

THE CATALYST REVIEW

November 2010

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Independent Catalyst Test Report 2010

The industry's first open market catalyst testing program

Photo Credit: Mike Cohea, Brown University

Acquisition Activity Increases in Both the Catalyst and Chemical Industries...

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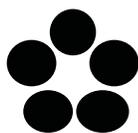
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The Catalyst Review is designed to provide readers with a global overview of events impacting the \$18 billion catalyst industry, through selected abstracts, company interviews, and original articles. There is also a special "Industry Rumors" column 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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INDUSTRY RUMORS

Acquisition Activity Increases in Both the Catalyst and Chemical Industries...

It has been interesting to observe the acquisition activities increase over the last six (6) weeks or so with two catalyst industry announcements Johnson Matthey's (JM) acquisition of Intercat for \$56MIL, plus \$29 MIL in debt from Reggis Lippert, which undoubtedly was motivated by the access to zeolite manufacturing capacity, as well as the strengthening of their refining catalyst portfolio. What most probably didn't notice was the increased demand for zeolite catalysts in the diesel automotive sector which was probably the strategic driver for the price. It is interesting also to note that increasing competition from PRC zeolite producers in the U.S. and European market over the last eighteen months, as they have more aggressively entered the market. Sinopec has been trying to enter the U.S. market via a distribution agreement with Hermes, but other sales representative agreements and efforts by Tricat are also notable.

Dupont's recent acquisition of MECS (Monsanto Environmental Catalyst Services) for an undisclosed amount via auction bid from American Securities LLC was also a case of interest because of the natural strategic fit with their sulfuric acid business and the growing portfolio within DuPont Sustainable Solutions, which includes STRATCO (sulfuric acid alkylation), BELCO Clean Air technologies, the Isotherming HPC process and DuPont Global Engineering Solutions (GES) which has been targeting and servicing the refining industry with Spent Acid regeneration (SAR) and Sulfur Gas recovery (SGR) technology to eliminate elemental sulfur Claus tail gas treatment. It is clear there is value added by producing and selling sulfuric acid (as opposed to sulfur) because of the large market sink (being the largest used chemical worldwide) by not flip-flopping on the elemental step.

We expect ongoing acquisitions with the aim to consolidate in the chemicals and the catalysts industries, as growing profits seek a home, at a time when margins and revenues are improving.



Clyde Payn, CEO
The Catalyst Group, Inc.

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Celanese Develops Advanced Technology for Production of Industrial-Use Ethanol...

Celanese Corporation announced its intention to construct manufacturing facilities in China and the U.S. to utilize recently-developed advanced technology for the production of ethanol for chemical applications and other industrial uses. Celanese's process technology builds on the company's industry-leading acetyl platform and integrates new technologies to produce ethanol using basic hydrocarbon feedstocks. Following necessary approvals, Celanese intends to construct one, and possibly two, industrial ethanol complexes in China to serve the fast-growing Asia region. Initial annual production capacity of each complex is expected to be approximately 400,000 tons. The company could begin industrial ethanol production within 30 months after project approvals. Current chemical application demand for ethanol in China is approximately 3 million tons annually and is expected to grow between 8% and 10% per year. Celanese's technology allows capacity to be more than doubled at significantly less than the original investment to meet future demand. The China units would utilize coal as the primary raw material. Source: Celanese, 11/9/2010.

Avener Key to Evonik's Future...

The global market for methyl methacrylate (MMA) is estimated to be growing at around 5-6%/year, and Germany's Evonik Industries intends to spearhead this growth. The company's Avener process will be used for the first time in a new 150,000-200,000 tonne/year production plant set to go on stream in 2014 at an undisclosed location. After three years of testing the upgraded C₁ process and catalysts in a pilot facility at Worms, Germany, Evonik is making final preparations for its worldscale unit. A location will be selected next year, and all production sites in Europe, North America and Asia, as well as a greenfield site close to customer industries, are under consideration, says Thomas Muller, head of the acrylic monomers business line. Investment costs for the facility will mostly depend on where it is built and what resources are available at the site. Facilitating the search for a suitable location is the fact that Avener can use starting materials available at all sites with "attractive C₁-based feedstock opportunities," says Steffen Krill, Evonik's director of process research and development. There are no plans to license the technology. The key to Avener's promise, Evonik says, is a new type of heterogenous inorganic catalyst developed in-house that is claimed to have a life cycle of about two years. Like the sulfo process, Avener is based on ammonia, methane, acetone and methanol. The significant difference is that it does not produce sulfuric acid as a by-product. This, Evonik says, will allow production costs to be substantially slashed and flexibility to be increased. Source: ICIS Chemical Business, 10/25-31/2010, p. 32.

DuPont to Acquire MECS...

DuPont has signed a definitive agreement to acquire MECS, Inc., from affiliates of American Securities LLC. Terms of the agreement were not disclosed. According to James R. Weigand, president, DuPont Sustainable Solutions. "MECS' technologies and services will expand and strengthen DuPont Sustainable Solutions business' clean air and clean fuel offerings and provide access to markets beyond those we now serve. We estimate that this acquisition will increase the addressable market for our clean air and clean fuel offerings from approximately \$200 million to \$1 billion." MECS is a global provider of process technology, proprietary specialty equipment, and technical services to the sulfuric acid industry. A large share of the world's sulfuric acid producers use MECS technology to capture sulfur that would otherwise become a pollutant and transform it into sulfuric acid, the most widely used chemical in the world and a vital part of virtually every industry. Source: DuPont, 11/10/2010.

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SPOTLIGHT: New Catalyst Development...**Emissions Technology, Inc. Develops New UltraBurn™ Combustion Catalyst System for Large Diesel Engines...**

Emissions Technology, Inc. (ETI), the maker of the patented UltraBurn™ Combustion Catalyst System, announced their new "Direct Injection" Series catalyst delivery system to serve diesel engines up to 30,000 horsepower. The UltraBurn product line reduces engine fuel consumption and lowers emissions. "The new DI system further expands the usefulness of the UltraBurn catalyst into performance enhancement when used with biodiesel or heavy fuel oil," said Mark Spoon, CEO of Emissions Technology. "It employs a novel injection technology coupled with new catalyst formulations and was extensively tested at CEE labs in California earlier this year," Spoon added. Patents are pending on the new delivery system. Source: Emissions Technology, Inc., 11/9/2010.

Topsoe Launches New Sulfuric Acid Catalyst...

Topsoe has developed a new sulphuric acid catalyst for operation in converted strong gases. The catalyst, designated VK-701 LEAP5™, has shown significant activity advantages compared to existing potassium and cesium-promoted catalysts. The high activity offered by VK-701 LEAP5™ presents new conversion opportunities for any single- and double-absorption plants. The catalyst has been developed in-house by Topsoe's researchers, and the new VK-701 LEAP5™ exhibits a major leap in activity based on physical and chemical changes enhancing the amount of the active vanadium in oxidation state V⁵⁺. Source: Haldor Topsoe, 11/2/2010.

BASF Adds Molecular Sieve Products to its Adsorbents Solution Portfolio...

BASF's Catalyst division has entered into an original equipment manufacturing (OEM) agreement with Chemiewerk Bad Köstritz GmbH (CWK), Germany, to market molecular sieve products targeted at the natural gas, refining, petrochemical and air drying markets. BASF will manage the business through its Adsorbents group, which is part of the Process Catalysts and Technologies business. The molecular sieves associated with this agreement are complementary to BASF's existing adsorbent product portfolio, which includes proprietary aluminas; specialty alumino-silica gels, such as Sorbead® and KC-Trockenperlen®; petrochemical purification products, such as Selexsorb® and PuriStar®; and bentonites, such as F-24 and NovaSil™. As part of this OEM arrangement, BASF will assume full responsibility for sales, distribution and technical support of the molecular sieve products. Source: BASF, 11/8/2010.

Mitsui and Sinopec to Form Joint Venture for EPT Project in China...

Mitsui Chemicals says it will establish a 50-50 joint venture with Sinopec, tentatively dubbed Shanghai Sinopec Mitsui Elastomers, for an ethylene-propylene-diene terpolymer (EPT) plant to be located at the Shanghai Chemical Industry Park in Shanghai, China. The two companies had signed a letter of intent in December 2009 to conduct a study for the EPT JV project. The JV will be established in the second half of 2011 and the EPT plant will have a capacity of 75,000 m.t./year. The plant will begin commercial operation in the first quarter of 2014. The project will involve a total investment of about ¥27 billion (\$333 million). This new plant will adopt metallocene catalyst technology. Source: Chemical Week online, 10/28/2010.

Albemarle Announces Completion of R&D Facility in South Korea...

Albemarle announced it has completed the R&D laboratory facilities and begun construction on its Yeosu, South Korea manufacturing facility. The completion of the Yeosu site R&D lab facility enables the production of metallocene polyolefin catalyst lab samples incorporating Albemarle's ActivCat™ technology for qualification trials with local customers. Pilot plant facilities will be completed in 2010. Intermediate commercial operations will begin in mid-2011, with the commercial facility being fully operational in 2012. The site will produce finished catalysts, activators like methylaluminoxane (MAO) and metallocene components, as well as High Purity Metal Organics for the HBLED market. Source: Albemarle, 10/20/2010.

Picosun Develops ALD-enhanced Processes for Chemical and Pharmaceutical Industries...

Picosun Oy, (Finland) will take part in Polycat, a major 2010 -2014 EU funded research project, aiming at reducing the environmental footprint of chemical and pharmaceutical industries by studying methods towards creating zero-waste processes. The European Union has allocated seven million euros from its 7th European Research Programme for the ten million euro budget of Polycat. Picosun's industrial partners in Polycat include Thales Nanotechnology from Hungary, Ehrfeld Mikrotechnik, Bayer Technology Services and Evonik Degussa, all three from Germany, Sanofi-Aventis from France, and a Ukraine/Russia based joint venture by German Süd-Chemie and Estonian Alviso. Polycat's scientific partners include universities and research institutions from Finland, France, Germany, Greece, Italy, the Netherlands, Russia, Switzerland, and the United Kingdom. Polycat is coordinated by the Institut für Mikrotechnik Mainz, in Mainz, Germany. Picosun's speciality as part of Polycat is in the process development for catalyst preparation and, towards 2014, also in process optimization and scale-up for industrial scale use. It aims at improving the competitiveness and sustainability of the European chemical industry through two key innovations. The first innovation is a new class of polymer-supported nanoparticle catalysts with their embedment in innovative microstructured flow chemistry reactors. The second innovation is a modular, least-investment-cost plant in container format (so-called 'Factory of the Future'). The development of highly efficient heterogeneously catalyzed fine chemical processes possess several process advantages, most notably reducing the use of solvents and eliminating reaction steps. Polycat also aims at improving the yield of processes, reducing the product costs by at least 10 % and cutting piloting times by almost a third. An important goal is to reduce process waste by 40 % through elimination of metal leaching into the products. Source: Picosun, 11/10/2010.

