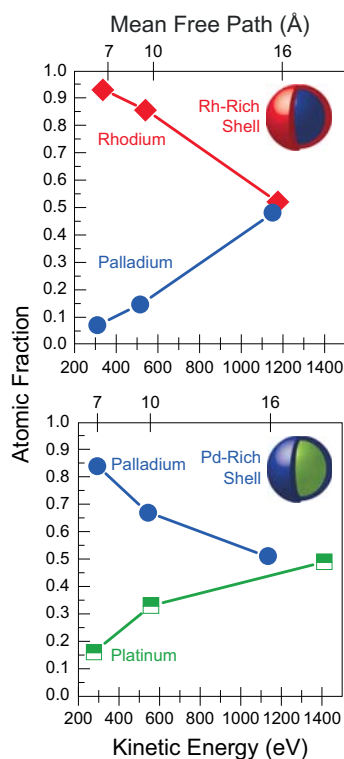


Reaction-Driven Restructuring of Bimetallic Nanoparticle Catalysts

Catalytic systems based on bimetallic particles with controlled size, composition, and structure dispersed on a high-surface-area support are widely used for catalytic reforming, pollution control, alcohol oxidation, and electrocatalysis in fuel cells. Owing to the nanoscale size of the particles, the modification of the surface structure and composition that may occur when reaction conditions change can have dramatic effects on catalyst activity and selectivity. Working at the ALS, a University of California, Berkeley-Berkeley Lab group has used an ambient-pressure x-ray photoelectron spectroscopy (APXPS) apparatus to demonstrate that bimetallic nanoparticle catalysts can undergo profound structural and chemical changes in response to reactive environments at ambient pressures, thereby opening the way for engineering catalysts with enhanced activity and selectivity.

Bimetallic catalysts (featuring active sites with two or more metallic elements) provide examples of some of the most active and selective catalysts yet discovered. Their performance advantages derive from a kind of "synergy": the two active metals somehow cooperate to enhance activity and/or selectivity relative to catalysts with only one metal. Nanoscale features such as surface structure and the distribution of the metals between the



nanoparticle surface and core are known to control their activity, selectivity, and lifetime, but these features can change dramatically during the course of a reaction. Monitoring the changes has not been possible, owing to the combination of the nanometer dimensions of the catalyst particles and the pressures and temperatures typical of the reaction environment, but without this information it is difficult to design a catalyst that responds optimally to the shifting conditions.

To investigate bimetallic catalysts under reaction conditions, the Berkeley group turned

Core-shell structure of nanoparticles. Dependence of rhodium and palladium atomic fractions of as-synthesized Rh_{0.5}Pd_{0.5} nanoparticles (top) and Pd and platinum atomic fractions (bottom) of the as-synthesized Pt_{0.5}Pd_{0.5} measured at 25 °C in UHV as a function of photoelectron kinetic energy and mean free path. Schematics showing the core-shell structures of the Rh_{0.5}Pd_{0.5} and Pt_{0.5}Pd_{0.5} nanoparticles are included (these schematics do not represent the shape of the nanoparticles).

to x-ray photoemission spectroscopy on ALS Beamline 9.3.2, where there is a unique ambient-pressure photoemission chamber that allows measurements at pressures up to 10 Torr, owing to the very small distance (less than one electron mean free path) through which the easily scattered photoelectrons travel in gas. The group prepared model catalysts consisting of rhodium-palladium (Rh_{0.5}Pd_{0.5}) and platinum-palladium (Pt_{0.5}Pd_{0.5}) nanoparticles arrayed on silicon dioxide wafers. Using a series of incident photon energies, which produced photoelectrons of dif-

ferent mean free paths (escape depths), made it possible to create depth profiles of the particle composition and chemical state. The profiles roughly corresponded to a surface shell, which is usually the catalytically active area, surrounding an interior core.

Measurements for each system began with as-prepared samples at room temperature in

