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"Abhaya is without question the best microscopist in catalysis and the best in chemical engineering."

Lanny D. Schmidt
Professor of Chemical Engineering
and Materials Science at the University
of Minnesota

# Microengineering for the Macroworld

**Abhaya Datye**, director of UNM's Center for Micro-Engineered Materials, has been a driving force towards understanding heterogeneous catalysts at the atomic level.

NEVER HAS so much depended on so little. Our ability to derive energy from biomass, to make fuel cells, to cleanly liquefy coal, and to meet the dramatically increasing global demand for automobile exhaust catalytic converters hinges on tiny nanoparticles that catalyze enormous volumes of reactants. Catalysis plays a key role in the global economy, accounting for 90% of manufacturing processes in the $375 billion U.S. chemical industry alone.

Understanding how heterogeneous catalysts work—especially the relationship between their atomic structure and function—will enable us to design materials with better reactivity, selectivity, and stability. At the forefront of this endeavor is Abhaya Datye, Director of UNM's Center for Micro-Engineered Materials and Associate Chair of Chemical and Nuclear Engineering.

"Abhaya is an outstanding catalytic scientist who has made exceptional contributions to our understanding and description of catalytic sites and species," says D. Wayne Goodman, Robert A. Welch Chair and Distinguished Professor of Chemistry at Texas A&M University.

With over 2,426 citations of more than 200 papers (66 of which have been cited between 10 to 76 times), Datye has exerted an enduring influence in the catalysis community. His seminal work in catalyst imaging has helped moved catalysis from an empirically-leaning "black art" towards a fundamental science of catalysis's atomic underpinnings. Due to this research, Datye has been invited to contribute to archival volumes such as the 40th anniversary issue of the *Journal of Catalysis*, two editions of the *Handbook of Heterogeneous Catalysis*, as well as a special issue of *Advances in Catalysis*. He has also given over 100 invited talks.

Datye's leadership is evidenced by his tenure as Program Co-Chair for the Snowbird North American Catalysis Society Meeting and his election to Vice-Chair and Chair of the next two Gordon Research Conferences on Catalysis, respectively. He sits on the editorial boards of *Applied Catalysis A, Catalysis Letters, Topics in Catalysis* and *Catalysis Communications.*

Datye has been awarded more than $16 million to investigate a broad range of topics including emissions control, methane combustion, selective hydrogenation, Fischer-Tropsch synthesis, methanol steam reforming, and electron holography. There is particular excitement about his recent forays into novel approaches to catalyst microengineering. Datye has a gift for identifying real industrial problems and, with his students, defining fundamental studies to address them. So far 20 Ph.D. and 22 Masters students have graduated from his group.

Goodman notes that Datye's work has also received extensive enthusiasm abroad. He has been invited to speak at the 2003 Europacat VI in Innsbruck, Austria (where he was the only U.S. keynote speaker on catalysis), the 1995 Taniguchi International Conference on Catalysis in Kobe, Japan (one of only two Americans invited), and the 2005 Topsoe Frontiers of Catalysis conference in Havreholm, Denmark, to name a few. He is a member in the Topsoe Global Catalysis Forum and the SASOL (South Africa) heterogeneous catalysis advisory board.

## Better Chemistry Through Microscopy

When Datye first arrived at UNM in 1984, catalysis studies were limited by imaging techniques that could only determine the averaged properties of materials. Transmission electron microscopy (TEM) studies were plagued by poor contrast because imaging was done through the tortuous substrate. Moreover, only projections of catalytic nanoparticles could be seen, which is problematic because real catalysts are irregular and have three-dimensional pore structures. Edges, kinks, and different crystal faces can greatly affect reactivity. Since catalysis is driven by the atomic structure of the first one or two monolayers, it was clear that a more detailed picture of the microstructure was needed.