Sinopec to Purchase 40% Stake in Repsol Brazil...

Sinopec International Petroleum Exploration and Production Corporation (SIPC), a subsidiary of China Petrochemical Corporation (Sinopec Group) has signed a definitive agreement with Repsol Brazil S.A., under which SIPC will purchase new shares comprising 40% of the share capital of Repsol Brazil (on a fully diluted basis) for an aggregate base consideration of US\$7 billion, resulting in a company valued at approximately US\$18 billion. The transaction is subject to certain governmental approvals but is not conditional on financing. "With the acquisition, Sinopec Group will strengthen its presence in South America and optimize its offshore oil and gas asset portfolio, which is in line with the international growth strategy," Sinopec Group said. Source: China Chemical Reporter, 10/21/2010, p. 4.

CB&I in Deal to License BP's PX Technology...

US engineering firm CB&I has won an agreement to license paraxylene (PX) technology from UK producer BP. Under the deal, CB&I's Lummus business unit has the exclusive right to license and market BP's PX recovery and isomerization technology and catalysts. The agreement marked CB&I's entry in the polyester chain and would strengthen its technology portfolio in aromatics. Source: ICIS Chemical Business, 10/18-24/2010, p. 15.

Shell Explores Refinery Streams...

UK-based Shell Chemicals wants to capitalize on what it calls "advantaged" feeds from the refinery, both liquids and gases. Shell is likely to stick with its "cracker plus one" business model, which means it generally only ventures as far as first-line ethylene derivatives. "If you want to be in upgrading hydrocarbons, adding a petrochemicals part to it does make lot of strategic sense," said Ben van Beurden, Executive Vice President for Chemicals, London. Continued stress and strain on the refining system is pointing up chemical opportunities. "If you play the game very well, the whole envelope becomes more robust," he said of Shell's oil and gas-to-chemicals business strategy. Chemicals at Shell can capitalize on low-value and other refinery streams and add value to the whole, he suggested. Shell has almost completed getting its portfolio in the right place, he said. The refinery divestment and closure program affects chemicals in a minor way - the loss of some capacities in Europe, when divestments are completed, will not have a major impact on the overall picture. Shell's strategy in petrochemicals is to become the "highest-profit hydrocarbon upgrader," said van Beurden. "We have discovered a whole seam of feedstock advantage." Tapping into those seams takes time. Shell has reconfigured its crackers at Deer Park and Norco on the US Gulf Coast to crack more gas, lower quantities of liquids and more "advantaged" feeds. It is closing a cracker in Germany and looking at upgrading another to take a modified feedstock slate. Its cracker at Moerdijk, the Netherlands, has been given the capability to crack hydrowax, a heavy-refinery product that is difficult to transport. The shift towards advantaged feeds at the cracker could be significant by the middle of the decade. Source: ICIS Chemical Business, 10/11-17/2010, p. 13.

A Modular SMR Unit Provides Onsite Hydrogen Production...

Standardized steam-methane-reforming (SMR) reactor units recently commercialized by Air Liquide allow direct hydrogen production at customer sites at costs much lower than those associated with alternative H₂ supply modes, including electrolysis and transporting compressed or liquefied H₂. Air Liquide says that onsite hydrogen-generation technologies previously available had not generally met the H₂ needs for typical photovoltaic (PV) cell producers. The compact HYOS-R-10k modular hydrogen-production unit is constructed on a unique skid that contains all system components. To generate hydrogen, natural gas is mixed with steam and fed into high-alloy reformer catalyst tubes, where synthesis gas is produced. This process stream enters a shift converter, where additional H₂ is produced via a water-gas shift (WGS) reaction and CO is converted to CO₂. The gas stream is then cooled and fed into a pressure-swing adsorption (PSA) purification system, where carbon dioxide and water are removed, leaving H₂ gas with less than 10 ppm impurities (that is, an H₂ purity of 99.999%). The standardized skidded HYOS-R-10k allows lower capital and installation costs, and the unit's efficiency and flexibility can mean reduced operating expenses. The system is capable of generating 268 m³/h of H₂ gas per unit at standard temperature and pressure. The modular nature of the technology allows installation of several units to match requirements for H₂ generation. Source: Chemical Engineering, 10/2010, p.

Shaw Licenses FCC Propylene Technology...

The Shaw Group has licensed two refining technologies from Sinopec designed to help refiners meet environmental regulations for cleaner gasoline as well as increase propylene production. The two technologies reduce olefins, sulfur and benzene from gasoline and also increase the yields of premium components, including iso-paraffins and propylene. The technologies are designed for installation in either existing or grassroots fluid catalytic cracking (FCC) units, Shaw says. FCC operators will have the flexibility to switch the unit's operating mode based on market demand for increased gasoline production or increased propylene production. Source: Chemical Week, 10/11/2010, p. 37.

Avantium Builds YXY Pilot Plant for Green Materials and Fuels...

Avantium announced that it has started with the construction of a pilot plant at the Chemelot site (Geleen, the Netherlands). The pilot plant will produce YXY building blocks for making green materials and fuels. Avantium has developed a novel and proprietary catalytic process to convert carbohydrates into furanic building blocks under the brand name YXY. The pilot plant is expected to become operational in the first quarter of 2011. The pilot plant marks a major milestone in the commercialization of a new generation of renewable materials and fuels. The pilot plant will demonstrate the breakthrough process developed in Avantium's labs at larger scale. Furthermore, it will produce several tons of YXY building blocks per year to support product development. Avantium is collaborating with industrial partners such as NatureWorks (a subsidiary of Cargill) and Teijin Aramid to develop novel materials on basis of its YXY building blocks. The company expects to use YXY building blocks for the production of green and recyclable materials such as water and soft drink bottles, carpets, textiles, high-performance fibers, coatings and plasticizers. The pilot plant is partly funded by a EUR 1 million grant from the Dutch Ministry of Agriculture. The Ministry had a total budget of EUR 10 million for projects to realize pilot plants for the production of sustainable bio-based products and energy for the European market. To run the pilot plant and to further accelerate the commercialization of YXY, Avantium is raising additional private funding. Source: Avantium, 10/14/2010.

Siluria Technologies Secures Funding to Advance First Direct, Economic Process for Converting Natural Gas to Chemicals...

Siluria Technologies announced the close of its Series A round of funding. The investment allows the company to optimize its natural-gas-to-materials platform to meet the performance levels required for commercialization. Its technology to create materials from natural gas will first target the \$160 billion annual market for ethylene. Siluria's investors include Alloy Ventures, ARCH Venture Partners, Kleiner Perkins Caufield & Byers, Altitude Life Science Ventures, Lux Capital, and a strategic investment from Presidio Ventures, the venture arm of global trading and operating firm Sumitomo Corporation. The total raised in the round comes to \$13.3 million. In place of resource-intensive processes based on petroleum, the Siluria platform offers a more cost-effective process that is directly compatible with the same industrial chemical manufacturing equipment used today. This breakthrough is made possible by Siluria's novel synthetic technology, which produces inorganic materials in the same way nature makes them: by growing metals and metal oxide crystals on a biological template. The technology offers unique ways to manipulate catalyst surfaces, thus improving catalyst performance in structure-sensitive reactions, such as selective oxidations of light alkanes to olefins and oxygenates. This enables Siluria to optimize a chemical manufacturing process which many have tried to crack: methane activation. Source: Siluria Technologies, 10/19/2010.

Bayer MaterialScience to Employ Uhde's EnviNOx Process...

BMS's conversion of a large chemical plant in Dormagen includes the installation of Uhde's EnviNOx process for use in the manufacture of nitric acid. The process uses catalysis to convert nitrous oxide into nitrogen and water. Conversion work on the Dormagen plant operated by chemical company INEOS was carried out at a cost of EUR 6.5 million and is expected to reduce nitrous oxide emissions by 98 to 99%. That means preventing a further 220,000 metric tons of CO₂ equivalents per year. The EnviNOx reactor replaces a conventional catalyst, which already converted a significant proportion of the nitrous oxide. Source: India Info online, 11/10/2010; TCGR.

MIT's Solar Power Thermo-Chemical Breakthrough...

Researchers at the Massachusetts Institute of Technology (MIT) have perfected a way to control the capture and release of solar energy through thermo-chemical technology. The essential element needed to allow the thermo-chemical technology to both absorb sunlight and release it, ruthenium, was too rare to ever be cost effective. The MIT research team say they have uncovered exactly how the essential molecule responsible for absorbing, storing, and releasing solar energy works. This understanding, they said, should make it possible to find similar chemicals based on more abundant, less expensive materials than ruthenium. According to Jeffrey Grossman, Associate Professor of Power Engineering in the Department of Materials Science and Engineering, when the molecule - fulvalene diruthenium - absorbs solar energy, it goes into a higher-energy state where it can remain stable indefinitely. Then, triggered by a small addition of heat or a catalyst, it snaps back to its original shape, releasing heat in the process. Source: Energy Matters Online, 11/1/2010.

Sinopec ZRCC Plant Begins Operations with METEOR™ EO/EG Process...

Sinopec Zhenhai Refining & Petrochemical Co. Ltd. (ZRCC) has launched a new ethylene oxide/ethylene glycol (EO/EG) plant in China utilizing the METEOR™ EO/EG process. Licensed through The Dow Chemical Company, the METEOR process integrates process simplicity, inherent safety and superior catalyst technology into a single reactor design. The ZRCC Plant, which first started up in April 2010, is the second plant in China to utilize the METEOR process. The first, operated by Sinopec-SABIC (Tianjin) Petrochemical Co. (SSTPC), began production in February 2010. Together, these METEOR plants attain significant reductions in feedstock consumption and greenhouse gas emissions when compared to industry averages. Based on 2010 figures to date, these METEOR plants are anticipated to curb feedstock consumption and greenhouse gas emissions over the course of a calendar year as follows: 1) Ethylene feedstock reduced approximately 50,000 metric tons per year; 2) Oxygen feedstock reduced approximately 165,000 metric tons per year; and 3) Carbon dioxide (CO₂) emissions reduced approximately 150,000 metric tons per year. The ZRCC plant located in Ningbo, in China's Zhejiang province, is the first METEOR™ dual-reactor plant ever built and has a capacity of 650 kta of ethylene glycol (EG) and 100 kta of pure ethylene oxide (EO). Source: Sinopec Zhenhai Refining & Petrochemical Co. Ltd., 11/3/2010.

