid separations. The nature of the cation and the anion determine the physicochemical properties of the ionic liquid. Therefore, tailoring of both the cation and anion can be manipulated to provide unique physiochemical properties when a chemical reaction or a specific affinity and selectivity are required. In this regard ILs have been applied in different areas of separation technology (Han and Row 2010).

Liquid-Liquid Extraction
The higher solubility of unsaturated compounds in various ILs compared with their saturated counterparts has been explained by the favorable electrostatic interactions between the cation of the ionic liquid and the π-system of the solute (Gutel et al. 2009). Other interactions have been evoked to explain the solvation properties of hydrocarbons in ILs such as hydrogen bonding between the gas and the anion, anion-π interaction between the gas and the anion and/or π-π interaction between the gas and the cation (Lee et al. 2010). This has resulted in the functionalization of ionic liquids to improve gas separation.

An extensive study was presented on the evaluation of 24 alkylimidazolium-based ILs for the extractive distillation of propene/propane mixtures screened at ambient temperature and low pressures (Mokrushin et al. 2010). Screening results show that every tested IL showed entrainer properties. Optimal entrainers should provide a high solubility (circles) and a low separation factor (triangles) (see Figure 1). Within the ILs studied higher separation factors also resulted in low solubility. Despite this, it was found that shortening of the alkyl substituents of the imidazolium ions leads to a decrease in capacity and to an increase in the separation factor. Interestingly, ILs containing nitrile functionalities in either the cation or the anion or on both moieties showed enhanced separation ability compared with non-functionalized ILs. The functionalized anion-containing 1-ethyl-3-methylimidazolium tetracyanoborate [Emim][B(CN)₄] is the most promising candidate.
SPECIAL FEATURE

Xing et al. (2013) designed a symmetrical dual cation nitrile-functionalized IL 1,3-dibutyronitrile-imidazolium bis((trifluoromethyl)sulfonyl)imide for the separation of ethene/ethane mixtures. The experimental results showed that enhanced separation selectivity could be achieved with only a slight reduction of absorption capacity compared to the non-nitrile functionalized IL. Modeling using COSMO-RS calculations showed that the increased polarity of the functionalized IL and thus the large difference in interaction with the gases were the major factors in determining the solubilities of ethene and ethane. In addition, a silver-containing IL was also tested because of its higher absorption capacity for olefins. It was found that the silver-containing IL was superior to any of the common ILs in the separation of ethene/ethane, particularly 1-butyl-3-methylimidazolium bistri fluoromethanesulfonimide [Bmim] [NTf₂].

Ionic Liquids and Metal Salts

Although the olefin/paraffin separation by chemical absorption is feasible, the stability of the metal-cation and the high vapor pressure of common organic solvents are still concerns. In this regard, the separation of olefin/paraffin mixtures via the absorption of olefins with a transition-metal has also been studied in ILs. The effects of the ionic liquid structure on gas absorption for a number of pyridinium and imidazolium ILs that contained AgNO₃, Ag[OTf] and Ag[NTf₂] were investigated (Sánchez et al. 2009). Ethene absorption was chemically enhanced in the silver-based ILs and was therefore considerably higher than that observed in the non-silver based ILs. Therein, the olefin/paraffin selectivity at a pressure of 1 bar was ~30–50 higher in the ILs containing silver salts. In addition, higher absorption capacities were observed for ILs impregnated with Ag[NTf₂] compared to the corresponding Ag[OTf] or Ag[NO₃]. This was due to a decrease in the lattice energy of the Ag[NTf₂] salt leaving the Ag⁺ more available for olefin complexation.

A similar study by (Ortiz et al. 2008), reported the selective absorption of propene from a mixture with propane by chemical complexation with silver ions in 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF₄]. The IL-Ag⁺ system showed higher absorption capacity for propene compared to the corresponding Ag-based aqueous solution. The propene solubility increased with pressure and decreased with temperature indicating that propene complex formation with the Ag salt is an exothermic process and consequently the equilibrium constants will decrease with increasing temperature. In addition, complete regeneration of the IL-Ag⁺ reaction media can be carried out at room temperature using pressure-temperature technology. In a continuation of the studies, the kinetics of absorption of propene in Ag-[Bmim][BF₄] medium have been analysed in a stirred cell reactor (Ortiz et al. 2010). For concentrations equal to or higher than 0.25 M of Ag⁺ in the IL [Bmim][BF₄] it was possible to assume instantaneous chemical reaction between propene and the silver ions. Therefore, the rate of absorption is governed by the rate at which dissolved propene and Ag⁺ diffuse to the reaction plane from the gas-liquid interface and liquid bulk, respectively. Thus, for instantaneous reactions of propene in Ag⁺ in IL media, absorption equipment would be designed for high mass transfer coefficients with short contact times to selectively absorb more olefin than paraffin.