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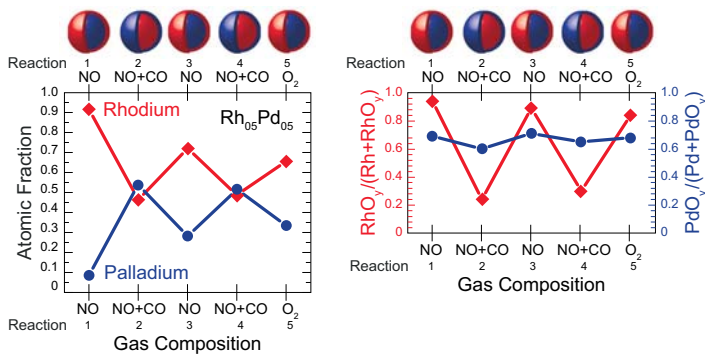
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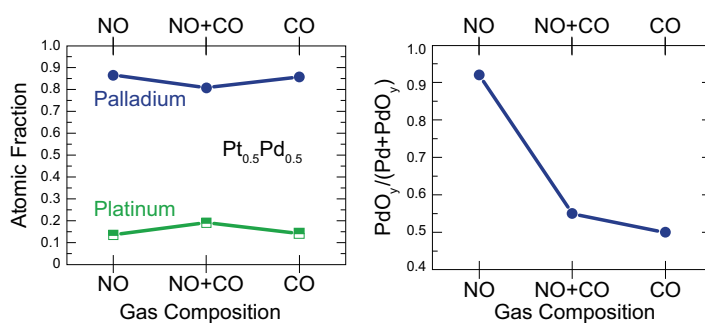
Watching Catalysts at Work

Catalysts—substances that speed up chemical reactions without themselves being consumed—are essential to the production of many industrially important chemicals. They also play a large role in environmental chemistry, most famously exemplified by the catalytic converters that reduce toxic emissions from vehicle tailpipes. Because of their importance, researchers all over the world are working to better understand how catalysts work and how to improve them, a stiff challenge both because many catalysts come in the form of tiny nanometer-sized particles and because they operate in gaseous atmospheres at high temperature that complicate probing. As a result, such nanoscale catalysts could until recently only be observed before and after, but not during, a reaction.

Bimetallic catalysts—small nanoscale metallic particles arrayed on a solid support—are a particularly important case in point. The distribution of the two metals composing the particles can shift between surface and interior during the catalysis process, but exactly how has not been known. At the ALS, Tao et al. have used an x-ray spectroscopy technique with a unique sample chamber to probe tiny catalyst particles under realistic conditions. This new window could give scientists the ability to develop cheaper and smarter catalysts that are fine-tuned to drive the chemistry of everyday life, such as reactions that sweep toxins from pollutants, feed hydrogen fuel cells, and drive fuel-refinement techniques.



Restructuring of $Rh_{0.5}Pd_{0.5}$ nanoparticles. Left: Evolution of Rh ($Rh^0 + Rh^{2+}$) and Pd ($Pd^0 + Pd^{2+}$) atomic fractions in the $Rh_{0.5}Pd_{0.5}$ at 300 °C under oxidizing conditions (100 mtorr NO or O_2) and catalytic conditions (100 mtorr NO and 100 mtorr CO). Right: Evolution of the fraction of the oxidized Rh (left y axis) and Pd atoms (right y axis) under the same reaction conditions. Schematic diagrams above the top of the figure show the reversible segregation of Rh and Pd under alternating oxidizing and catalytic conditions.



Lack of significant restructuring of $Pt_{0.5}Pd_{0.5}$ nanoparticles. Left: Evolution of the Pd and Pt atomic fractions in $Pt_{0.5}Pd_{0.5}$ NPs at 300 °C under oxidizing (100 mtorr NO), catalytic (100 mtorr NO and 100 mtorr CO), and reducing (100 mtorr CO) conditions. Right: Evolution of the atomic fraction of the oxidized Pd atoms under the same reaction conditions.

ultrahigh vacuum and continued with a sequence of measurements under oxidizing conditions (10 mTorr O_2 or NO) at 300 °C, catalytic conditions (100 mTorr of NO and 100 mTorr of CO), and reducing conditions (100 mTorr CO or H_2). The catalysts were also cycled between oxidizing and catalytic conditions to determine the reversibility of any composition changes observed. The group found that the as-prepared $Rh_{0.5}Pd_{0.5}$ nanoparticles had rhodium-rich shells and

$Pt_{0.5}Pd_{0.5}$ nanoparticles had palladium-rich shells. Thereafter, the composition of the shell and the core-shell distribution of the constituent elements of the $Rh_{0.5}Pd_{0.5}$ nanoparticles changed dramatically but reversibly in response to changes in the ambient gas composition, whereas no substantial composition shifts occurred in the $Pt_{0.5}Pd_{0.5}$ nanoparticles other than oxidation of the palladium at the surface under oxidizing conditions.

The divergent restructuring

behaviors of the two catalyst systems under the same reaction conditions illustrate the flexibility and tunability of bimetallic nanoparticle catalysts during catalytic reactions. The group believes that the restructuring offers an interesting way of controllably engineering the nanostructures for catalysis (or

other applications) with the use of reactive gases. Designing new catalysts and shaping the catalytic properties of nanomaterials by structural engineering in reactive environments could ultimately yield “smart” catalysts whose structures change advantageously depending on the reaction environment.