Datye pioneered the use of nonporous oxides as model supports for heterogeneous catalysts that greatly facilitate imaging. Fabricated in spheres and other simple shapes, the supports do not interfere with the TEM beam, enabling Datye to easily image an abundance of nanoparticles in profile, discerning their atomic-scale structure, exposed crystal facets, and metal-support interfaces. The result of his work was a community-wide burst of surface data that could be directly correlated with catalytic behavior, laying the groundwork for greater theoretical understanding of surfaces at the atomic scale. His technique is now routine and widespread, and his early images of rhodium (Rh) particles deposited on titanium dioxide ($TiO_2$) are ubiquitous, appearing in a multitude of textbooks, handbooks, review articles and lectures (Figure 1). This work also garnered Datye the first of three invitations to speak at the Gordon Research Conference on Catalysis.

**Figure 1.** This textbook is just one of many examples that reproduce Datye's early transmission electron microscope images of rhodium particles. His technique has been instrumental in advancing understanding catalysis at the atomic level.

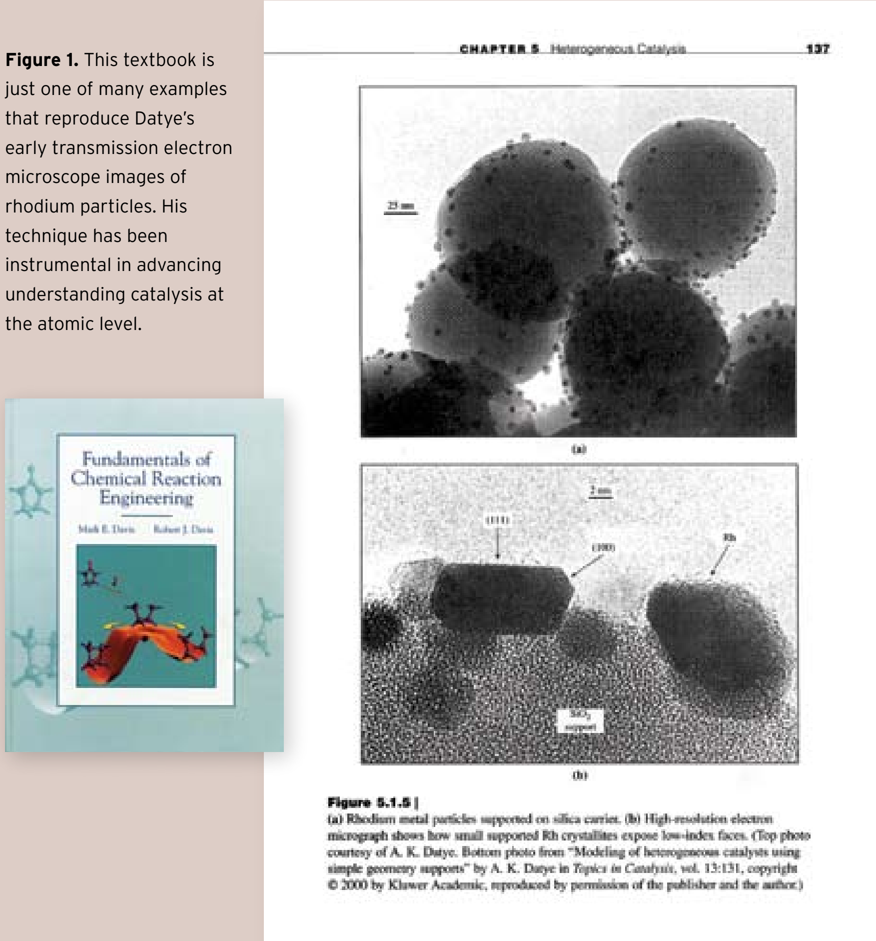

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**Figure 5.1.5 |**
(a) Rhodium metal particles supported on silica carrier. (b) High-resolution electron micrograph shows how small supported Rh crystallites expose low-index faces. (Top photo courtesy of A. K. Datye. Bottom photo from "Modeling of heterogeneous catalysts using simple geometry supports" by A. K. Datye in *Topics in Catalysis*, vol. 13:131, copyright © 2000 by Kluwer Academic, reproduced by permission of the publisher and the author.)

"Abhaya is without question the best microscopist in catalysis and the best in chemical engineering," notes Lanny D. Schmidt, a professor in the Department of Chemical Engineering and Materials Science at the University of Minnesota. "His papers have provided definitive results on the relationship between structure and reactivity in heterogeneous catalysis. He is one of the most creative scientists in catalysis today."