Incorporating Chromophores Into a Polymerization Catalyst...

By incorporating a chromophore into an aluminum polymerization catalyst, chemists can now prepare colored polymers in just one step. The so-called DyeCat process places the dye directly into the backbone of poly(lactic acid), or PLA, thereby circumventing current coloration techniques in which polymers must be scoured, dyed, and then treated for colorfastness. "Hence the consumption of energy, water, chemicals, and time, as well as effluent production, are all avoided," writes the research team from the University of Leeds, in England, led by Patrick C. McGowan. The dye molecule can be incorporated in three different ways: It can be appended to the ligand framework that stabilizes the aluminum center, designed to act as the aluminum-stabilizing ligand, or used to initiate polymerization. With the latter method, the researchers prepared yellow, red, and purple PLA. Mixing the yellow and purple polymers, McGowan's group made black PLA filaments, a color that is popular in textiles but tough to prepare because it requires high dye loading and tends to leach. Source: Chemical & Engineering News, 11/8/2010, p. 48.

Easily Recycled Coupling Catalysts...

Matthias Beller and colleagues at the Leibniz Institute for Catalysis at the University of Rostock, in Germany, have developed recyclable imidazolium phosphanes that work well in palladium-catalyzed C–O, C–N, and C–C bond-forming reactions. The sterically hindered ligands are insoluble in 1,4-dioxane at room temperature, but their cationic nature drives the formation of a soluble complex at 100 °C. In the case of palladium-catalyzed hydroxylation, Beller's group found that this solubility helps the complex remain in solution, ready to be reused, once the phenolate reaction products are removed via precipitation. In the case of Sonogashira coupling, where the product was soluble in 1,4-dioxane, the ligand precipitated out in the reaction flask by simply cooling it down. Beller notes that the ligands are stable to air and moisture and can be recycled several times without significant loss of reactivity. Source: Chemical & Engineering News, 10/25/2010, p. 44.

Monolayer of Platinum Atoms on a Tungsten Carbide Support Catalyzes the Electrolytic Production of H₂ Effectively and Cheaply...

Jingguang G. Chen and a team at the University of Delaware have introduced a new method for reducing the use of platinum in electrolysis catalysts without losing efficiency: the layering of an atomic layer, or monolayer (ML), of platinum on low-cost tungsten monocarbide (WC) substrates. Chen said that his team's aim was to deposit a single layer of platinum atoms onto an inexpensive planar support so that all the platinum atoms can participate in the reaction. If a monolayer of metal atoms is deposited onto a support, the atoms interact with the substrate. The electronic structure of the atoms can change because the distances between the individual atoms in the layer can be different from those in the pure metal. In addition, bonding between the platinum and atoms of the support can lead to undesired effects. This can greatly disrupt the catalytic properties. Chen and his team selected tungsten carbide as a carrier. They deposited thin films of tungsten carbide onto a tungsten substrate and added platinum atoms by vapor deposition. The chemical and electronic properties of these atomic platinum monolayers on tungsten carbide did not differ significantly from those of a block of pure platinum. The catalytic efficiency of the supported platinum monolayer is also correspondingly strong. These ML Pt-WC catalysts represent a significant decrease in platinum loading and associated platinum cost compared to that currently used in many electrolysis applications. Source: Green Car Congress online, 10/17/2010.

Georgia Tech Develops System for Recycling Precious Metal Catalysts...

Researchers at the Georgia Institute of Technology (Georgia Tech; Atlanta), say they have developed a novel organic solvent system that significantly enhances the recyclability of precious metal catalysts including gold, palladium, platinum, and silver. The novel approach uses a combination of two chemicals; thionyl chloride; and a variety of organic reagents such as pyridine, N,N-dimethylformamide (DMF), pyrimidine or imidazole. A paper outlining the research was published recently in the journal *Angewandte Chemie*. Concentrations of the chemicals can be adjusted to preferentially dissolve gold or palladium. The solvents do not dissolve platinum. This ability to preferentially dissolve noble metals creates a customized system that provides a high level of control over the process, Georgia Tech says. In contrast to the system developed by Wong and his colleagues, standard recycling processes use a combination of nitric and hydrochloric acids, known collectively as 'aqua regia,' to dissolve noble – or precious – metals. However, as the metals are often dissolved together, impurities may be introduced into the recycling process. These impurities may harm the efficiency of catalysts produced from the recycled materials. The system developed by Wong and his colleagues could be particularly useful given that industrial catalyst systems increasingly use more than one metal, such as palladium with a gold core. In this specific case, the Georgia Tech solvent system – dubbed 'organic aqua regia' – could first use a combination of thionyl chloride and DMF to dissolve out the gold, leaving hollow palladium spheres. The palladium spheres then could be dissolved using a different combination of the solvents, the researchers say. To date, the researchers have demonstrated that the solvent system can selectively dissolve gold and palladium from a mixture of gold, palladium and platinum. They have also used it to remove gold from a mixture of gold and palladium. Details about the commercialization of the technology have not been disclosed. The new highly efficient recycling system could open up new possibilities for using precious metals in cancer therapeutics, microelectronics and other applications, Georgia Tech adds. Source: Chemical Week online, 11/1/2010.

Chemists Improve Synthesis of Biodiesel...

Two chemists from Brown University have developed a more efficient way to produce biodiesel from waste vegetable oil. Using two catalysts common in organic chemistry, Assistant Professor of Chemistry Jason Sello and Postdoctoral Fellow Aaron Socha were able to synthesize biodiesel in a single reaction vessel. Traditional methods of synthesizing biodiesel from waste oil require two reaction vessels. The method is six times faster than current methods, consumes less energy overall and is more environmentally friendly, according to the release. In developing the new procedure, the chemists considered catalysts that could complete the reaction in a single vessel and that were readily available, low in cost, low in toxicity and stable in the presence of water and air that might be in the waste oil after cooking. They opted to use bismuth triflate and scandium triflate, in part because bismuth was relatively cheap and their lab had experience with scandium. When the catalysts did not yield biodiesel under standard conditions, Socha suggested using a microwave reactor. The combination of the two catalysts and the microwave reactor successfully yielded biodiesel at 150 °C. The catalysts in the free fatty acid reaction can be recycled up to five times while still obtaining a 97% yield. Source: Brown Daily Herald online, 10/21/2010.

Coal to Chemicals Gains in China...

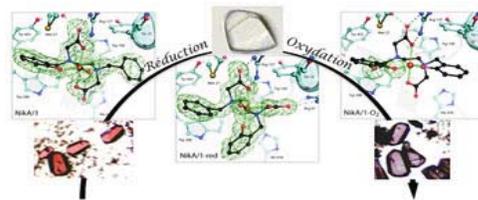
All indications are pointing to a booming coal-to-chemicals industry in China. Domestic shortages and the rising price of crude oil have rendered coal a favorite alternative. From the perspective of cost, coal to chemicals enjoys an obvious advantage as oil is four times as expensive as coal. Developing coal to chemicals is an inevitable choice in China, a nation characterized by the real nature of "insufficient oil, little gas and ample coal". CTO projects enjoy considerable economical efficiency when international oil prices stand above \$80/bbl. China uses coal or natural gas as a feedstock to produce methanol. Methanol units that consume coal as the raw material occupied 66.6% in the total output in 2009. In the petrochemical stimulus plan that was announced at the end of February 2009, the section on coal to chemicals mandated "controlling the total volume, phasing out laggard capacities, stopping approvals on coking and carbide expansions, and firmly containing pell-mell [unplanned] developments." In the middle of 2010, the National Development and Reform Commission issued the Notice on Rationalised Development of Coal-to-Natural Gas Sector. The country now strictly limits the development of coal-to-chemicals in the consuming regions that are short of resources but encourages such development in the producing, resource-rich regions in western China. The twelfth Five-Year Plan (2011-2015) stresses that mergers and restructuring in the coal industry is an important mandate, aiming to reduce the number of coal enterprises to 4,000 from the existing 11,000. At the end of the forthcoming five-year period, there will remain only six to eight coal groups in China, further concentrating coal resources. The coal-to-chemicals industry must be in control of the scale, resources and environmental capacity while complying with ecological requirements, as well as the status of water and coal resources. Source: ICIS Chemical Business, 11/8-14/2010, p. 33.

Exploring the Catalytic Deoxygenation of Bio Liquids to Form Liquid Hydrocarbons...

Researchers from Tuskegee University, the Air Force Research Laboratory, Applied Research Associates and Florida State University report on efforts to develop an efficient method of removing oxygen from liquid biomass to produce petroleum-comparative liquid hydrocarbons using hydrogen and a NiMo/ γ -Al₂O₃ catalyst. The researchers report on their efforts in terms of various oxygen removal conditions such as reaction temperature and pressure, catalyst amount, and hydrodynamics of heterogeneous reaction mixture in the batch reactor. Methyl laurate was converted mainly to undecane and dodecane in the presence of hydrogen and the catalyst. Lauric acid is formed as a major intermediate product. Formation of the two primary hydrocarbon products and CH₄ increased with increased catalyst amount, increased H₂ pressure, and increased reaction temperature over the range of 300-350°C. Formation decreased with higher temperatures. Formation of heptadecane, octadecane, and heptadecanic acid increased with catalyst amount, reaction temperature, and H₂ pressure. Elevated hydrogen pressures and prolonged reaction durations were required in the presence of a catalyst to increase conversion of canola oil to hydrocarbons such as heptadecane and octadecane. Source: Green Car Congress online, 10/27/2010.

Artificial Metalloenzymes, the Chemical Synthesis of the Future...

Researchers at Commissariat à l'Energie Atomique et aux Energies Nouvelles (CEA), Joseph Fourier University and Centre National de la Recherche Scientifique (CNRS) have developed a new approach combining protein crystallography and biomimetic chemistry for observing oxygen activation. This was achieved by creating a complex artificial metalloenzyme composed of a chemical catalyst and a protein and observing it via X-ray crystallography at the European Synchrotron Radiation Facility (ESRF). The results obtained constitute an essential step towards the development of artificial metalloenzymes capable of producing various molecules of industrial interest more efficiently and at a lesser cost. In order to study this reaction, the researchers have mimicked it by introducing an aromatic cycle in an iron complex and then incorporating this complex into a protein whose sole function is nickel transport in *Escherichia coli* bacteria. This protein therefore does not disturb the chemical oxygen activation reaction. The researchers have then crystallized this artificial metalloenzyme and directly observed the evolution of the reaction within the crystal via X-ray crystallography. "The crystal enables the diffusion of the reaction substrates and intermediaries. The enzyme remains active in the crystal, and the various steps of the reaction can be observed directly therein", explains Christine Cavazza, CEA researcher at the Protein Crystallography and Crystallography Laboratory of the Institute of Structural Biology (IBS). "We can thus observe the incorporation of oxygen atoms into an aromatic core". Source: Physorg online, 10/21/2010.