The effect of ionic liquids on the formation of a partial positive charge on the surface of silver nanoparticle and its subsequent effect on facilitated olefin transport were investigated by Kang et al. (2008a). The 1-butyl-3-methylimidazolium cation was paired with various anions to form the corresponding, tetrafluoroborate [Bmim][BF₄], triflate [Bmim][OTf] and nitrate [Bmim][NO₃] ILs were investigated. These ILs were employed to control the positive charge density of the surface of silver nanoparticles. The positive charge density of the silver nanoparticles, as characterized by the binding energy of the silver atom, was in the following order: [BF₄]/Ag >> [OTf]/Ag > [NO₃]/Ag. This order was consistent with the tendency of the IL to form free ions and create a higher positive charge on the Ag and, therefore, improve the propene/propane separation. A similar study was also undertaken with the same Ag-IL mixtures impregnated into the polymer poly(2-ethyl-2-oxazoline) (Kang et al. 2008b). The anion type negligibly affected the initial
separation performances; however, it significantly affected the long-term operation stability. Additionally, UV and TEM confirmed the long-term operational stability was strongly associated with the reduction rate of the silver ions. The reduction rate of the silver ions in the polymer/silver salt/ionic liquid complex was observed in following order: [Bmim][BF$_4$] > [Bmim][OTf] > [Bmim][NO$_3$], suggesting that among the ionic liquids investigated, [Bmim][NO$_3$] had the most improved separation performance.

In addition to silver, copper also has been investigated in ionic liquid media. Copper nanoparticles in 1-Methyl-3-octyl imidazolium tetrafluoroborate [Ommim][BF$_4$] ionic liquid was introduced for olefin/paraffin separation (Hong et al. 2013). When the copper nanoparticles were generated in the IL 1-octyl-3-methylimidazolium tetrafluoroborate [Ommim][BF$_4$] the separation performance was twice that of the neat IL and the mixed gas permeance increased from 6.9 to 12 GPU due to facilitated olefin transport. A similar mechanism was proposed, whereby the enhanced separation performance was attributed to both the free imidazolium ions and the positively polarized copper nanoparticles, which favorably interact with the olefin molecules.

A more detailed study into the effects of imidazolium-based ionic liquids on dissociation of micrometer-sized copper flakes into copper nanoparticles and on facilitated olefin transport was investigated (Han et al. 2011). Again, FT-Raman spectroscopy evidenced that the positively charged surface on the copper was induced by interactions with anion of the IL. TEM images and UV–vis spectra have been confirmed by the intensity of the copper-ionic liquid interactions depending on the size and distribution profiles of the nanoparticles. The separation performance of the ionic liquid/Cu metal composite membranes for olefin/paraffin mixtures was in the following order: [Eminim][BF$_4$]/Cu < [BMIM][PF$_6$]/Cu < [BMIM][BF$_4$]/Cu. Surprisingly, the binding energies of the copper atoms in the ionic liquid/Cu metal composites were strongly correlated with the separation performance. Consequently, it was concluded that facilitated olefin transport was consistent with the trend of increasing binding energy of copper atoms.

Silver Containing Ionic Liquids

In general, liquid membranes have higher selectivity values than the non-porous solid membranes and because of the higher liquid phase diffusivities the economic efficiency of membrane processes is determined by the membrane selectivity and the membrane productivity (i.e., the flux that can be realized through the membrane). For the separation of olefin/paraffins, selectivity is the most important factor as low capacity can be compensated by a bigger membrane area but the low selectivity still requires a multi-component process.

The use of ionic liquid-silver complexes has been recently studied and patented by Dai et al. (2011) along with the US government. This is the only ionic liquid-based patent for olefin paraffin separation.

