BOOSTING CATALYST PRODUCTIVITY

Companies are finding different pathways to increase catalysts' ability to produce

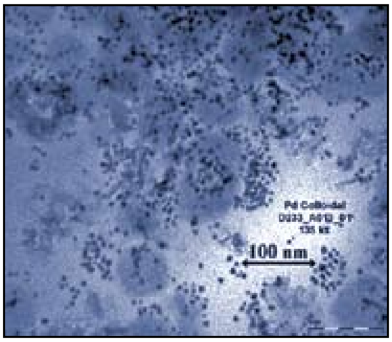

FIGURE 1. Metal clusters with a narrow size distribution, such as these produced on BASF's Nanotechnology platform improve activity while reducing metal content

BASF

For the better part of a century, chemical process industries (CPI) have depended on catalysts to make their processes viable. Current efforts toward process efficiency and environmental innocuousness have placed more demands on catalysts to produce more with less.

Industrial catalyst manufacturers are partners in the effort; they are pursuing several different pathways to maximize their products' ability to boost output for those who use them. Among the strategies are to find ways to maintain product yields with less catalyst, and to improve catalyst activity without sacrificing selectivity.

There have been several recent examples where new catalysts have helped realize manufacturing advantages. Success has been reached through the use of alternate catalyst materials, new support designs and new manufacturing methodology.

Engineering particle size

Heterogeneous catalyst activity and selectivity are affected strongly by catalyst particle size. One strategy to improve productivity is to find ways to make uniform-sized catalyst particles that are optimally sized to perform the needed reactions. The BASF (Ludwigshafen, Germany; www.basf.com) catalyst division is applying that approach in its NanoSelect platform, a commercially viable process for manufacturing metal crystallites of a specific size. The first two products under the NanoSelect umbrella are LF100 and LF200, which are the world's first lead-free alternatives to Lindlar catalysts. Lindlar catalysts are lead-modified heterogeneous palladium catalysts that, for example, hydrogenate alkynes to selectively produce *cis*-, rather than *trans*-alkenes.

BASF Catalysts global product technology manager Hans Donkervoort explains that standard heterogeneous catalysts have metal crystallite sizes varying from <1 to 100 nm. The NanoSelect platform is designed to make metal colloids with metal crystallites sized in a very narrow, almost unimodal size range — for example, 7.0±1.5 nm.

"For the LF 100 and 200 catalysts, we are able to produce metal crystallites in a specific narrow range, which allows BASF to achieve the same functionality with the NanoSelect catalyst as that of a Lindlar catalyst," Donkervoort says. In addition, these catalysts require less palladium metal to achieve the same hydrogenation activity, which leads to significant cost reductions in the hydrogenation process. "Palladium content of Lindlar catalysts is about 5% by weight, while the LF 100 and 200 have around 0.5 or 0.6% palladium by weight," Donkervoort explains, "but hydrogenation activity levels are similar."

The BASF LF Series catalysts also eliminate the need for lead. The role of lead in Lindlar-catalyzed reactions is important, but not well understood.

For developing the lead-free hydrogenation catalysts, BASF won a "Green Excellence Award" from Frost & Sullivan (San Antonio, Tex.; www.frost.com) in August 2009.

"Feedback from [LF catalyst] users in the market has been good," Donkervoort says. "Performance is the same [as existing Lindlar catalysts], including selectivity for the *cis* versus *trans* double bond."

The two catalysts constructed on the NanoSelect platform differ in the support material used — in the case of LF 100, the support is activated carbon, and for LF 200, the support is alumina-silicate powder.

BASF's catalyst division is currently working on producing other catalysts on the NanoSelect platform, including multimetallic systems. The company is also seeking collaborations with university research groups to learn more about the fundamental chemistry of the catalyst systems.

In addition to working on new NanoSelect catalysts, BASF engineers are also developing catalysts that are compatible with other strategies manufacturers may be pursuing toward achieving higher productivity in their processes. Succeeding in doing so could include moving from a batch-production model to continuous production, Donkervoort explains. Companies are looking to downsize their equipment and make more product with smaller process hardware, Donkervoort says, and "it's up to us to develop catalysts that will be effective" in such a scheme.

Catalysts for a new reactor

Catalyst particle size figures prominently in another effort where increased productivity is coupled with downsized capital equipment. Oxford Catalysts Ltd. (Oxford, U.K.; www.oxfordcatalysts.com) has developed a method with a goal similar to that of BASF's NanoSelect platform — achieving a narrow, catalyst-particle-size distribution.