Example of chemical kinetics observed within a crystal. Left: Iron complex in a protein crystal. Centre: Conformational modification of the complex after iron reduction. Right: Incorporation of oxygen into the complex after molecular oxygen activation. Credit: CEA

Special Feature

Independent Catalyst Test Report 2010



The industry's first open market catalyst testing program

Open-market catalyst testing

If you have shopped for a new car recently, you have probably looked at consumer buying guides for comparative data to help with your decision. When it comes to making an important purchase like this, you want hard data to compare your options. For most high-budget consumer products, you can go on the internet and find data and ratings from independent labs that do side-by-side testing of competitive brands. This is also true for thousands of industrial products like electronic components, medical equipment, and building products.

It is not true for refining catalysts. Refinery engineers often spend months sorting through plant data, vendor data, glossy brochures, and hearsay, trying to assess product claims and make a fair assessment of competitive catalysts. Usually, the best they can do is an apples-to-oranges comparison. Hard data from side-by-side testing is generally not available.

In 2009, as part of starting up a new business, we approached fifteen independent refiners and six catalyst suppliers with a proposal to run a shared-cost independent test program on diesel hydroprocessing catalysts. We asked them to provide samples of catalysts to be tested side-by-side at an independent lab using a standard 12-day activity test. Our goal was to develop a database of comparative test results that would be readily available and affordable to any independent refiner.

Our request drew a wide range of responses from catalyst suppliers and refiners; this article tells the story of our first year developing this new product.

The evolution of catalyst testing



The refining industry is fortunate to have many capable catalyst suppliers who serve as partners in meeting the demands of today's refineries. They continue to develop improved products, enabling clean fuels to be produced at much lower cost than would otherwise be possible.

Fifty years ago, catalyst technology was a cornerstone of refining research. Catalysts were developed within the walls of the major oil companies' R&D departments. Amoco, Chevron, Exxon, Mobil, Shell, and others had large proprietary catalyst development programs that were internally funded with tens of millions of dollars per year. New catalysts were screened mostly in small test rigs, and commercial products were tested in large pilot plants.

As the industry matured, catalyst technology became a business in itself. The work of catalyst testing gradually shifted to smaller catalyst companies who emerged as important technology suppliers to the refining industry. Eventually, most major oil companies shut down their large pilot plants to save costs, and some quit testing catalysts altogether.

Today, most catalyst testing is done by the catalyst suppliers who compete in the \$4 billion per year refining catalyst market. These suppliers are high-tech companies with extensive testing capabilities. The cost of product testing is borne by the suppliers as an internal cost that is passed on in the price of catalyst.

Refiners remain very interested in catalyst technology - but their main focus is on catalyst selection. They want to find the best catalysts, choose the right product for the service, and buy it at a good price. Catalyst is a very high leverage product in terms of value added for the cost. A small improvement in catalyst performance can easily contribute \$20 million per year bottom line improvement, for just one unit. Catalyst is also an important cost item, attracting the attention of procurement managers. A large independent refiner with dozens of hydroprocessing units can easily spend over \$100 million/year on catalyst; hence there is a big payoff for leveraging competition.

With no practical option for independent testing of competitive products, most refiners are forced to rely on their catalyst suppliers for test data. Catalyst selection then becomes a difficult task – when considering different suppliers' products, engineers must sort through dozens of available product options amidst a confusing array of conflicting vendor data and product claims, with no common frame of reference.

The work of catalyst testing

What is involved in the work of catalyst testing? It requires a bank of test rigs, infrastructure for hydrogen supply, feed supply, product handling, storage, and disposal. You need access to a modern analytical testing laboratory. You need an operations staff, an analytical services staff, and a variety of technical support services – mechanical, electrical, instrumentation, process control, and information technology. You must always operate these systems safely, with highest precision, on a wide variety of feeds. It is, at minimum, a several million dollar per year operation.

Catalyst testing becomes a business - CPERI Solutions

Independent catalyst testing became a standalone business when CPERI Solutions was formed in 2005. CPERI Solutions is an independent lab with operations at the Chemical Process Engineering Research Institute (CPERI), in Thessaloniki, Greece. CPERI Solutions is a successful for-profit business, having done testing for thirty different companies on five continents and showing profits every year.

CPERI Solutions' customers include refiners and catalyst suppliers. Some customers have long-term contracts providing several months per year of pilot plant time. They schedule blocks of time each year to run their projects, up to their contracted limit. Spot customers buy one pilot plant run at a time – this is usually a site-specific test involving selection of catalyst for a particular commercial unit. Whether done on a contract or spot basis, a customer can test catalysts at CPERI Solutions for a small fraction of what it cost to maintain internal testing capability.



There are no industry standards for testing hydroprocessing catalysts. The experimental tools and work methods are similar throughout the industry, but each refiner and supplier has his own preferences on test protocols, and each holds the data closely as proprietary information. The technical culture of the catalyst industry is still highly secretive. In this sense, even while the business has undergone huge structural change, there has been little change in the culture of product testing.

Standardized, open-market catalyst testing

In 2009, Hoekstra Trading LLC contracted with CPERI Solutions to run side-by-side independent tests on a set of diesel hydrotreating catalysts we collected from refiners and catalyst suppliers. Our goal was to lay the groundwork for standardized, open-market catalyst testing. With standardized testing, instead of doing custom pilot plant tests for particular hydroprocessing units, a single pilot plant protocol is used to evaluate a large number of catalysts for a whole category of units, in this case, high pressure diesel hydrotreaters. Open-market testing means that the test results are available to anyone willing to pay a share of the cost. This approach is fast, easy, and inexpensive for our clients; and compared to relying on vendor data, it is very effective in positioning them for informed catalyst selection.

Testing diesel catalysts with the “10-20 test”

Our standardized pilot plant test is called the “10-20 test” – the name indicates a target product specification of 10 ppm sulfur on a feed containing 20% light cycle oil (LCO). It is a twelve day test consisting of four run conditions, three days per condition. Two standard test feeds are used, a light gas oil (0% LCO) and a blend containing 20% light cycle oil. Pressure, gas-to-oil rate, and space velocity are held constant through the test. Temperature is varied at three levels as shown in Table 1.

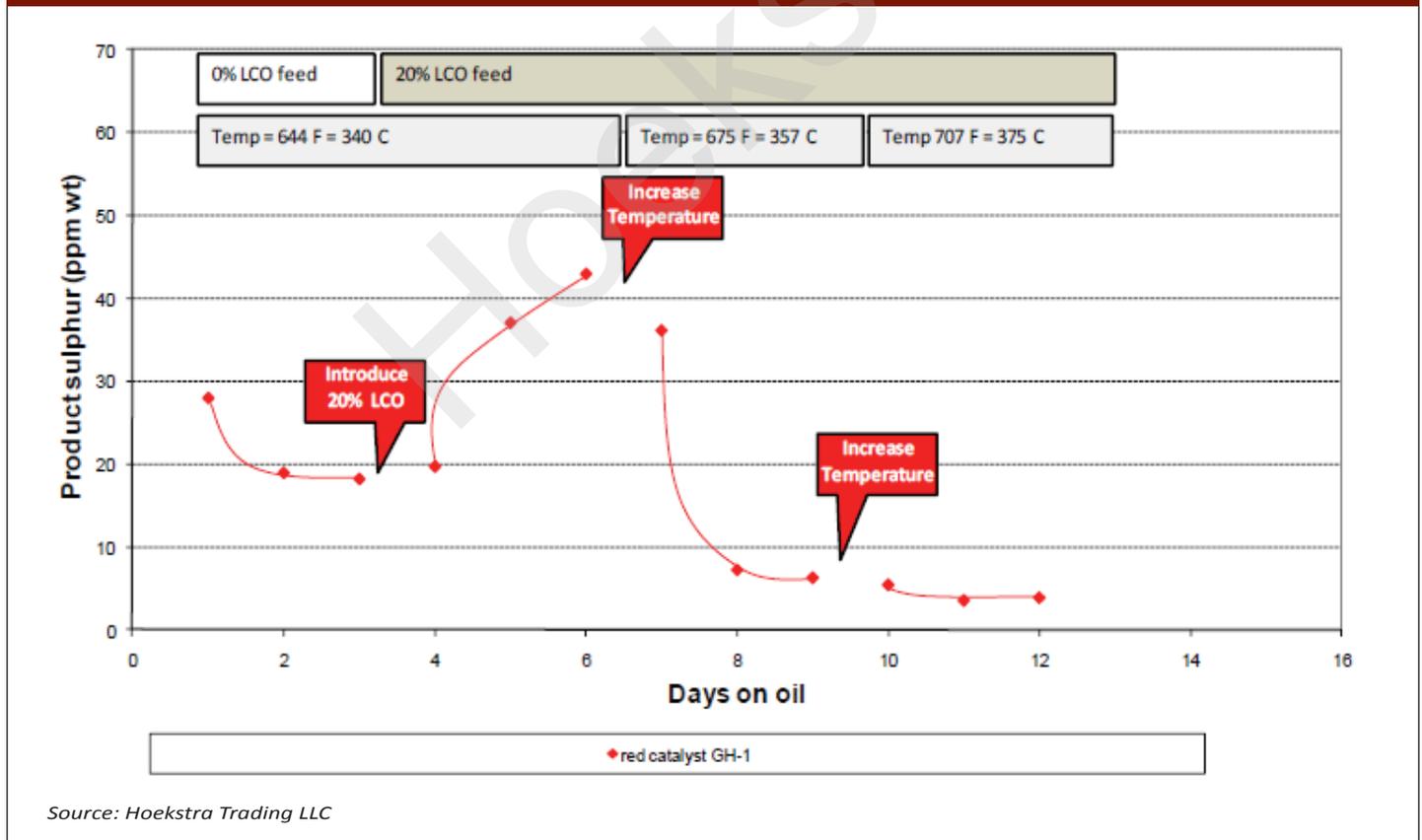
Figure 1 shows test results on a sample of a typical high-performing catalyst we have used as a benchmark for this test. The product sulfur is charted for each day of the 12-day test. During the first 3 days, the product sulfur stabilizes at 19 ppm product sulfur on the light gas oil (0% LCO) feed. On day 4, the 20% LCO feed is introduced at constant temperature and the catalyst responds to the more difficult feed, with product sulfur increasing to 43 ppm by day 6. On day 7, the reactor temperature is increased to 675°F (357°C), and the catalyst responds with product sulfur decreasing to 6 ppm by day 9. On day 10, temperature is increased to 707°F (375°C), and product sulfur comes down to 4 ppm.

