

Hunting for the hidden chemistry in solid catalysts

Advances in analytical techniques uncover subtleties of these essential industrial catalysts

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Bert M. Weckhuysen has a dream. Someday he'd like to produce a movie showing what happens on a catalytic solid at a submolecular level.

That dream remains out of reach, he admits. But after more than 20 years of work on the analytical techniques required to make a movie of a solid catalyst in action, Weckhuysen, a chemistry professor at Utrecht University, thinks its time will come.

He's not alone in the quest. Simon R. Bare has spent the past 30 years developing ways to uncover hidden details of commercial solid catalysts as an industry scientist—first at Dow and then at UOP, an oil-refining technology company. He is now continuing that work at Stanford Synchrotron Radiation Lightsource, where he serves as codirector of the chemistry and catalysis division.

Bare, Weckhuysen, and other catalysis aficionados gathered in Denver last month at the North American Catalysis Society meeting to discuss some of the latest developments in catalyst characterization. The researchers described techniques based on X-ray analysis, electron microscopy, atom probe tomography, and other methods for studying never-before-seen nanosized structural subtleties and chemical features that directly control the way

catalysts do their job. These scientists aim to exploit that information to design better-performing and longer-lasting catalysts.

It's hard to exaggerate the importance of solid-state catalysts. "We could not have the standard of life we're used to on this planet without these catalysts," Bare asserts.

For decades, solid catalysts have driven the overwhelming majority of industrial chemical processes. According to industry estimates, more than 80% of today's large-scale chemical processes depend on solid catalysts, which are also known as heterogeneous catalysts because these solids are a different state of matter than the gas and liquid reagents they transform.

For example, most transformations in petroleum refining, pollution abatement, and production of fuels and chemicals are

In brief

The work of solid catalysts

is responsible for trillions of dollars' worth of chemical processes such as oil and gas refining. Typically consisting of metal nanoparticles attached to high-surface-area supports, these catalytic materials are complex, nonuniform, and challenging to analyze. But because even modest improvements in catalyst performance could substantially reduce the cost, energy requirements, and waste associated with catalytic processes, researchers strive to develop new analytical techniques that can reveal hidden details of the way solid catalysts work and eventually lose their potency. Some of the latest advances draw on X-ray methods, electron microscopy, and atom probe tomography.

facilitated by supported catalysts. That term refers to composite materials typically consisting of nanometer-sized metal particles attached to porous metal oxides, zeolites, and other high-surface-area materials.

Although these kinds of catalysts have been used for decades on the multi-ton scale, they are complex materials, and many key details of the way they convert reactants to products remain unknown. To begin with, their atomic structure is difficult to pin down. Solid catalysts differ substantially in that regard from enzymes and from organic compounds that function as homogeneous catalysts. With enzymes and small-molecule catalysts, the positions of all atoms, including those directly involved in catalysis, are often known, and they are identical from molecule to molecule.

Not so with solid catalysts. As Bare points out, the catalytic particles in a single batch of these materials come in a variety of sizes and shapes. Stig Helveg, a research scientist at Danish catalyst manufacturer Haldor Topsoe, adds that even if they were truly monodisperse or single-sized, which they aren't, each particle would have numerous types of surface sites, such as corners, edges, and terraces, that differ from one another in their atomic structure and coordination and therefore also differ in their catalytic activity.

Adding to the complexity, some of these surface sites undergo changes in response to the reaction environment, forming catalytically active sites on the fly in the presence of a pool of chemical species, including reactants, products, and reactive intermediates. Figuring out which surface sites and chemical species are the players and which are spectators is like piecing together a big jigsaw puzzle, Bare says. To locate those pieces and figure out where they fit in the puzzle, many researchers apply multiple analytical techniques, often simultaneously.

That's the approach Helveg took to study a poorly understood phenomenon called catalytic oscillation, in which the transformation of reactants to products varies with time, even though reaction conditions remain constant. Working with Patricia J. Kooyman of the University of Cape Town and other researchers, Helveg probed oscillations in CO oxidation on platinum nanoparticles, a key reaction in catalytic converters to clean up vehicle emissions.

