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ACS Meeting News

### Perfecting Solid-Catalyst Synthesis

ACS Meeting News: Researchers strive to devise methods that provide molecular-scale control

[Mitch Jacoby](#)

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## Videos

### Rotations

By analyzing a series of high-resolution micrographs of a porous particle of silica, researchers can produce computed three-dimensional images and videos of the particle (top) and of the pores inside the particle (bottom). Gold particles, which appear as dots scattered throughout the images, are embedded to aid in image alignment.



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Krijn de Jong \* Macromedia Flash Player 8 is required to view video.

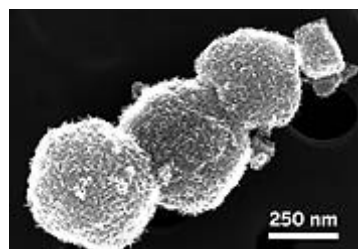
**IN THE COMPLEX WORLD** of catalysis, solid catalysts stand out as especially complex. Compared with liquid-phase catalysts, which generally are discrete molecules with clearly defined structures, solid catalysts can be more complicated to describe and more difficult to prepare, because they often consist of particles of one material in intimate contact with other materials.

Most researchers who study solid catalysts focus on the reactions they mediate. But some scientists in that field are developing molecular-level understanding of the synthesis steps by which those composite materials are made. They are devising new procedures to probe and control the size, dispersion, morphology, stability, and other properties of catalytic solids, and they are trying to encourage others to join them in their quest.

"More and more these days, we hear the call to transform the art of catalyst preparation into a science. Yet that call isn't being heeded as closely as it should be," said [John R. Regalbuto](#), a professor of chemical engineering at the University of Illinois, Chicago. Regalbuto, who presently is serving as a National Science Foundation catalysis program director, is one of several scientists who presented recent findings on catalyst synthesis last

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 insoluble in the gas and liquid reagents they transform. For example, most transformations in petroleum refining, pollution abatement, and production of fuels and chemicals are facilitated by supported catalysts. These composite materials typically consist of nanometer-sized metal particles attached to porous metal oxides, zeolites, carbon, and other high-surface-area supports and other combinations of solids.

Manufacturers have been making some very good catalysts for the past century, remarked Ferdi Schüth, director of the Max Planck Institute for Coal Research, in Mülheim, Germany. "But more or less they've been making them by trial and error," he said. By developing the skills and dexterity needed to control catalyst composition on the nanometer scale at will, the expectation is that researchers will be able to design and then synthesize new catalysts with greater activity and selectivity and make products with less energy input than the ones used today. Additionally, as Regalbuto pointed out, moving from a "largely empirical" discovery process to a more systematic theoretical approach will reduce the funds, time, and manpower currently invested in developing new catalysts.

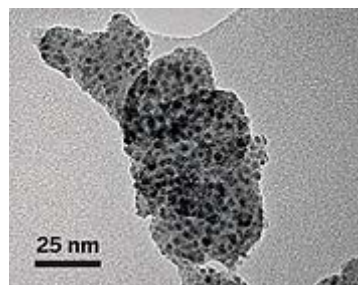


Harun Tüysüz & Hans Bongard  
Nanocasting The structure and porosity of these Co<sub>3</sub>O<sub>4</sub> particles can be tuned on the nanometer scale by controlling the morphology of the porous silica cast in which they were formed.

**A SYSTEMATIC APPROACH** to catalyst synthesis is exactly the tack followed by Krijn P. de Jong, a chemistry professor at Utrecht University, in the Netherlands. His group examined one of the most common large-scale methods for making catalysts: impregnating a porous support with a metal-nitrate or other catalyst precursor solution, followed by drying and heat-treatment steps. One of de Jong's objectives is to develop synthetic tools that can fine-tune catalysts for Fischer-Tropsch chemistry, which is a carbon-carbon coupling process for making synthetic fuels and chemicals.

Previously, the Utrecht group found that roughly 6 nm is an ideal size for supported cobalt Fischer-Tropsch catalyst particles. But making particles that size isn't the only challenge to preparing effective catalysts, de Jong said. The particles need to be uniform in size, evenly spaced to avoid agglomeration (clumping) and undesirable sintering (fusing into larger particles), and loaded into the support at high concentrations—on the order of 20% by weight. In general, Fischer-Tropsch catalysts described in research papers and symposia do not meet those criteria, de Jong pointed out.

To tackle those synthesis challenges, the team selected a model support material, a porous silica known as SBA-15, and began by examining the material's pore structure in detail. Those pores or hollow channels are often depicted schematically as simple and uniform in shape. But from a detailed electron tomography study, which recorded numerous images of a single particle at various sample-tilt angles, the group produced computed three-dimensional images and videos showing that those pores are rough and highly corrugated (*Chem. Mater.*, DOI: [10.1021/cm803092c](https://doi.org/10.1021/cm803092c)). Controlling the corrugation of the pores could provide a new handle for narrowing the size distribution of the particles contained therein, de Jong said.



Johan den Breejen  
Uniform species New synthesis methods yield silica-supported cobalt Fischer-Tropsch catalyst particles that are uniform in size (5 nm) and evenly distributed.