Table 1: “10-20 test” protocol.

Condition	Feed	Temperature		Days
		(°C)	(°F)	
1	Light gas oil	340	644	3
2	20% light cycle oil	340	644	3
3		357	675	3
4		375	707	3

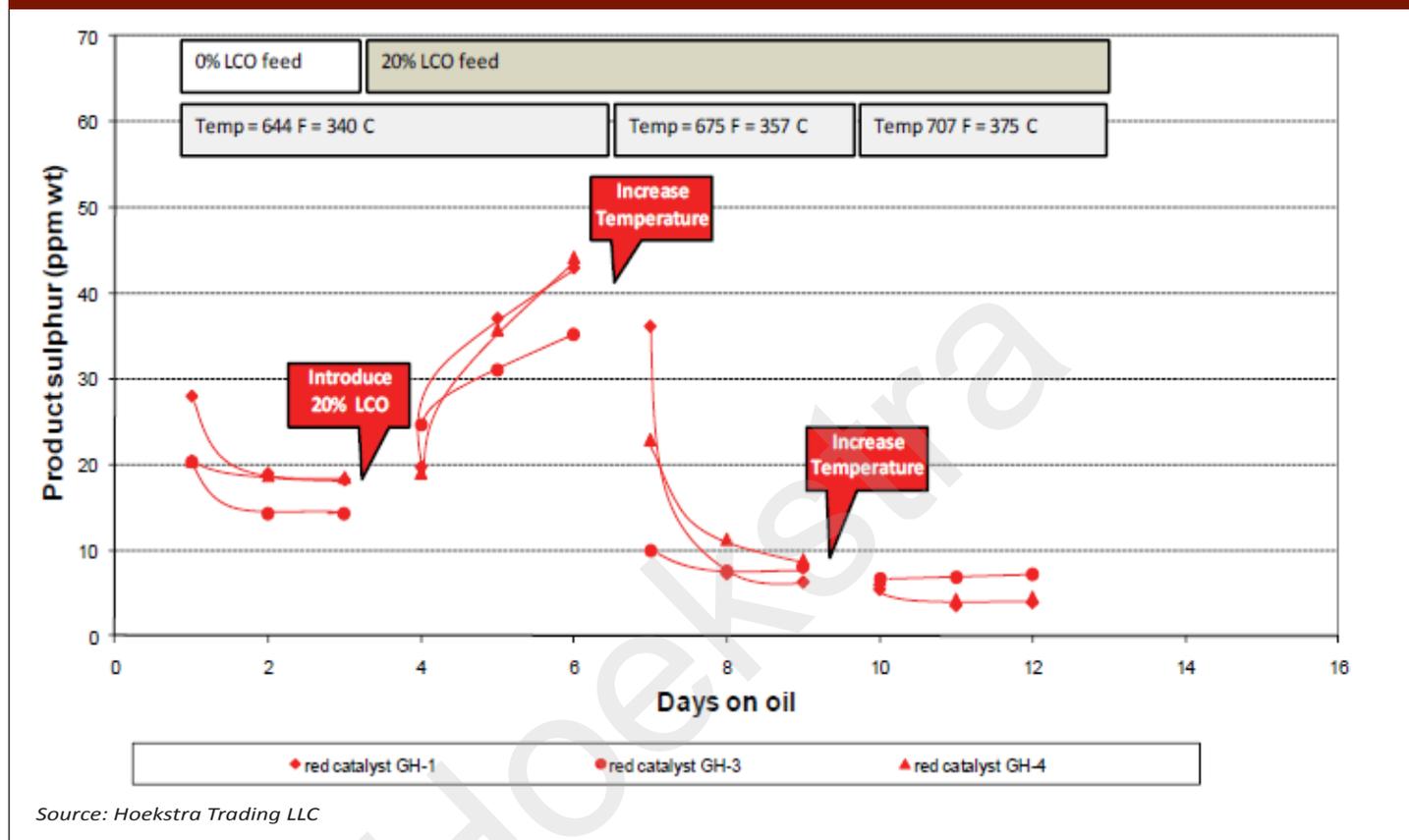
Source: Hoekstra Trading LLC

Figure 1: Hoekstra Trading “10-20” test”, plot of daily sulphur.



In order to rank the relative performance of different catalysts, it is necessary to know the repeatability of the test. Figure 2 shows the result of repeat tests on this sample of our reference catalyst. The three data sets came from three different pilot plant runs which were made six months apart from one another, in two different pilot plants, over a time period of one year.

Figure 2: Hoekstra Trading "10-20" test", plot of daily sulphur.



Source: Hoekstra Trading LLC

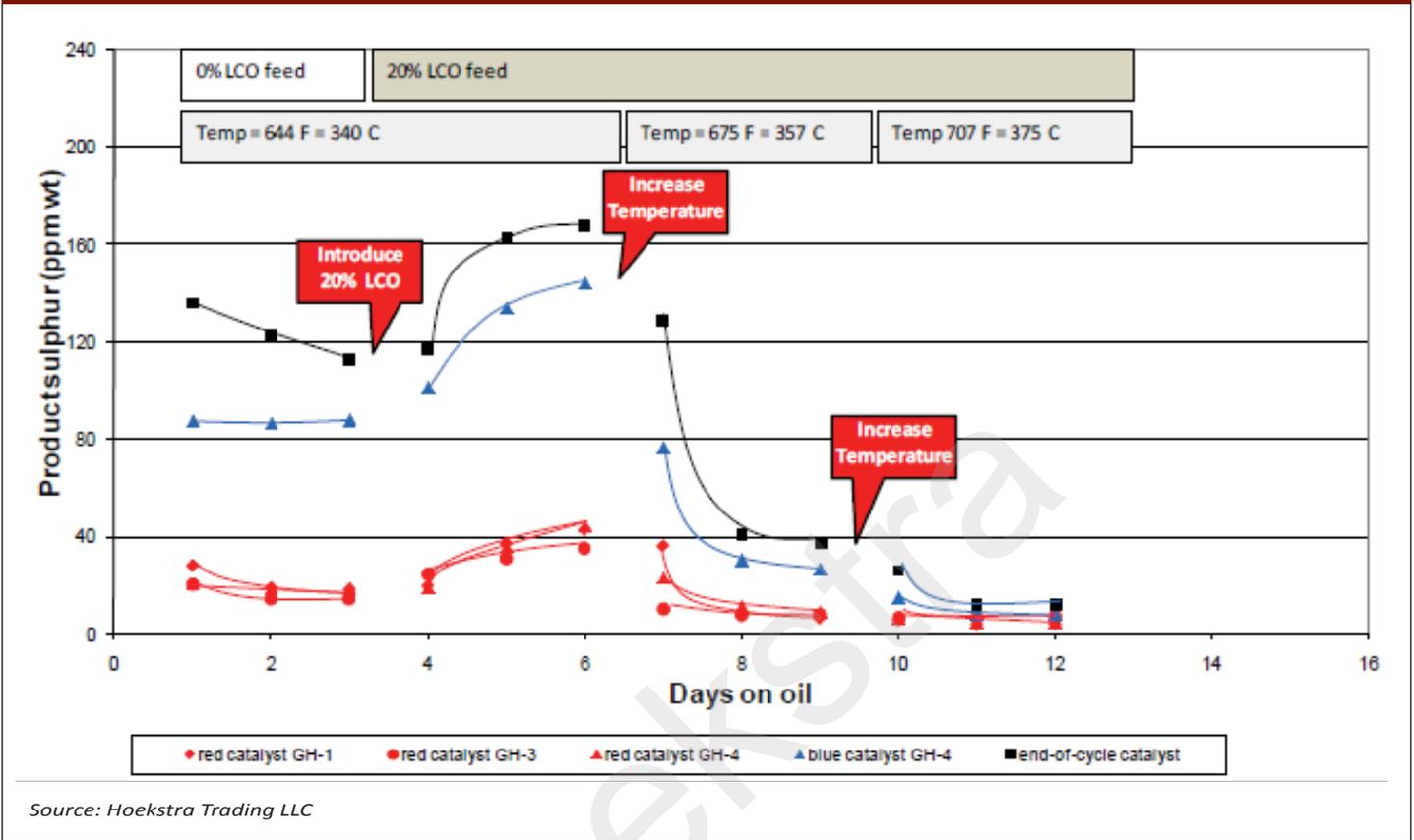
The differences seen in repeat tests on the reference catalyst represent experimental error due to inherent variance in measurement, as catalysts are tested in multiple pilot plant runs over time. Sources of error include differences in pilot plant hardware, temperature measurement, analytical measurement, feed properties, flow rates, and catalyst loading. It would be a mistake to try to totally eliminate these small differences. Instead, we take them to show the inherent range of testing error. Differences within this range cannot be attributed to true differences in catalyst performance.

In Figure 3, the above test results are shown on an expanded scale, along with the results for two additional catalysts. The black curve represents a catalyst with activity similar to an end-of cycle catalyst, and the blue curve represents a fresh catalyst with relatively low initial activity. Here, the separation of catalyst performance is clear, well outside the range of experimental error.

Figure 3 provides a framework for measuring the performance of different diesel hydrotreating catalysts. By running this test on different catalysts, we can position the catalysts into a relative activity ranking. We have done this with catalysts from all major suppliers. Our sample set includes some catalysts provided directly by catalyst suppliers, and some taken from commercial batches that had been previously sold to refiners.

This test program has shown the 10-20 test to be a sound method, with known repeatability, able to clearly distinguish differences in performance of competitive products. Product rankings and full test data were delivered to our clients in May, 2010. The report, Independent Catalyst Test Report 2010, is now available for immediate delivery to any independent refiner or catalyst supplier. We are continuing to expand our data base.

Figure 3: Hoekstra Trading "10-20" test", plot of daily sulphur.