In a pioneering 2014 study, the team used a nanoreactor specially designed to carry out reactions in view of a transmis-

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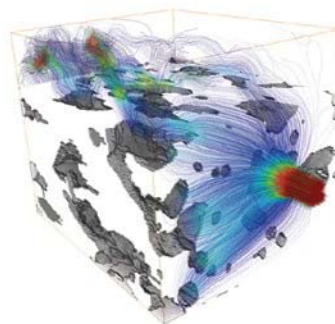
sion electron microscope (TEM) while maintaining gas pressures and catalyst temperatures at levels representative of automobile exhaust. The device enabled the team to record time-resolved TEM images and simultaneously measure mass spectrometry and calorimetry data during the oxidation reactions.

The investigation showed that the oscillatory behavior of the CO oxidation reaction is synchronized with a periodic, reversible change of the Pt nanoparticle shapes—going from rounded to faceted. The team found that when CO conversion was at its peak, the particles adopt highly faceted structures, proving experimentally that nanoparticle shape dynamics plays a key role in the reaction mechanism (*Nat. Mater.* 2014, DOI: 10.1038/nmat4033).

More recently, Helveg and coworkers coupled TEM analysis with surface X-ray

Video
online

Red, green, and blue lines represent pathways along which molecules can travel through a solid catalyst containing an internal network of interconnected channels. The network was exposed by using an ion beam to remove a layer of the material, then imaging the resulting exposed surface with electron microscopy, and repeating layer by layer. To see a video version of this graphic, visit cenm.ag/solidcat. White = solid regions; gray = pores and channels.



diffraction to study NO reduction, another key piece of automotive emissions cleanup chemistry. Again the team found that platinum catalyst particles undergo various types of reversible reconstructions and faceting during reactions at high temperatures and pressures. They also found that the changes, which alter the coordination and catalytic potential of surface atoms, depend on the composition of the engine exhaust. A hydrogen-rich atmosphere causes substantial faceting. In contrast, NO-rich environments induce particle rounding (*Phys. Chem. Chem. Phys.* 2017, DOI: 10.1039/c6cp08041c).

Emissions cleanup isn't the only vehicle-related process dependent on catalysts. About half the world's gasoline production comes from fluid catalytic cracking (FCC), a process that converts long-chain molecules in crude oil to shorter, more valuable compounds. Recently, Weckhuysen developed new imaging techniques to understand how FCC particles lose their catalytic prowess, a first step toward mitigating the problem and extending catalyst lifetimes.

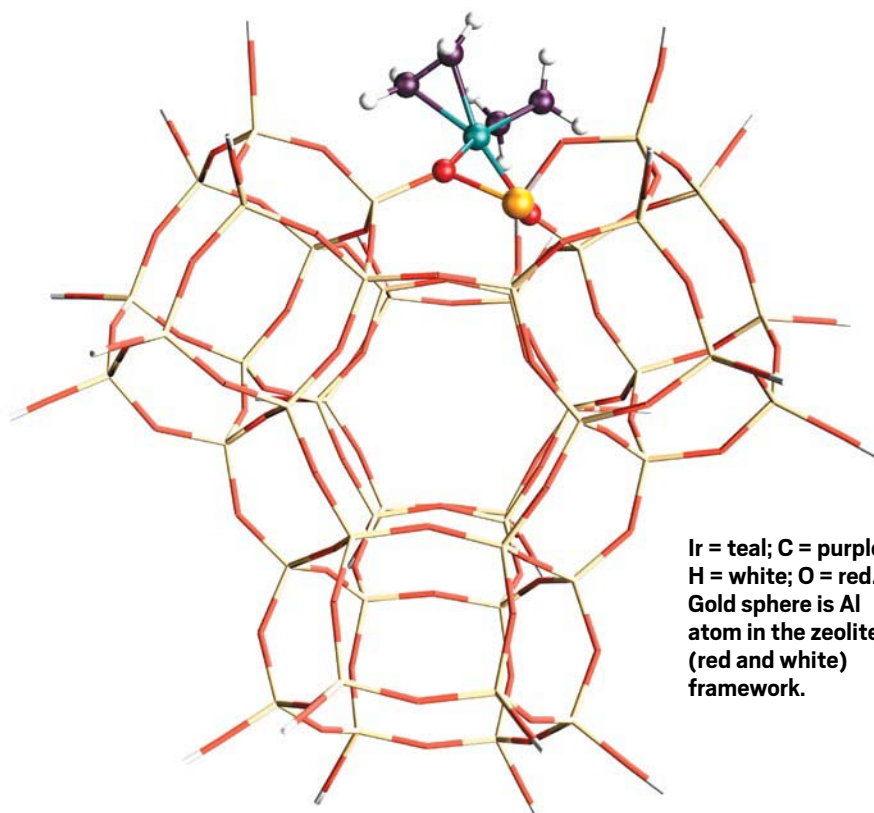
In one synchrotron-based study, Weckhuysen and coworkers used X-ray nanotomography to examine a series of fresh and used FCC catalysts. The catalysts typically consist of two active components held together by a binder: a zeolite, which is an aluminosilicate material with roughly 1-nm-wide pores, and a clay with larger pores. The aim of the study was to quantify changes in the porosity of individual FCC particles.