Agel et al. (2011) measured physical properties and complex stabilities of [Ag(C$_{5}$H$_{11}$)][NTf$_{2}$] to determine gas solubilities and diffusion coefficients of propene and propane in order to calculate selectivities for membrane separation. The complex-ionic liquid[Ag(propene)][NTf$_{2}$] formation at ambient temperatures formed a stable liquid membrane. Importantly, the system contained no additional volatile membrane components such as molecular solvents or water that can get lost during the separation process or contaminate the gas streams. Due to the higher silver content the propene capacity is much higher compared to those measured for silver salt solutions in standard ionic liquids, resulting in a solubility selectivity as high as 40 at 1 bar mixed propene/propane pressure.

Silver salt containing ionic liquids were also employed in the liquid-liquid olefin/paraffin separation. The extraction of C$_{5}$-C$_{8}$ linear α-olefins from olefin/paraffin mixtures of the same carbon number using silver(l)/N,N-dimethylbenzamide bis(trifluoromethylsulfonylimide ([Ag(DMBA)$_{2}$][TF$_{2}$N]) or silver(l)/propylamine bis(trifluoromethylsulfonylimide ([Ag(PrNH$_{2}$)$_{2}$][TF$_{2}$N]) as the extracting agent was investigated (Wang et al. 2014). The separation performance of the system increased with increasing chain length of the olefin/paraffin mixture with the [Ag(DMBA)$_{2}$][TF$_{2}$N] ionic liquid outperforming [Ag(PrNH$_{2}$)$_{2}$][TF$_{2}$N] in terms of both selectivity and distribution coefficient. Modeling using the universal quasi-chemical activity coefficient (UNIQUAC) model suggested that the silver cation interacts more strongly with the PrNH$_{2}$ compared with the DBMA, meaning in the latter IL the silver can interact more freely with the olefin. In addition, doping of the IL with water also improved performance with selectivities as high as 38 being observed for the octene/octane system.

Ionic Liquid Membranes

An adaptive self-healing ionic liquid nanocomposite membrane comprising a multi-layer support structure impregnated with [Ag][NTf$_{2}$] hs been used for propene/propane separation (Pitsch et al. 2012). The ionic salt renders liquid like upon complexation with propene increasing the olefin solubility Figure 2. This results in facilitated transport of propene over propane at benchmark-setting selectivity and permeance levels. Importantly, the membrane showed a regenerative or self-healing when recontacted with propene after desorption.

SPECIAL FEATURE

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Polymeric ionic liquid membranes have also been impregnated with ionic liquid-silver complexes for ethylene/ethane separation (Tomé et al. 2014). Therein, the use of protic-ionic liquids as alternative polymer matrices were employed a new series of facilitated transport membranes of a polypyrrolidinium type ionic liquid (PIL) incorporating different amounts of the pyrrolidinium ionic liquid (PIL) and the silver salt Ag[NTf₂]. The membranes were prepared by a film casting process and their ethene and ethane permeation properties were measured at 293 K using a time-lag apparatus. The preparation of PIL/IL composite membrane increased the permeability of both ethene and ethane, compared to the poor mass transfer observed in the pure PIL. Nevertheless, the presence of the IL in the composite membrane significantly reduced C₂H₄/C₂H₆ permselectivity which was greatly improved by the addition of the silver salt. Furthermore, increasing the silver ion concentration in the PIL/40% IL system resulted in enhanced overall ethane/ethylene permselectivity, surpassing the upper bound for conventional polymeric membranes, indicating that PILs have interesting potential as polymer matrices for olefin-facilitated transport membranes (Figure 3).

Conclusions

Due to the special features of ionic liquids, such as high thermal and chemical stability, low vapor pressure, non-flammability, tunable physicochemical properties ionic liquids are considered good candidates for the substitution of organic membrane phase in liquid membranes. Although somewhat in its infancy, the use of ILs for olefin/paraffin separations is in some cases achieving better results compared to conventional membrane separation processes. However, a recent review by Faiz and Li (2012) for the application of ionic liquid/metal salt composite membranes for olefin/paraffin separations concluded that even though the concept was successfully applied for separation, the long term stability of the membranes is still a major issue. Despite these initial concerns, the use of ionic liquid technology has been almost exclusively conducted in research laboratories. However, the future of olefin/paraffin separation is particularly exciting, and the space for industry driven research is still rich with opportunity especially in the field of IL technology.