Client response

Among our clients, without exception, there has been enthusiastic response to our report. All of them eagerly awaited the test results, took part in face to face meetings or web conferences at the first possible opportunity upon release of the data, and had several people join in engaging discussion of the results. Some of our results were surprising. We know that, in every case, our testing has enhanced our client’s understanding of competitive product performance, influenced the direction of their catalyst strategy, and opened new opportunities to improve bottom line performance.

Independent Catalyst Test Report 2010 is the first product of its kind. The technical credibility of our program is not seriously questioned; it has been accepted and endorsed by experts through every sector of the industry. The cost and ease of doing business are unmatched - by contrast, most go it alone options require at least several months lead time to just work out feed sourcing, feed transport, catalyst sourcing and legal agreements, before any testing has started.

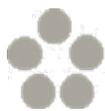
We are now well into our second year of product testing for diesel hydroprocessing catalysts. Our immediate goals are to expand our database and add more independent refiners to our client list. For the future, we hope to help many hydroprocessing engineers with the important job of choosing a new catalyst – in much the same way that Consumer Reports helps them choose a new car.

Source: George Hoekstra, Hoekstra Trading, LLC, 1961 Dorset Drive, Wheaton, IL, Phone: +1 630 330 8159, E-mail: george.hoekstra@hoekstratrading.com.

Author Biography



George Hoekstra retired from BP in April 2009 after a 35 year career as a chemical engineer with BP and Amoco. George’s career was mostly in refinery process R&D and technology management. As an independent consultant, his company currently offers an open-market catalyst testing program to help independent refiners select hydroprocessing catalysts. George can be reached via his website, <http://www.hoekstratrading.com>.



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Renewable High-Octane Gasoline by Aqueous-Phase Hydrodeoxygenation of C₅ and C₆ Carbohydrates over Pt/Zirconium Phosphate Catalysts...

Aqueous phase processing (APP) is a promising option for the conversion of aqueous biomass derived feedstocks (including sugars, sugar alcohols, bio-oils, cellulose, or even lignin) into hydrogen, light alkanes, liquid alkanes, and oxygenates. Recently it was shown that sorbitol could be converted into C₁ to C₆ straight alkanes over bifunctional Pt/SiO₂-Al₂O₃ catalysts by aqueous-phase hydrodeoxygenation (APHDO). This finding pointed to the possibility of making gasoline from aqueous carbohydrate solutions. However, the C₅ and C₆ alkane mixtures produced by this process have a low research octane number (ca. 37) and these straight-chain alkanes cannot be used directly as a gasoline range fuel without further upgrading.

In this work the authors show how APHDO can be modified to selectively produce gasoline-range molecules with high research octane numbers from 71 to 89, from both C₅ and C₆ aqueous carbohydrate solutions at high carbon yields (73%) using a stable Pt/Zirconium phosphate (Pt/ZrP) catalyst.

Table 1 shows the results obtained for the APHDO of sorbitol using a series of bifunctional catalysts with the same Pt loading (4%). Pt/ZrP was found to be stable under the reaction conditions with no significant deactivation after 200 h TOS. No Pt, Zr, or P were detected (<7 ppm) in the product stream, indicating no leaching occurred. In addition, Pt/ZrP had almost twice the C₅ and C₆ alkane selectivity compared to Pt/SiO₂-Al₂O₃.

Although additional catalyst development needs to be carried out, Figure 1 shows a conceptual process for APHDO. In the first reactor the carbohydrates are reacted with hydrogen to hydrogenate the carbohydrates into sugar alcohols. The outlet stream from this reactor is sent to a second reactor, which contains the Pt/ZrP catalyst. The outlet from this second reactor is fed into a separation system. The system separates the gases, the gasoline phase, the aqueous phase, and a water stream. The gasoline phase is then blended with a petroleum-based feedstock. Part of the gas phase stream is recompressed and fed back into the first reactor. Alternatively, the gases can be combusted to provide process heat, or reformed to produce hydrogen. The aqueous phase can be recycled back into either reactor 1 or 2 or purged into a wastewater treatment facility. APHDO could also be used for the upgrading of bio-oil. Source: ChemSusChem 2010, 3, 1154-1157; Ning Li et al.

Figure 1: Block flow diagram for the APHDO of carbohydrates and aqueous phase bio-oil

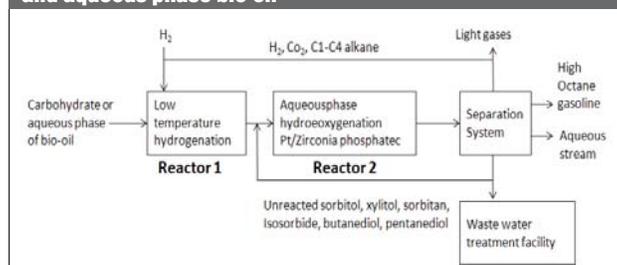


Table 1: Carbon conversion and selectivity over different Pt/acid catalysts for aqueous-phase hydrodeoxygenation of sorbitol. Reaction conditions: 518 K, 2.93 MPa, WHSV=2.91 h⁻¹ with 5 wt% sorbitol solution as feedstock, H₂ flow rate 40 mLmin⁻¹.

Catalyst	C _{gas} ^[b] [%]	S _{alkane} ^[b] [%]	Specific alkane selectivity ^[c] [%]					
			C1	C2	C3	C4	C5	C6
Pt/SiO ₂ -Al ₂ O ₃	25.8 ^[d]	45.8	13	20	14	17	14	22
	23.6 ^[d]	43.2	14	19	14	19	13	21
Pt/H-ZSM-5	86.5 ^[d]	75.4	4	9	14	21	16	36
	28.9 ^[d]	22.7	12	16	12	14	18	29
Pt/HY	26.9 ^[d]	45.4	8	14	13	19	22	24
	12.1 ^[d]	20.8	30	26	14	13	12	6
Pt/WO ₃ /ZrO ₂	34.2 ^[d]	50.6	4	8	12	20	23	34
	7.5 ^[d]	16.0	17	26	17	10	20	10
Pt/MoO ₃ /ZrO ₂	7.3 ^[d]	13.5	9	18	15	7	31	19
	4.6 ^[d]	25.4	3	8	9	7	29	43
Pt/Nb ₂ O ₅	33.4 ^[d]	29.3	30	28	17	12	8	5
	33.6 ^[d]	25.7	32	29	18	12	5	4
Pt/zirconium phosphate	32.8 ^[d]	52.5	4	9	12	20	22	33
	34.2 ^[d]	50.6	3	8	12	20	23	34
Pt/titanium phosphate	47.1 ^[d]	41.6	10	18	21	20	16	16
	28.3 ^[d]	26.9	17	24	20	16	10	12
Pt/niobium phosphate-1	33.7 ^[d]	73.6	1	3	6	11	24	56
	15.0 ^[d]	12.9	15	20	16	16	20	12
Pt/niobium phosphate-2	23.3 ^[d]	43.9	12	19	15	22	18	15
	24.3 ^[d]	26.1	21	30	18	14	10	7

[a] C_{gas}: percent of carbon converted to gas phase. [b] S_{alkane} = carbon in alkanes/carbon in gas phase × 100%. [c] Specific alkane selectivity = (carbon in specific alkanes)/(carbon in all alkanes detected) × 100%. [d] Activity at 12 h. [e] Activity at 36 h.

A Recyclable TEMPO Catalyst for the Aerobic Oxidation of Sulfides to Sulfoxides...

The selective oxidation of sulfides into the corresponding sulfoxides is one of the most important transformations in organic synthesis because of its usefulness for the preparation of biologically and medicinally valuable intermediates. The chemoselective oxidation of sulfides to sulfoxides can be achieved directly with molecular dioxygen, requiring high pressure and elevated temperature conditions. Consequently, a number of alternative methods have been developed for this transformation, among them a few catalytic systems that allow the use of atmospheric oxygen as secondary oxidant. In the course of ongoing studies to develop environmentally benign catalytic processes for the oxidation of alcohols, the authors found that the aerobic oxidation of alcohols with TEMPO (2, 2, 6, 6-tetramethylpiperidine-1-oxyl) in the presence of catalytic amounts of manganese and cobalt nitrate, can be extended to the oxidation of sulfides.

Choosing thioanisole as a model substrate, they investigated a catalyst mixture comprising TEMPO (1 mol %), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2 mol %), and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2 mol %) in acetic acid at 40 °C (Scheme 1). Under the optimized conditions, a representative range of sulfides was evaluated and it was found that diaryl- and dialkyl- as well as arylalkylsulfides were smoothly converted into the corresponding sulfoxides in high yields. This was also true for electron-rich sulfides; further oxidation to sulfones was not observed (Table 1).

Because both alcohols and sulfides can be oxidized under the reaction conditions described here, the authors subsequently investigated the chemoselectivity (Scheme 2) and found a high preference for alcohol oxidation when both functional groups were present in a substrate. Use of the heterogeneous, readily recoverable, and reusable TEMPO derivative 7 (Figure 1) yielded results identical to unmodified TEMPO. Source: ChemSusChem 2010, 3, 1040 – 1042; Chinnusamy and Reiser.

Scheme 1: Aerobic oxidation of sulfides.