The team found that the catalysts fail because iron and nickel impurities from crude oil accumulate at the entrances to the clay's large pores. The metal particles prevent crude oil molecules from reaching

the zeolites' catalytic sites, which are located in narrow channels in the interior (*Sci. Adv.* 2015, DOI: 10.1126/sciadv.1400199). Modifying FCC catalysts with a higher concentration of a macroporous, clog-resistant clay in the outer layer might extend catalyst lifetimes, Weckhuysen suggests.

To learn more about the ability of FCC catalysts to shuttle reactant and product molecules through a particle's system of interconnected channels and pores, Weckhuysen and coworkers developed two additional three-dimensional imaging methods.

In one, they simultaneously recorded X-ray fluorescence and transmission X-ray microscopy data from single, whole FCC



Ir = teal; C = purple;
H = white; O = red.
Gold sphere is Al
atom in the zeolite
(red and white)
framework.

particles obtained from a commercial plant. Coupling data from both techniques provided a detailed picture, complete with nanoscale structural data and element mapping for six metals. The team used the results to virtually slice through a particle and simulate gradual aging and clogging of its pore network due to metal contamination (*Nat. Commun.* 2016, DOI: 10.1038/ncomms12634).

The other 3-D imaging method relies on a focused ion beam to sputter—basically sandblast with ions—a layer of material from an FCC catalyst followed by scanning electron microscopy imaging of the resulting exposed surface. By repeating the sputtering-imaging sequence numerous times, researchers can virtually restack the layers of images to provide a complete picture of the hidden interconnected and dead-end pathways through the channel network (*ACS Catal.* 2016, DOI: 10.1021/acscatal.6b00302). Both 3-D methods provide new ways to evaluate mass transport through today's porous catalysts and offer predictive tools for designing improved catalysts, Weckhuysen says.

X-ray absorption spectroscopy (XAS) ranks as one of the most popular methods for analyzing solid catalysts. And among XAS techniques, the variant known as

The iridium diethylene complex shown here bound to a zeolite surface serves as a reference structure for XANES spectroscopy and extends that method's analytical capabilities.