One objective of this method, known as organic matrix combustion (OMX), is to help generate catalysts suitable for a process-intensification technology, called microchannel reactors, developed by Oxford subsidiary Velocys (Plain City, Ohio; www.velocys.com).

Microchannel reactors and the catalysts inside were developed, in part, as a way to make the distributed production of biofuels feasible. Biomass density is low compared to petroleum; it takes about one ton of biomass to yield a single barrel of liquid biofuel. To make a biomass-to-liquid-fuels process practical and economically feasible, production facilities need to be small and located near the source of the biomass. A spin-off from the Battelle Memorial Institute (Columbus, Ohio; www.battelle.com), Velocys devised microchannel reactors to enable small biomass-to-liquid production facilities that could be located near biomass sources.

Microchannel reactors are designed to intensify catalytic reactions, such as Fischer-Tropsch (F-T) reactions, allowing for higher productivity with less equipment. Microchannel reactor blocks (Figure 2) are ideally suited to catalytic reactions that are highly exothermic or highly endothermic, and could benefit those for which a conventional reactor architecture limits the reaction equilibrium.

But to take full advantage of the microchannel technology, heterogeneous catalysts need to be extremely active. Oxford's OMX process enables higher activity by manufacturing catalyst particles in a narrow, nanoscale metal-crystallite-size distribution around the optimal size for a particular reaction. The narrow particle-size-distribution curve allows the highest activity while still maintaining sufficient stability, Oxford says. In the OMX method, an organic component forms a complex with the metal salt that effectively stabilizes the metal. The complex undergoes a rapid calcination process that blocks the metal crystallite from growing larger.

The process also generates particles with an ideal surface configuration. OMX produces metal crystallites with "terraced" surfaces to enhance activity, the company explains.

Microchannel reactors contain stacked arrays of parallel reaction channels with sizes in the range of 0.1 to 5.0 mm. Smaller diameter channels dissipate heat more quickly than those in conventional fixed-bed or slurry reactors. By significantly reducing distances required for heat and mass transfer, microchannels help accelerate processes. Oxford Catalysts has been working on new designs for highly active catalysts specifically for F-T chemistry. When coupled with the microchannels, the catalysts help processes realize 50 times higher productivity per gram of catalyst.

For example, in F-T reactions carried out in 1–2-mm microchannels, heat can be removed 20 to 100 times faster than in a conventional reactor. This limits competing reactions, such as those that generate methane. "Microchannels allow you to work under conditions that are more favorable for reaction kinetics," remarks Derek Atkinson, business development director for Oxford Catalysts.

Temperature differences across microchannel reactors are small — typically 1°C, compared to a 20 to 40°C differential often observed in conventional reactors. Also, conversion rates for carbon monoxide of greater than 70% per pass have been observed, compared to 45–60% in fixed bed or slurry bed reactors.

Oxford and Velocys are building an installation to demonstrate the microchannel technology at a biomass gasification plant in Gussing, Austria. The facility will use gasified woodchips as a feedstock for F-T chemistry and will have a capacity of about 10,000 gal/yr.

The plant is expected to be operational in early 2010 for the beginning of a six-month demonstration period, after which the reactor skid will be moved to Wright-Patterson Air Force Base near Dayton, Ohio to test its applicability to producing synthetic jet fuel. Goals of the demonstration plant are to learn about process upsets and catalyst poisoning.

Optimizing performance

Efforts aimed at squeezing more productivity from processes using heterogeneous catalysts can focus on other areas, including tweaking catalyst crystal structure, reducing energy requirements and refining catalyst selectivity.

Süd-Chemie AG (Munich, Germany; www.sud-chemie.com) found a way to improve productivity in traditional ammonia synthesis by stabilizing a new catalyst crystal structure. The new catalyst contains less oxygen in its crystal structure than its predecessors, and therefore shortens the reduction time. It also exhibits up to 40% higher activity. Combined, the advantages in the new ammonia synthesis catalyst improve energy efficiency significantly for ammonia producers and could boost ammonia production by up to 5%.

"A 5% increase in ammonia production can translate into millions of dollars annually in a typical-sized plant," remarks Yvonne Zhang, vice president for global marketing in the catalyst technology unit of Süd-Chemie. The better-performing crystal structure was discovered by a China-based academic research group and was licensed by Süd-Chemie from Zhejiang University of Technology.

Oxford Catalysts/Velocys

FIGURE 2. Velocys microchannel reactors have improved heat transfer properties and require highly active catalysts

Improving the selectivity of catalysts that are marketed is being pursued by a number of companies in the catalyst business, including CRI Catalyst, a subsidiary of Royal Dutch Shell Group (London, U.K.; www.shell.com) and Grace-Davison (Columbia, Md.; www.gracedavison.com). In many cases, improved selectivity means higher productivity, in the form of higher yields of desired products versus side products.