Impregnation is widely used to deliver catalyst precursor solutions to the interior surfaces of porous support materials. But few researchers routinely check whether that method actually fills the pores with solution. By and large, it does, de Jong concluded on the basis of calorimetry and microscopy studies of SBA-15 and other support materials. His group found that about 90% of the pores in various support materials are filled by that method.

After a catalyst precursor solution impregnates a porous solid, drying and heating steps convert the catalyst precursors to products. The steps generally include a high-temperature treatment known as calcination, which is often carried out by heating the sample in air. According to de Jong, X-ray and microscopy studies show that air calcination can reduce a catalyst's activity by driving the particles to agglomerate and cluster. To sidestep those harmful effects, the group searched for alternative calcination conditions and found that a dilute mixture of NO in helium does the job well by reducing the decomposition rate of metal nitrate precursors (*J. Catal.* **2008**, *260*, 227).

Demonstrating that various strategies for drying, calcining, and other preparation steps can be exploited to improve catalysts, the Utrecht team synthesized an 18 wt % cobalt Fischer-Tropsch catalyst on a commercial silica support. De Jong reported that the material consists of nearly uniformly sized and uniformly spaced 5-nm particles that exhibit some 50–60% greater activity for Fischer-Tropsch chemistry than other highly active catalysts studied by the Utrecht group.

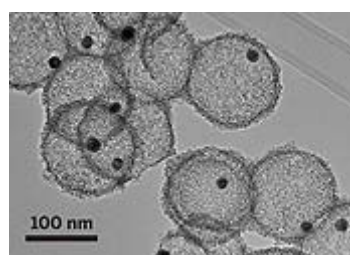
Like de Jong, Schüth also is devising synthesis methods that stabilize precious-metal catalyst particles against clustering. If particles remain small, a large fraction of the atoms are exposed at the surface and are available to mediate pollution-control and other types of reactions. But as particles begin clustering and fusing into larger particles, would-be catalytic sites become inaccessible in the particle's interior.

Recently, Schüth's group developed a way to protect gold particles from that fate by encapsulating them in a hollow oxide sphere. The procedure combines synthesis steps developed in Schüth's lab and elsewhere.

First, the team synthesized monodisperse gold particles roughly 16 nm in diameter and coated them with silica. That step yielded uniformly sized composite particles, 95% of which contained exactly one gold nanoparticle in the center. Then, the group formed a porous zirconia shell around the intermediate product and finally removed the silica by treating the material with sodium hydroxide. Displaying micrographs reminiscent of frog eggs, Schüth noted that the procedure resulted in hollow zirconia spheres containing a single off-center gold nanoparticle.

**"Moving to a more systematic theoretical approach will reduce the funds, time, and manpower currently invested in developing new catalysts."**

The encapsulated gold particles formed in this way are effectively separated from other particles but are highly accessible to gas molecules, which is crucial for heterogeneous catalysis, Schüth said. Indeed, he reported that these particles are remarkably active CO-oxidation catalysts and that they resist sintering even when exposed to high temperatures (800 °C) for an extended period. Schüth acknowledged that the multistep synthesis is time consuming and expensive but noted that it can be simplified in several ways and applied to other types of catalysts.



M. Paul & B. Spliethoff

**Caged gold** Each 16-nm gold particle (dots) sits in a hollow zirconia shell, leaving plenty of room for catalysis and almost no chance for sintering.

**STAYING WITH CO** oxidation but switching to another catalyst, Schüth described a nanocasting method for customizing ordered, highly porous oxides, such as  $\text{Co}_3\text{O}_4$ . The strategy in this case calls for fine-tuning the cast, which imparts structural properties to a material formed inside.

To make the casts, the Max Planck team prepared several samples of a porous silica known as KIT-6 by varying the temperature at which the material was "aged." Increasing the temperature increases the size and volume of the pores and decreases the thickness of the silica walls. In addition, it causes the two otherwise unconnected pore systems in KIT-6 to become connected through micropores.

The group impregnated the casts with a cobalt nitrate solution, dried and calcined the intermediate products, and subjected them to other treatments. Then, they removed the silica with alkaline solution and analyzed the catalysts. The investigation showed that by synthetically controlling the extent to which the pore systems of the nanocasts interconnect, the group could customize the structure, porosity, density, and surface area of the  $\text{Co}_3\text{O}_4$  product. Schüth noted that catalysts with the least connected pore systems and the highest surface area were the most active for low-temperature CO oxidation (*Chem. Commun.* **2008**, 4022).

Heterogeneous catalysis is especially tricky because the field is a hybrid of several chemistry disciplines, said Stuart Soled, a senior researcher at ExxonMobil who organized the symposium. As he explained it, the field draws from coordination chemistry, solid-state chemistry, inorganic and organic chemistry, surface chemistry, and chemical engineering.

Catalysis researchers would like to be able to specify and control the position of every atom in a catalyst, Soled said. They would like to design, a priori, molecular bonds, particle sizes, morphology, and other catalyst properties. That is one tall order, he acknowledged, adding, "We've made a lot of progress in that direction in recent years, but we still have a long way to go."

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