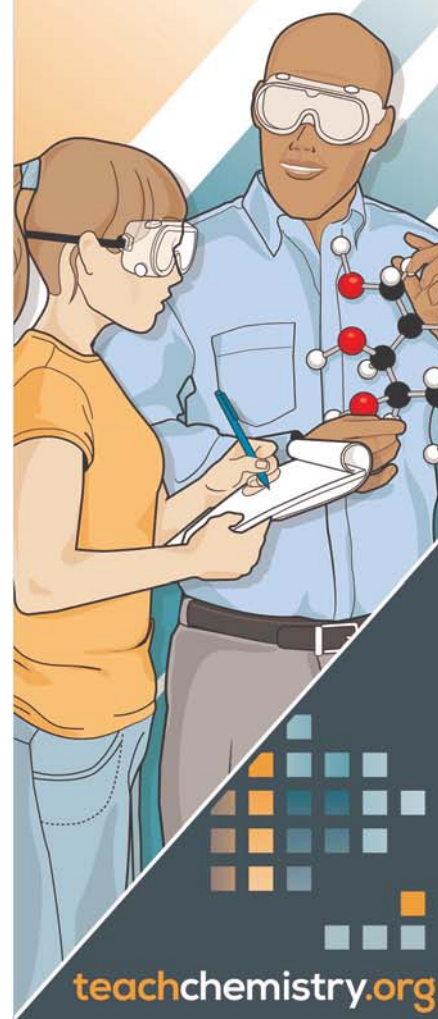
X-ray absorption near-edge structure (XANES) spectroscopy tops the charts. That method may soon become even more widely used thanks to an advance that overcomes one of its limitations.

Compared with a related method known as extended X-ray absorption fine-structure (EXAFS) spectroscopy, XANES is easier and faster. It also gives high-resolution, high-quality results under a variety of reaction conditions, even when being used to probe low-quality catalysts, according to Bare, who specializes in XAS methods. When applied to catalytic metals, XANES provides chemical information, including the metal atom's oxidation state and bonding geometry. But unlike EXAFS, XANES does not indicate what is bonded to the metal atom or provide other types of structural information.

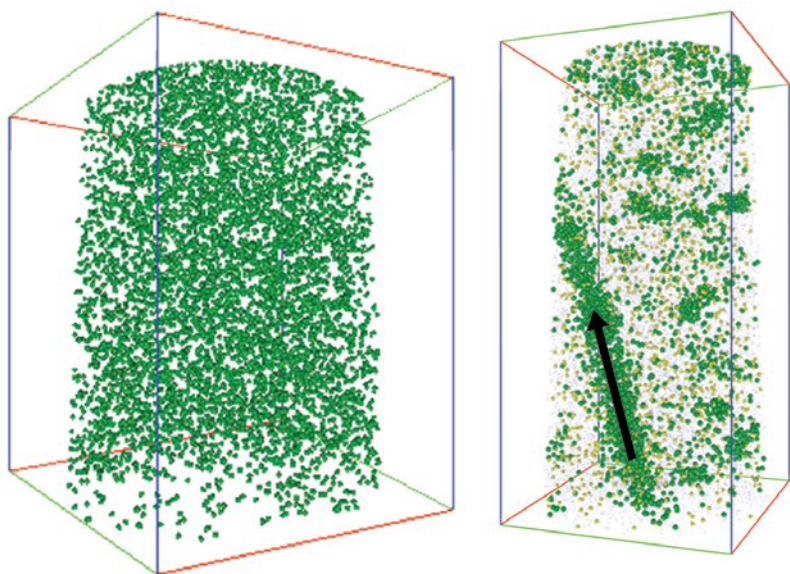
Bare is trying to change that. In a study conducted with Bruce C. Gates of the University of California, Davis, and others, he showed that XANES spectra recorded from carefully prepared reference complexes— $\text{Ir}(\text{C}_2\text{H}_4)_2$ and $\text{Ir}(\text{CO})_2$ bound to zeolite and MgO surfaces—contain unique fingerprints that unambiguously tie XANES data to the molecular structure of each of those complexes (*Chem. Eur. J.*