Datye's technique soon helped clarify thinking about a number of key topics in catalysis, such as strong metal-support interactions (SMSI). There is considerable interest in SMSI because it can be used to fine-tune catalytic selectivity, increasing the relative hydrogenation of carbon-oxygen bonds over that of carbon-carbon bonds, for instance.

Researchers knew that the activity of Group VIII metals deposited on $TiO_2$ changes significantly after the system is reduced in hydrogen at high temperatures, but they were not sure why. Previous micrographs suggested that the change might be due to a flattening of the metal particles. Datye's Rh images ruled out that hypothesis and provided the first visual and direct evidence that a suboxide of titanium covers the rhodium particles. His 1988 paper was cited 53 times.

Datye's group also elucidated why oxidation-reduction cycling, which industry uses to regenerate catalysts, increases their activity. The researchers studied the breakdown of n-pentane ($C_5H_{12}$) to methane and other hydrocarbons in the presence of Rh on silica as well as Rh in the (111) and (100) orientations. They found that the particles, which increase in size due to oxidation, are unable to shrink back into a single crystal during mild reduction, but instead form an aggregate of crystals in different orientations. As a result, the Rh surface is roughened, increasing the particle's surface area and hence its catalytic activity.

Datye is now interested in the restructuring of bimetallic catalyst particles such as those made from palladium (Pd) and silver, which are used in the conversion of acetylene to ethylene. As with rhodium catalysts, regeneration by oxidation (to remove hydrocarbon deposits) changes the activation energy for ethylene production as well as the relative selectivity of various other reactions. Datye's group has found the conditions for regeneration that promote the highest selectivity by breaking up ensembles of Pd atoms.

## Sinister Sintering

One of the big challenges for catalyst engineers is to reduce dependence on precious metals like platinum (Pt), Rh, and Pd, which are growing more scarce as demand for catalytic converters and other devices skyrockets globally. Current catalytic converters waste more than 90% of these metals because over time, and at elevated temperatures, small particles combine into larger particles, decreasing overall surface area and, hence, catalytic activity. Some of Datye's newest and most innovative work is to understand the forces behind this sintering as well as how to microengineer against it.

Utilizing a Hitachi S-5200 in-lens scanning electron microscope—the only one at a U.S. research university—Datye's group discovered that in addition to Ostwald ripening, sintering occurs also by the motion of large particles. (Ostwald ripening is atomic attrition from the relatively high surface area of small particles to less useful large particles.) It was previously thought that only small particles can move in a concerted fashion, but Datye's group has found that Pd particles as large as 30 nanometers can migrate over an oxide during heating (Figure 2). Subsequent in-situ studies in collaboration with Haldor Topsoe A/S in Denmark have confirmed this surprising result in real catalysts and have revealed a totally new sintering mechanism: Brownian motion. Much of this work is as yet unpublished. Datye's group has also studied the dynamics of individual Pd

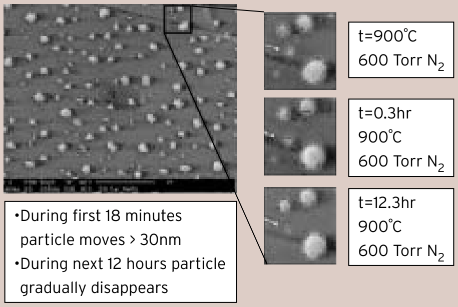

**Figure 2.** Datye discovered that during sintering, surprisingly large palladium particles can move over an oxide. The insets at right show three scanning electron microscope images of the same area over time.

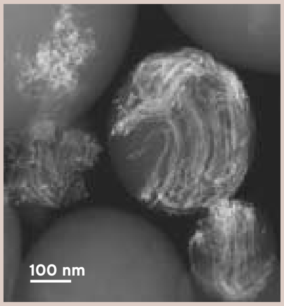

**Figure 3.** This scanning transmission electron microscope (high angle annular dark field) image shows platinum nanowires deposited inside the closed pores of silica spheres made by Evaporation-Induced Self-Assembly.