References


SPECIAL FEATURE


About the Author

Dr. Peter Goodrich is a Senior Research Fellow at Queen’s University Belfast, where he is currently researching the use of ionic liquids as alternative media for petroleum, vegetable oil and fats upgrading, metal catalyzed transformations relating to bulk and intermediate chemicals and liquid-liquid and gas-liquid separations. He previously worked at AstraZeneca and Randox Laboratories synthesizing drugs and novel ligands for asymmetric catalysis. He holds a PhD in Chemistry from Queen’s University Belfast where he studied chemoenzymatic synthesis for the production of pharmaceutically active molecules. Email: p.goodrich@qub.ac.uk
EXPERIMENTAL

Uptake of One and Two Molecules of CO$_2$ by the Molybdate Dianion: A Soluble, Molecular Oxide Model System for Carbon Dioxide Fixation...

Metal oxides are well known as economically viable catalysts for bringing about various transformations of CO$_2$. Herein, the authors set out to investigate salts of the molybdate dianion, in order to determine the behavior and mode of reaction of a simple oxoanion with carbon dioxide. In this quest to discover either a new homogeneous catalytic system or a soluble model for known heterogeneous oxide catalysts, they found that molybdate absorbs not just one but two equivalents of CO$_2$ and were able to completely characterize the resulting mono- and dicarbonate complexes.

Initially the authors sought to employ commercially available sodium molybdate as a catalyst but determined that it does not react with CO$_2$ under aqueous conditions. In order to endow the molybdate dianion with solubility in organic media, they prepared [PPN]$_2$[MoO$_4$] (PPN$^+ = (\text{Ph}_3\text{P})_2\text{N}^+$) which, when dissolved, readily reacted with CO$_2$ to form an addition product subsequently identified as the k$^2$-bound carbonate moiety [PPN]$_2$[MoO$_3$(k$^2$-CO$_3$)] possessing the structure shown in Figure 1.

Curious to see whether the new molybdenum carbonate complexes could serve as a source of activated CO$_2$, they subjected [PPN]$_2$[MoO$_3$(k$^2$-CO$_3$)] to the mild hydride donor triethylsilane, resulting in the formation of formate. The production of formate improved from 16% to 71% when the reaction was run under an atmosphere of CO$_2$, raising the question of whether the active species facilitating CO$_2$ reduction was the monocarbonate complex [MoO$_3$(k$^2$-CO$_3$)]$_2^-$ or the dicarbonate complex [MoO$_2$(k$^2$-CO$_3$)$_2$]$_2^-$.

After optimization of reaction conditions, [PPN][OCHO] and [PPN][MoO$_3$(OSiEt$_3$)] were obtained as the sole products. This system thus illustrates both the reversible binding of CO$_2$ by a simple transition-metal oxoanion and the ability of the latter molecular metal oxide to facilitate chemical CO$_2$ reduction.

Characterization (including computational energy calculations) of the two molybdenum oxo carbonate species obtained from the uptake of CO$_2$ by the molybdate dianion (Figure 2) suggests that the first binding event to form [MoO$_3$(k$^2$-CO$_3$)]$_2^-$ is irreversible, while the second CO$_2$ molecule binds in a reversible process. Source: Knopf I, Ono T, Temprado M, et al. (2014). Chem. Sci., 5: 1772–1776.

A Radical Twist to the Versatile Behavior of Iron in Selective Methane Activation...

Recent discovery and development of significant reserves of shale gas have added to the vast quantity of methane available for conversion into base chemicals and transportation fuels and has spurred great interest in developing economically viable, large-scale routes for its selective activation. Current commercial routes involve the conversion of methane into syngas, which is subsequently converted into hydrocarbons using methanol-to-hydrocarbon (MTH) catalysis or into transportation fuels via Fischer–Tropsch synthesis (FTS). Unfortunately, both routes are complex, multistep catalytic operations, which are energy intensive. In this mini-review, the authors chose to focus on recent developments from the Zhang Research Group (Nanyang Technological University)
dealing with a novel catalyst consisting of lattice-confined single iron sites (Figure 1), capable of converting methane into ethylene, benzene, and naphthalene—in high yield and in a non-oxidative manner. Based upon X-ray absorption fine structure (EXAFS) studies, complemented with high-angle dark field (HAADF) scanning transmission electron microscopy (STEM) measurements, it is proposed that the active site in this catalyst material consists of a single iron atom, coordinated to one silicon and two carbon atoms.