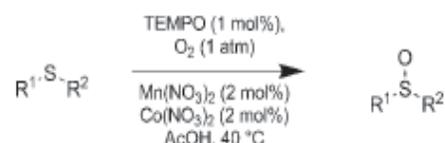
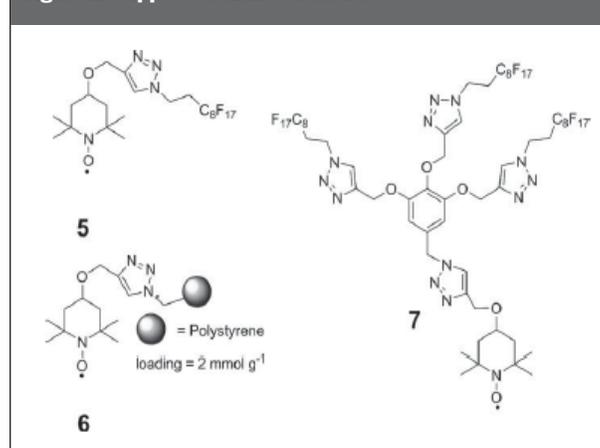


Table 1: Aerobic oxidation of sulfides with TEMPO (Scheme 1).^[a]

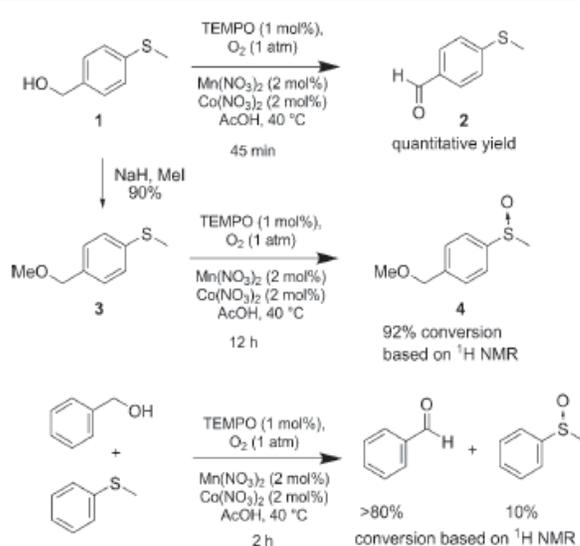
Entry	R ¹	R ²	Time [h]	Yield [%] ^[b]
1	Ph	Me	1.5	58 ^[c]
2	Ph	Me	4	94
3	Ph	C ₂ H ₅	4	96
4	Ph	<i>i</i> Pr	6	91
5	2-Naphthyl	Me	5	89
6	4-Me-C ₆ H ₄	Me	3	92
7	4-OMe-C ₆ H ₄	Me	3	93
8	4-Cl-C ₆ H ₄	Me	15	79
9 ^[d]	PhCH ₂	Ph	12	81
10 ^[d]	Ph	Ph	24	68
11	4-CHO-C ₆ H ₄	Me	24	0
12	C ₃ H ₇	C ₃ H ₇	7	98
13	C ₂ H ₅	C ₂ H ₅	6	92
14	<i>i</i> Pr	<i>i</i> Pr	6	86

[a] Sulfide (1.0 mmol) in AcOH (2 mL), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2.0 mol %), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.0 mol %), TEMPO (1.0 mol %), oxygen atmosphere, 40 °C. [b] Isolated yield. [c] Determined by ¹H NMR. [d] 5 mol % each of TEMPO, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Figure 1: Supported TEMPO derivatives.



Scheme 2: Chemoselectivity between alcohols and methyl sulfides in aerobic TEMPO oxidations.



Hydridoboranes as Modifiers for Single-Site Organochromium Catalysts: From Low- to Ultrahigh-Molecular-Weight Polyethylene...

Molecular single-site catalysts allow the precise synthesis of polyolefins with a range of specific properties. Organochromium complexes show advantageous properties in the polymerization and copolymerization of ethylene. Depending on the catalyst system used, low-molecular weight (MW) up to ultrahigh-molecular weight polyethylenes (UHMW-PEs) with a narrow molecular weight distribution can be obtained. The molecular weight of the polyethylene produced by a single catalyst system can be reduced by the use of chain transfer reagents. Herein the authors report on the use of hydridoboranes as additives which, in the presence of single-site cyclopentadienyl-chromium complexes, are able to increase the molecular weight of polyethylene accurately up to the UHMW-PE range.

The influence of several modifiers on ethylene polymerization was investigated by using structures **A** and **B** as catalyst precursors and methylaluminoxane (MAO) as the activator and compared with the results obtained with zirconocene dichloride **C** (Figure 1). Although 200–300 equivalents of the respective modifier were used, this amount did not result in a considerable decrease in the catalytic activity, as noted in Table 1, indicating that the chosen modifiers readily allow the coordination of the incoming ethylene monomer.

As expected, organoaluminum compounds tend to lead to lower molecular weight as a result of chain-transfer reactions from Cr to Al. Whereas trimethylaluminum (AlMe_3) has little effect (Table 1, entries 2 and 8), triethylaluminum (AlEt_3) leads to a strong decrease in the PE chain lengths. Of significance is the fact that boranes display considerable influence such that while trialkylboranes lead to lower MW, the use of 9-borabicyclo[3.3.1]nonane (9-BBN) as an additive produces high-molecular-weight polyethylenes up to the ultrahigh range (Table 1, entries 6 and 12). The authors were able to control the increase in MW by using different amounts of 9-BBN such that by varying the amount and nature of the modifiers the MW could be selectively controlled over a broad range from 50,000 up to 5,000,000 g mol^{-1} without changing the reaction conditions or the catalytic system.

Figure 1: Catalyst precursors in ethylene polymerization.

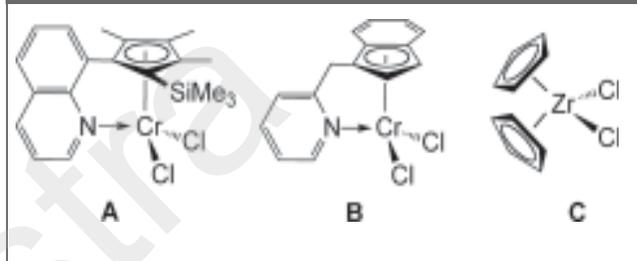


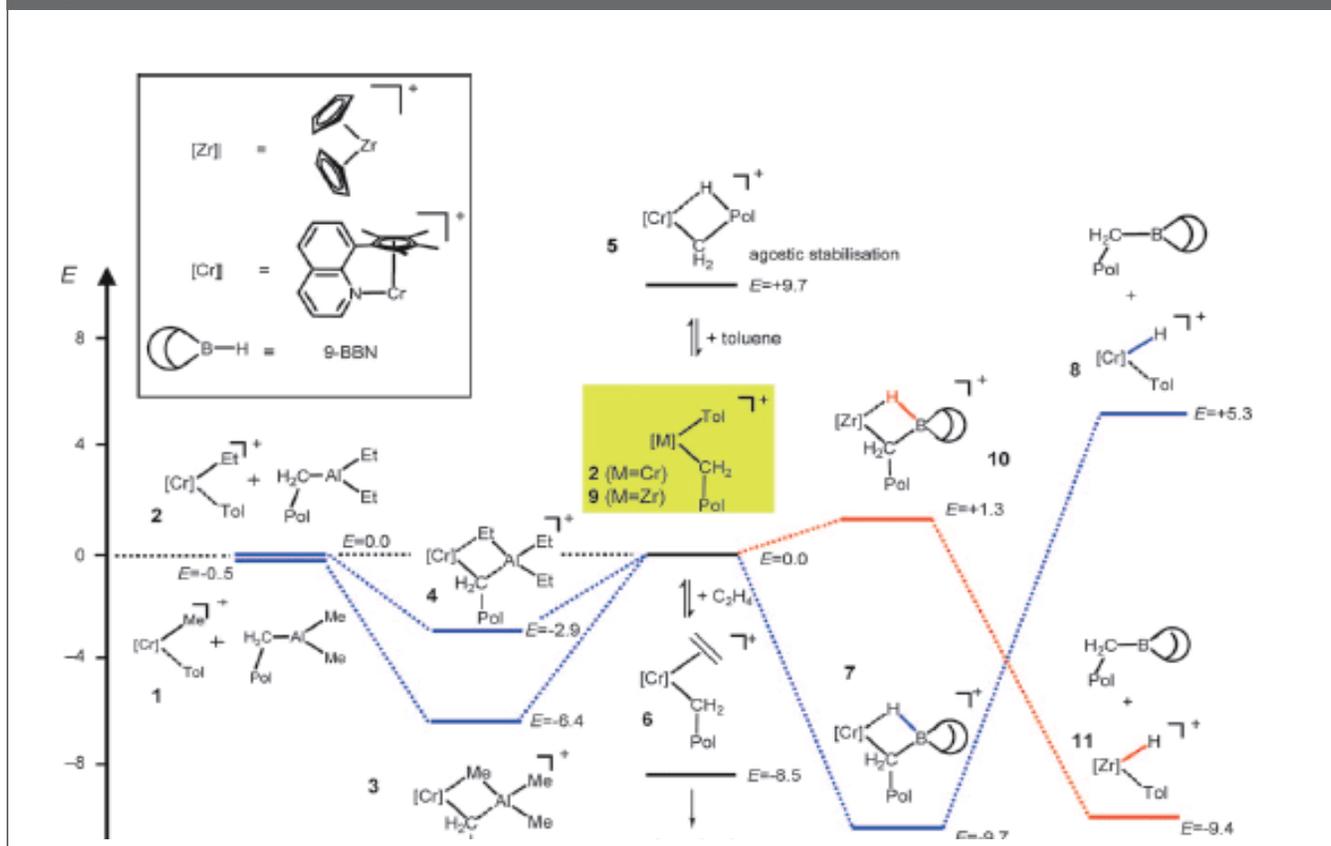
Table 1: Ethylene polymerization with A, B, and C as a catalyst precursors and various modifiers.^[a]

Entry	Pro-catalyst	c_{cat} [μmol]	Modifier	Modifier/Cr	Activity [$\text{g mmol}^{-1} \text{h}^{-1}$]	$M_w^{\text{[b]}}$ [10^5 g mol^{-1}]	PE [g]	$t_{\text{polym.}}$ [min]	$M_w/M_n^{\text{[b]}}$	Crystallinity ^[c] [%]	$T_m^{\text{[c]}}$ [$^{\circ}\text{C}$]
1	A	4.42	–	–	3243	5.3	2.9	12	3.1	65	135.4
2	A	5.82	AlMe_3	290:1	2200	3.2	4.3	20	3.4	74	133.3
3	A	5.36	AlEt_3	200:1	3298	0.5	5.9	20	3.2	80	130.5
4	A	5.36	PhSiH_3	200:1	2972	4.7	4.0	15	3.1	63	134.0
5	A	6.05	BEt_3	250:1	3529	3.1	7.1	20	3.7	68	134.0
6	A	4.66	9-BBN	200:1	2908	31.4	2.7	12	5.1	53	133.9
7	B	6.99	–	–	3017	13.1	4.2	12	2.9	53	132.4
8	B	6.07	AlMe_3	280:1	3553	12.8	4.3	12	2.5	57	133.9
9	B	6.38	AlEt_3	200:1	3439	0.9	4.4	12	2.4	81	131.9
10	B	6.38	PhSiH_3	200:1	2850	13.5	3.6	12	3.0	56	133.7
11	B	8.51	BEt_3	200:1	2731	4.2	7.8	20	3.0	60	132.9
12	B	6.38	9-BBN	200:1	2834	48.9	6.0	20	3.5	51	134.7
13	C	10.30	–	–	2332	6.0	4.8	12	2.4	57	132.3
14	C	10.30	9-BBN	200:1	1181	4.3	3.4	17	3.7	67	133.6

[a] Conditions: co-catalyst PMAO, Al/Cr 1000:1, RT, 150 mL toluene, 1 bar C_2H_4 . [b] Determined by GPC. [c] Determined by differential scanning calorimetry.