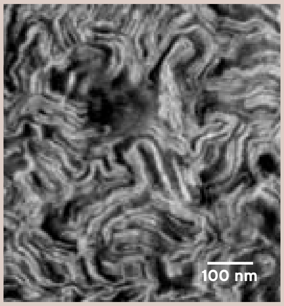

**Figure 4.** The platinum nanowires in this high resolution scanning electron microscope image follow a swirl-like pattern inside a silica sphere. By folding over into lamellar regions this configuration of pores may provide a new way of confining and protecting catalytic particles.

nanoparticles using an atom-tracking scanning tunneling microscope in collaboration with Brian Swartzentruber at Sandia National Laboratories. (Both Sandia and Los Alamos National Laboratories have afforded Datye many opportunities for collaboration, one of the reasons he originally chose to join UNM).

Thinking of new ways to prevent sintering, Datye has made "clever use of mesoporous silica," says Goodman. Datye's group has tested different porous structures to see how well each prevents particle migration and constrains particle growth. The best structure consists of one-dimensional pores within mesoporous silica particles, made by a technique called Evaporation-Induced Self-Assembly invented by UNM researchers Jeff Brinker (see accompanying profile on page 2) and Tim Ward. Remarkably, the catalyst particles are confined *inside* the closed sphere in a network of winding, folding tubes that appear to keep particles from aggregating or escaping (Figures 3 and 4). Nonetheless, the silica walls are thin enough to allow gases to permeate and react with the trapped catalyst. Datye shares a patent that utilizes these mesoporous silica to form attrition-resistant catalysts for Iron Fischer Tropsch catalysis in the production of synfuels. An exciting possibility for other applications is that engineers might be able to deposit a material on the outside of the spheres to absorb molecules like hydrogen sulfide that poison or inactivate the catalyst inside, greatly extending its life.

Datye's group has made scanning electron microscope images of the circuitous tube formations by synthesizing Pt nanowires inside the spheres. But Datye is also exploring whether these cylindrical wires would be more stable catalysts than spherical Pt nanoparticles by lowering the surface energy while sacrificing only a small amount of surface area. The group has also discovered how to make the silica itself thermally stable up to 800°C and how coating the pores with an oxide increases the number of nucleation sites for gold. Datye has been using gold because, while fairly inert in bulk, it is highly reactive on the nanoscale. In fact, it displays more reactivity at lower temperatures than Pt or Pd, making it an ideal candidate for removing car emissions when the engine is cold and for lowering energy costs associated with other high temperature processes. Best of all, gold is not in short supply. Datye hopes that these and other studies will eventually lead to a "self-healing" catalyst.

On another microengineering front, Datye's group has improved the activity of molybdenum sulfide ($MoS_2$), which is commonly used to clean sulfur or other contaminants from fossil fuels. In this case, the group increased $MoS_2$'s ability to remove nitrogen from pyridine by a factor of ten. This was accomplished by first depositing nanoscale dots of $TiO_2$ on a silica support. The layers of $MoS_2$ that were subsequently deposited were then confined to these tiny islands, limiting their size. Since the Mo atoms in the $MoS_2$ layers are only active at the edges, this serves to create more active Mo sites. But Datye's group also showed that the reactivity increased because the $MoS_2$ layers were curved over the nanodots, possibly because the curvature creates more strain in the $MoS_2$ layers, making the top surface more active too.

## Industrial Ties

Datye first became interested in catalysts after receiving a B.S. from the Indian Institute of Technology in 1975. While working for Hindustan Organic Chemicals (HOC), he was struck by the enormous expense and inconvenience incurred by the company each year when it had to shut down for several weeks to replace the degraded catalyst. No catalyst companies were able to come up with a better system at the time. Interestingly, on a later visit to HOC, Datye found that a consultant had discovered the mode of deactivation and devised a simple corrective method which restored the old catalysts that the company had luckily stored in barrels over the intervening years.