CRI Catalyst plans to introduce a product early this year that will improve selectivity in styrene production. The catalyst is designed to maintain the activity of its predecessors while boosting selectivity, says Laurent Fenouil, global business director for CRI/Criterion's styrene catalyst unit. Fenouil says the driving force for the company's catalyst business is increasing catalyst activity and selectivity, along with lengthening product lifetimes to help its customers optimize efficiency. In the future, the styrene sector will see a "renewed emphasis" on energy cost and energy usage, Fenouil notes, adding that CRI will be working on catalysts that help users reduce energy use while retaining the same performance characteristics.

In many areas, productivity becomes an economic imperative based on feedstock costs. For example, producers of polyolefins are searching for catalysts that will allow them to improve both production and economics. Grace-Davison global marketing director for polyolefins Jewan Bae says his company is working to develop catalysts to do just that. The demand can especially be felt among resin producers in Europe, Japan and Korea, who must produce more to compete with companies in China and the Middle East, where feedstock costs are lower. Bae says for now, North American companies can compete on costs with Chinese and Middle Eastern firms, because the cost of natural gas is relatively cheap, but in a few years that won't be the case.

Bae and Grace are looking for the increased costs to push many companies toward producing specialty products instead of commodity polyolefins. Producers are already going in that direction, Bae says, because they can command premium pricing. Grace is looking to help in that effort also, by working with industry partners to develop and commercialize stereoselective catalysts based on metallocene chemistry, Bae explains. Metallocenes consist of a metal atom bound to, and sandwiched by, two cyclopentadiene rings.

Metallocenes are an example of metal-organic complexes, which may become increasingly common as industrial catalysts in the future as chemists and engineers learn the details of their function and work out viable production processes.

University catalyst research

Projected demand among CPI companies for catalysts that exhibit higher activities, enhanced selectivity, reduced environmental impact, or posess other desired performance parameters have many companies looking not only to recently developed technologies, but also to academia for new developments that could spur the next generation of industrial catalysts. A significant portion of industrially relevant catalyst work in academia is focused on engineering metal-organic complexes to serve as catalysts and supports. An example is work led by Ferdi Schüth at the Max Planck Institut für Kohlenforschung (Mülheim an der Ruhr, Germany; www.kofo.mpg.de). Researchers there, along with collaborators elsewhere, have developed a new catalyst for oxidizing methane into methanol. The new catalyst mimics a previously studied homogeneous catalyst based on platinum and bipyrimidine, but has the additional and important property of being a solid material that can act as a heterogeneous catalyst with much less energy required to separate it by filtration. The catalyst is characterized by a highly porous covalent triazine-based network into which platinum metal powder is added so that the Pt atoms reside within the lattice of the organic framework. The methane is oxidized into methanol in heated sulfuric acid. Schüth and colleagues are now trying to enable the process to work with reactants in the gaseous state. The work could eventually be used to make it cost-effective to monetize previously unused natural gas resources.

A research team at the University of California at San Diego (www.ucsd.edu) has demonstrated catalytic activity after post-synthetic modifications of metal-organic frameworks (MOFs). In synthesizing the hollow-latticed MOFs, the researchers substituted an amine-containing molecule for a similar molecule that served as a linker for the MOF structure. Including the amine group allowed the team to functionalize the MOF with other molecules that give rise to catalytic activity. They "bolted on" two cyclic anhydrides capable of chelating an iron atom, which can be used as a catalytic active site. The research could eventually give rise to a new type of tunable catalyst for specific synthetic tasks.

Meanwhile, Korean scientists have succeeded in making ultrathin zeolite sheets that may have advantages as efficient catalysts for hydrocarbon cracking and other petrochemical applications. The thinness of the zeolite sheets allows reactants to rapidly and easily diffuse into the zeolite structure while products diffuse out. Working at the Korean Advanced Institute of Science and Technology (Daejon, South Korea; www.kaist.edu), researchers directed the growth of a thin zeolite sheet with surfactant molecules that acted as templates. The polar end of the surfactant consists of two quaternary ammonium groups around which the zeolite crystal grows. The non-polar tails prevent the growing zeolite crystals from aggregating together into larger, three-dimensional crystals. The surfactant template is removed, leaving thin zeolite flakes, which pile up randomly with gaps to aid diffusion to the catalytic sites. ■

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