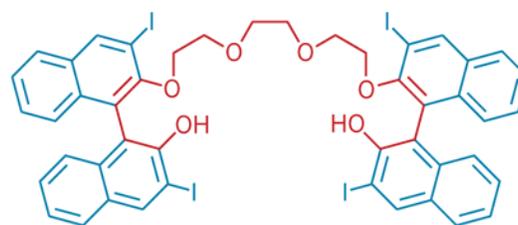
The role of 9-BBN compared to established chain-transfer reagents was investigated in a series of control experiments and a mechanism based upon Density Functional Theory (DFT) is proposed (Scheme 1) which explains earlier experimental observations concerning the formation of UHMWPE when organochromium catalysts are immobilized. Source: *Angew. Chem. Int. Ed.* 2010, 49, 8751-8754; Mark et al.

Scheme 1: Calculated energies of the proposed different influence of AIR and BH on the chain termination during ethylene polymerization. Method: DFT B3LYP/6-311g⁺. The profiles are plotted for zero-point-vibration-corrected energies. The relative energies are in kJmol⁻¹. Dimerization energies for AIR₃ and R₂BH were taken into account. CH₃CH₂ was used as a model for the polymer chain. CH₂Pol=growing polymer chain.



'Chiral Fluoride' Separates Alcohols...

Thanks to the unusual combination of a crown ether moiety and a chiral organocatalyst, chemists in South Korea have developed a simple method for separating enantiomers of silyl-protected secondary alcohols. In the presence of potassium fluoride, the mix-and-match molecule created by Choong Eui Song and colleagues at Sungkyunkwan University generates a "chiral fluoride" species that can selectively desilylate one enantiomer in a racemic mixture of silylated secondary alcohols. During the process of designing the catalyst, Song's team discovered it was necessary to incorporate halogens at the 3 and 3' positions of the BINOL (1,1'-bi-2-naphthol) organocatalyst. An X-ray crystal structure of the catalyst-KF complex reveals that the Lewis basic halogen atoms interact strongly with the potassium ion. "This study can open up a new avenue of research for chiral-fluoride-catalyzed asymmetric reactions, which have vast synthetic potential but remain a relatively undeveloped field," the researchers note. Source: *Chemical & Engineering News*, 10/18/2010, p. 27.



Chiral-anion generator

INEOS Bio JV Awards EPC Contract to AMEC for BioEnergy Center...

INEOS Bio's joint venture (INEOS New Planet BioEnergy) has awarded the EPC contract to build its bioenergy facility in Southeast Florida to AMEC of Tucker, GA. AMEC will provide engineering and construction expertise to build this first commercial scale facility, valued at over \$100 million. The facility will produce 8 million gallons (24 kta) of third-generation ethanol and 6 megawatts (gross) of renewable energy annually from renewable biomass including yard wastes and municipal solid waste, wood, and vegetative wastes. The heart of the INEOS Bio technology is a patented anaerobic fermentation step, through which naturally occurring bacteria convert gases derived directly from biomass into ethanol. Source: INEOS Bio and New Planet BioEnergy, 11/1/2010.

Envergent Providing Detailed Engineering to Build Pyrolysis Plant...

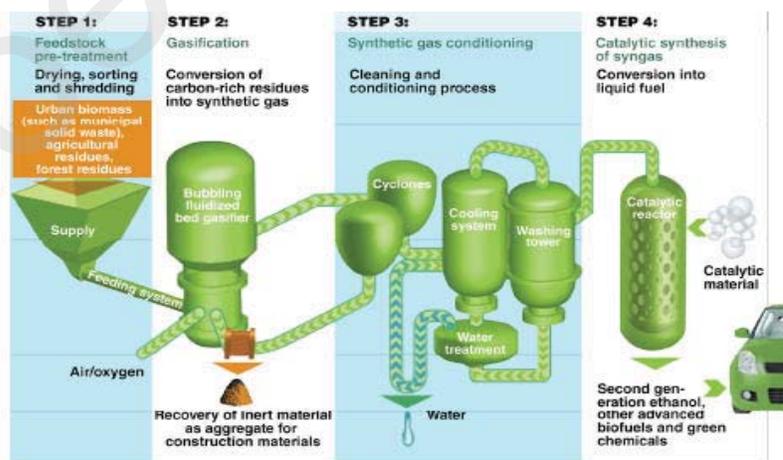
Envergent Technologies LLC, a Honeywell company, announced it has been selected by High North BioResources Ltd. Partnership to perform detailed engineering for a project to convert wood residuals to renewable heat and electricity. The High North facility, to be built in Alberta, Canada, will be a pyrolysis plant for renewable heat and power generation and is projected to process 400 bone-dry metric tons of sawmill residuals per day to produce over 20 million gallons of pyrolysis oil annually. The plant will use Rapid Thermal Processing (RTP) technology, which works by rapidly heating biomass such as wood chips or straw at ambient pressure to generate high yields of pyrolysis oil. The oil can be burned in industrial burners and furnaces for heat or to power electric generators. Source: Envergent Technologies LLC, 10/28/2010; TCGR.

Better Gas Storage Via MOFs...

Natural gas-powered vehicles may soon be able to travel double the distance on a single tank due to metal organic frameworks (MOFs). BASF research scientists have developed an innovative method for the solvent-free industrial-scale manufacture of those materials for better gas storage. MOFs produced by the new method are currently being trialed for natural gas storage in heavy-duty vehicles. With their special structure and large surface area, MOFs open up new opportunities for alternative propulsion systems, in catalysis, as nanoreactors, and in drug delivery, making them hugely interesting both BASF has been working toward industrial-scale synthesis of metal-organic frameworks for the past 10 years. Used as storage materials in the natural gas tanks of municipal utility vehicles, MOFs offer a docking area for gas molecules, which can be stored in higher densities as a result. The larger gas quantity in the tank increases the vehicle's range. An advantage of the production method developed by BASF is that it uses no organic solvents. The simple method gives a higher material yield from an aqueous medium and is suitable for existing BASF production plants. Source: Hydrocarbon Processing, 11/2010, p. 7.

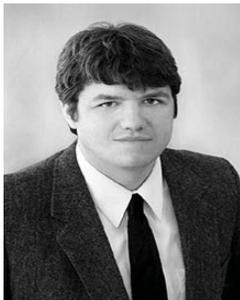
World's First Commercial Plant to Produce Biofuel from Municipal Waste...

Enerkem Inc. has broken ground in Edmonton, Alberta, on what is said to be the world's first industrial-scale plant to produce liquid fuel from municipal solid waste. When the plant starts up at the end of 2011, it will convert 100,000 m.t./yr of garbage into 10-million gal/yr of methanol, followed by ethanol, under a 25-year supply contract with the City of Edmonton. The garbage represents 40% of the city's waste that is currently landfilled because it cannot be recycled or composted.



In Enerkem's process, garbage is shredded and gasified in a bubbling fluidized bed at "low severity" (750–800°C and atmospheric pressure). The severity is increased in stages to produce a synthesis gas that is mainly carbon monoxide and hydrogen. Particulate matter is removed by cyclones, then the gas is water-scrubbed, compressed and converted sequentially, by proprietary catalytic processes, to methanol, acetate, and finally to ethanol. Early next year Enerkem will start construction on a similar plant in Pontotoc, Miss., supported by \$50 million in funding from the U.S. Dept. of Energy. Source: Chemical Engineering, 10/2010, p. 14.

Prof. Paul Dauenhauer, Ph.D.



Paul Dauenhauer received his B.S. in Chemistry and Chemical Engineering from the University of Wisconsin, Madison. He received a Ph.D. in Chemical Engineering from the University of Minnesota where he completed his thesis focusing on catalytic reforming of biomass-derived oxygenates under Professor Lanny D. Schmidt. During this time, he published ten articles, including publications in Science, Angewandte Chemie, and Journal of Catalysis. Additionally, he is a co-inventor of the 'Reactive Flash Volatilization' process to catalytically reform solid biomass, which currently has three patents pending. Until 2009, he was a Senior Research Engineer with the Dow Chemical Company as part of the Core R&D – Reaction Engineering Division in Midland, MI and the Hydrocarbons and Energy research division in Freeport, TX. In August of 2009, Paul Dauenhauer joined the faculty of Chemical Engineering at the University of Massachusetts, Amherst as an Assistant Professor where his research focuses on biomass conversion.

The Catalyst Review asked, “What are the newest and most promising process reaction technology efforts currently underway in your laboratory?”

On Biomass Conversion Chemistry: The thermo-chemical decomposition of biomass to bio-oils by pyrolysis occurs through the thermal degradation of biomass biopolymers including cellulose, lignin, and hemicellulose. These large biopolymers are known to react and fragment through hundreds of intermediate organic compounds, eventually forming volatile organics, gases, and solid products (char). During the decomposition process, we have recently shown that the solid biopolymers react through an intermediate liquid phase before eventually volatilizing to form vapor products. The diversity of products produced from biomass pyrolysis is determined predominately by the reaction chemistry occurring within the intermediate liquid phase. Additionally, natural biomass sources such as wood fibers and grasses contain inorganic materials which exist within the intermediate liquid and are known to naturally catalyze various isomerization, hydrolysis, and dehydration reactions. By studying the homogeneous decomposition chemistry and the role of inorganic catalysts within molten biomass biopolymers, we will eventually be able to develop molecular-level reaction models which are capable of predicting the production rates of gases, solid char byproduct, and different types of volatile organic compounds valuable for biofuels and/or chemicals.

On Catalytic Biomass Reactor Design: Thermo-chemical biomass reactor design differs significantly from conventional reactors due to the necessity for thermal degradation of solid particles such as fibers or wood chips. This requirement has led to three general classes of biomass reactors based upon the heat transfer mechanism: gas phase convection (fluid beds), radiation (focused solar), or conduction (particles/fibers on hot surfaces). Conduction between high temperature reactor surfaces and particles of biomass results in the highest rates of heat transfer and reduces production of char relative to convection. We aim to design continuous flow catalytic reactors that autothermally couple endothermic particle degradation with exothermic catalytic oxidation. This reactor concept exhibits tunability for control of the quantity and quality of produced bio-oils by manipulation of the ablation surface geometry, oxidation catalyst design, and thermal transport properties of the selected reactor materials. The compact design will potentially permit utilization of portable reactors capable of producing high quality bio-oils as part of a distributed network supplying a single bio-refinery.

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