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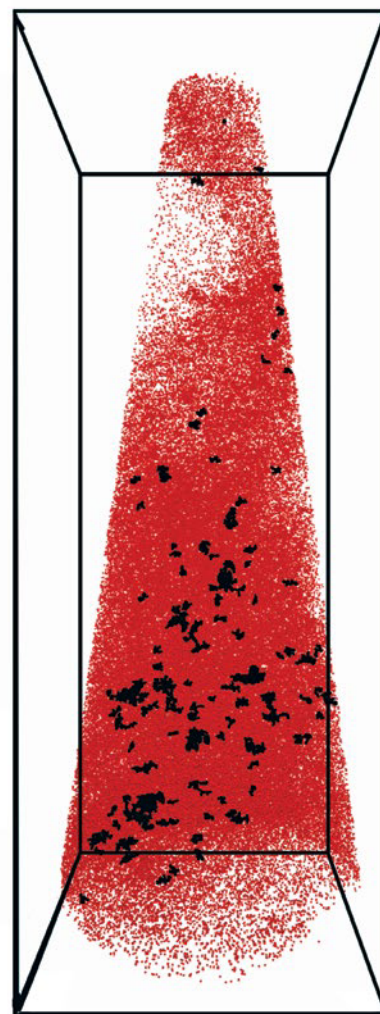
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Atom probe tomography images comparing an untreated zeolite crystal (left) with a steam-treated one (center, both images roughly 50-nm wide at base) show that aluminum atoms (green) cluster throughout the solid and accumulate along grain boundaries (arrow). The method also indicates that in a briefly used zeolite catalyst (right, 70-nm wide at base), carbon clusters (black) accumulate and potentially block the catalytically active aluminum atoms.



2017, DOI: 10.1002/chem.201701459).

The team used those complexes as references because they are typical of surface species encountered in reactions of organic compounds on solid catalysts. The plan now is to build a library of XANES reference spectra to help identify structures of unknown species that form on real catalysts.

Unlike X-ray methods, which are very popular for studying solid catalysts, atom probe tomography (APT) is rather uncommon. Nonetheless, APT is a powerful method. It provides, with subnanometer resolution, the 3-D position of atoms in needle-shaped specimens and indicates the chemical identity of those atoms.

Attracted by those capabilities, Bare and Weckhuysen teamed up with APT specialists to get an up-close look inside a commercial zeolite known as ZSM-5, which is used for hydrocarbon cracking, isomerization, and alkylation. They wanted to know where aluminum atoms reside within the zeolite. The locations are important because these atoms introduce negative charges that are typically balanced by protons. The resulting positive charges form Brønsted acid sites, which are responsible for much of zeolites' catalytic activity.

The group analyzed untreated and so-called steamed zeolites. Steaming is a standard procedure for activating zeolite catalysts. The researchers found that steam treating the zeolite leads to aluminum segregation and clustering, especially along crystal defects known as grain boundaries (*Nat. Commun.* 2015, DOI: 10.1038/ncomms8589). The finding shows that APT can pinpoint the location of aluminum atoms in zeolites, a technically challenging feat. It also suggests that the zeolite's catalytic properties may be tailored by tweaking synthesis conditions to control zeolite crystallization and the number of grain boundaries.

In a follow-up APT study, the team analyzed ZSM-5 catalysts that were briefly used to convert methanol to hydrocarbons. The researchers were looking for clues regarding the mechanism of coking, a process that harms catalysts by gunking up their surfaces with a layer of carbon. They used ^{13}C -labeled methanol to avoid ambiguities about the source of the carbon gunk. The team found that small carbon clusters—the first step in coking—formed and collected near the aluminum atoms, potentially blocking the catalytically active Brønsted acid sites (*Angew. Chem. Int. Ed.*

2016, DOI: 10.1002/anie.201606099). The team suggests that choosing conditions that minimize aluminum atom migration and clustering may be a strategy to impede accumulation of carbon particles and formation of coke.

“There is no shortage of innovation and new approaches when it comes to developing techniques for analyzing heterogeneous catalysts,” Bare says. “But with each new finding, we have to ask, ‘Are we studying something that’s truly meaningful? Is there a link between the data we just collected and the performance of that catalyst?’”

In some cases, the answer is clearly yes. In others, it’s hard to know, Weckhuysen says whimsically, because “heterogeneous catalysts are truly heterogeneous,” meaning they exhibit a headache’s worth of variation from particle to particle. That variation makes it tough to be certain that some newly observed feature or surface species on an isolated catalytic particle plays an important role in the reactions of all catalyst particles of that type.

“There’s still plenty of work to be done to pin down the important details in heterogeneous catalysis,” he adds. “But we’re definitely getting there.” ■