This experience points not only to the importance of understanding the atomic fundamentals of catalysis, but also to Datye's sensitivity to the problems encountered by industry. Indeed, Datye's impact in this commercially important field hasn't gone unnoticed by industry. He has given 25 invited talks to companies, from BP to UOP. He has also had significant collaborations and funded programs with companies such as Dow Chemical, Exxon, Allied Signal Environmental Catalysts, SASOL, and Catalytica. With his seminal scientific contributions, his eye for industrially relevant problems and his leadership in advancing the discipline, Datye proves the point that people can be catalysts too. ■

## For Further Reading

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### Electron microscopy of catalysts: recent achievements and future prospects

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**Abstract**

Electron microscopy is undoubtedly one of the most important tools for visualizing the morphology of industrial heterogeneous catalysts. With improvements in resolution, it is now possible to directly image the complex nanostructure of catalytic materials. Spectroscopic measurements performed in situ within the microscope provide elemental analysis and information on oxidation state and bonding. The development of in situ, controlled atmosphere instruments means that we can now study working catalysts, instead of simply doing postmortem examinations. In this review, we assess the state of the art and highlight some of the insights provided by microscopy in the study of catalysts. We then look to the future to see the developments on the horizon (notably aberration-corrected microscopy) that could have the largest impact on our ability to understand catalysts.

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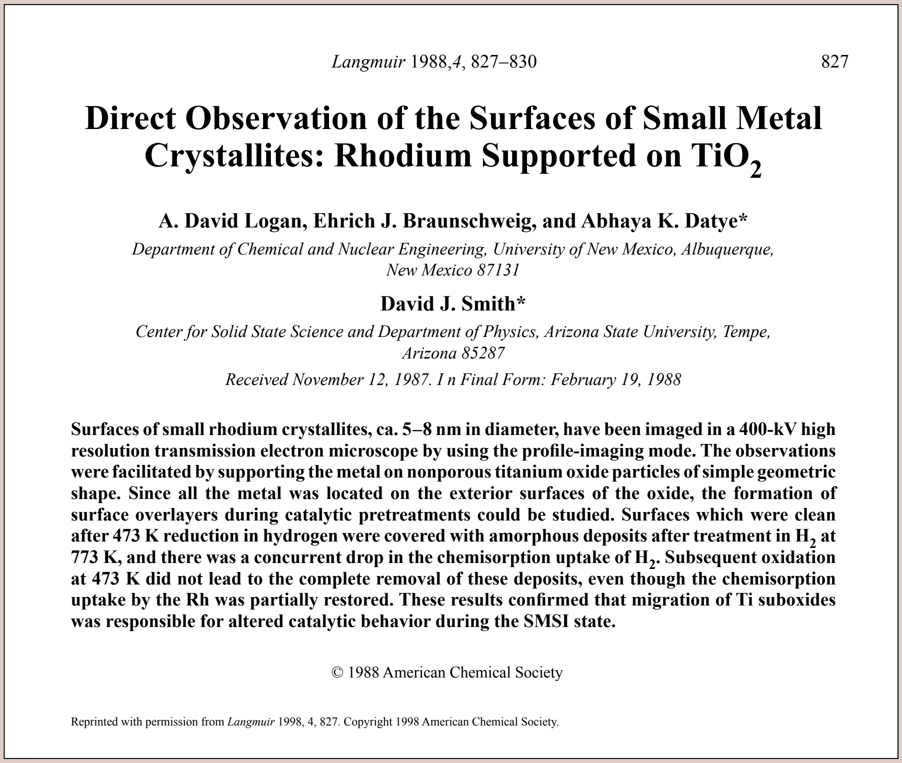

*Langmuir* 1988,*4*, 827–830 827

### Direct Observation of the Surfaces of Small Metal Crystallites: Rhodium Supported on $TiO_2$

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**Surfaces of small rhodium crystallites, ca. 5–8 nm in diameter, have been imaged in a 400-kV high resolution transmission electron microscope by using the profile-imaging mode. The observations were facilitated by supporting the metal on nonporous titanium oxide particles of simple geometric shape. Since all the metal was located on the exterior surfaces of the oxide, the formation of surface overlayers during catalytic pretreatments could be studied. Surfaces which were clean after 473 K reduction in hydrogen were covered with amorphous deposits after treatment in $H_2$ at 773 K, and there was a concurrent drop in the chemisorption uptake of $H_2$. Subsequent oxidation at 473 K did not lead to the complete removal of these deposits, even though the chemisorption uptake by the Rh was partially restored. These results confirmed that migration of Ti suboxides was responsible for altered catalytic behavior during the SMSI state.**

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