From the results of density functional theory (DFT) calculations, backed by vacuum ultraviolet soft photoionization molecular-beam mass spectrometry (VUV-SPI-MBMS) measurements (to determine the presence of methyl radicals in the gas phase above the catalytic surface), a mechanism has been proposed (Figure 2). Of interest is the fact that this conversion process closely resembles the commercial benchmark for ethylene production—the steam cracking of hydrocarbons. Unlike steam cracking, however, there is almost complete absence of coke deposits—a finding yet to be fully understood. In spite of this advantage, further improvements of the relative yields of ethylene, benzene and naphthalene will be required to make this novel catalytic cracking route attractive for implementation in the petrochemical industry. Source: Ruitenbeek M and Weckhuysen BM. (2014). Angew. Chem. Int. Ed. 53: 11137–11139.

Polar Group and Defect Engineering in a Metal–Organic Framework: Synergistic Promotion of Carbon Dioxide Sorption and Conversion...

Prompted by concerns about the effects of global warming, one of the suggested strategies for reducing concentrations of CO₂ involves carbon capture and sequestration (CCS). Newer, cost efficient techniques are currently being assessed including the use of porous sorbents that adsorb CO₂ preferentially over N₂ based on a physisorption mechanism. Herein, the authors propose the use of a new class of crystalline porous materials, metal–organic frameworks (MOFs) as viable candidates for CCS applications. These materials—with their very high surface areas and gas sorption capacity as well as a tailorable pore surface/environment—can facilitate selective CO₂ binding. Moreover, the effect of coordinatively unsaturated metal sites (CUSs) combined with the polarizing and alkaline functional groups can lead to enhanced CO₂ capture.

To test this premise, the authors prepared a stable Al-based MOF (USTC-253) by the reaction of Al(NO₃)₃·9H₂O and 4,4’-dibenzoic acid-2,2’-sulfone (Sbpdc). For comparison, Sbpdc was replaced with 4,4’-biphenyldi-carboxylic acid (bpdc) and 2,2’-bipyridine-5,5’-dicarboxylate acid (bpydc) under the same conditions to afford elongated MIL-53 (EL-MIL-53) and MOF-253. Introduction of trifluoroacetic acid (TFA) into USTC-253 leads to the formation of USTC-253-TFA, which has almost the same structure as USTC-253 with a certain amount of structural defects (Figure 1). The participation of TFA as a modulator in the reaction leads to the formation of vacancies and missing-linker defects in the structure (Figure 2), which will expose new coordinately unsaturated metal centers. These, in turn, expose new coordinately unsaturated metal centers that act as the desired Lewis acid sites for the enhanced CO₂ capture and catalytic conversion of USTC-253-TFA.
In addition to the CO₂ capture capability, CO₂ cycloaddition with propylene oxide as a model substrate was investigated to determine the viability of converting CO₂ to useful high-value chemicals. It was found that, in this application, USTC-253-TFA exhibits good catalytic activity and recyclability in the synthesis of cyclic carbonates at room temperature and 1 bar CO₂ pressure according to the proposed mechanism shown in Figure 3. Source: Jiang Z-R, Wang H, Hu Y, et al. (2014). ChemSusChem online preview, DOI: 10.1002/cssc.201403230.

**Controlled Surface Segregation Leads to Efficient Coke-Resistant Nickel/Platinum Bimetallic Catalysts for the Dry Reforming of Methane...**

Industrial reforming of natural gas with H₂O or CO₂ to produce syngas typically relies on the use of Ni catalysts due to its low cost and high activity relative to noble metals. However, Ni catalysts undergo deactivation due to coke formation, sintering, and metal oxidation, especially in CO₂ reforming. One approach to dealing with this problem involves modification of the metal surface to prevent C* nucleation and growth through modification of the metal surface.

Alternatively, enhancement of the gasification of carbon by addition of alkali or alkaline or rare-earth metal oxides has been shown to be effective. A third approach, which forms the basis of this work, involves the addition of secondary metals (e.g., Fe, Co, Pt, Ag, Au, and Mn) as promoters. Herein, the authors focus on the use of Ni/Pt bimetallic systems in which the surface is known to vary as a function of temperature and adsorbates (Scheme 1). They first undertook the preparation of “pure” supported Ni/Pt bimetallic NPs possessing a controlled surface composition and structure. The evolution of the surface composition and structure of the obtained bimetallic catalysts under simulated reaction conditions was then investigated by various microscopic and spectroscopic techniques. The authors went on to demonstrate that upon thermal treatment the
structure of the bimetallic catalyst evolves from Pt monolayer island-modified Ni nanoparticles to core-shell bimetallic nanoparticles composed of a Ni-rich core and a Ni/Pt alloy shell (Scheme 2).

Dry reforming tests showed that the surface modification of the Ni-based catalysts by adding Pt atoms can effectively enhance the catalytic activities and resistance towards carbon formation and may facilitate the CH oxidation pathway and inhibit the carbon oxidation pathway (Scheme 3), leading to an enhanced catalytic activity and suppressed carbon formation as the Pt coverage increases. Source: Li L, Zhou L, Ould-Chikh S, et al. (2014). ChemCatChem online preview, DOI: 10.1002/cctc.201402965.

**Scheme 3. Proposed mechanism for the dry reforming of methane.**
Biological catalysts are not functional above 200 °C, and there are often kinetic and thermodynamic incentives to run processes at higher temperature. The question then becomes, can we build a catalyst with enzyme-like functionality which is stable at higher temperatures? One strategy is to employ amorphous silica-aluminates coupled with molecular self-assembly to build multifunctional structures with enzyme-like specificity.

In our research, we focus on developing fundamental descriptions of the support-catalyst interactions using careful synthesis, advanced characterization methods, and catalytic studies. Collaborating with groups at Penn State, University of Pennsylvania, and the Fritz Haber Institute in Berlin, Germany, we recently found that the activation energy for the partial oxidation of methanol to formaldehyde catalyzed by vanadia, supported on smooth versus rough-textured silica surfaces, differed by 25 kJ/mol. We attribute this to differences in hydroxyl density distribution that resulted in different degrees of strain in the surface vanadia species. We proposed that differences in strain of these species resulted in different adsorption energy for methanol and thus different apparent activation energies for this reaction. We continue to investigate similar interactions; for example, we are currently investigating the effect of support roughness on the relative Lewis and Brønsted acidity of silica-supported zirconia. While still relevant to our long-term objectives, these intermediate results should provide insight into the design of catalysts for improving biomass conversion.

Vanadia proved useful for demonstrating the effect of surface texture on catalyst performance. However, perhaps more significantly, a consensus has emerged that supported vanadia at sub-monolayer coverage adopts an equilibrium configuration with its support. A consequence of this is that the structure of vanadia on surfaces below monolayer coverage should be a sensitive probe of surface structure. Can the careful characterization of submonolayer vanadia provide a tool to interrogate the surface of amorphous oxides, much as N₂, CO, and pyridine are probes for surface area, metal dispersion, and Brønsted acidity respectively? Significantly, supported vanadia is composed of a variety of monomers, dimers, or oligomeric species, thus unlike these other probes, vanadia should reveal details of the support surface at length scales larger than the single site. Certainly elucidating the relationship between oligomeric vanadia species and the underlying support is not trivial; this will require computational chemistry to map out these relationships. Nevertheless, if the catalysis community is to develop enzyme-mimic catalysts, then we need to develop methods to interrogate surfaces at length scales larger than single molecules.

Looking farther ahead, control of surface roughness by manipulating silica synthesis provides a means of manipulating hydroxyl density distribution. We propose the chemistry found in the cooperative self-assembly of mesoporous silica (SBA-15 and related materials) provides a toolkit with which to manipulate hydroxyl densities and distributions. Since these hydroxyls are responsible for chemical interactions with catalytically active species, control of hydroxyl distribution provides a means of tuning catalytic activity. We propose that deliberate control of these surface groups would be a major milestone toward achieving our grander vision to create local arrangements of catalytic sites that mimic the structure and behavior of enzyme catalysis.