

WHO SHRUNK THE CATALYST?

Smaller is better for a metal catalyst, but smaller also means more compact in terms of the metal's atomic structure. Chemical engineers often fabricate metal catalysts in the form of nanoparticles in order to increase their reactive surface area. However, the small size can lead to structural changes in how the metal atoms assemble together. A new suite of x-ray experiments on platinum (Pt) nanoparticles gives the most detailed picture yet of the consequences of going small. Measurements taken at three different x-ray beamlines at the APS confirm that atom-spacing becomes smaller as the size of a nanoparticle decreases, but the spacing expands back to near normal when gas molecules adsorb on the surface (Fig. 1). Because this contraction-relaxation affects the way reactants behave on the metal surface, the results of these experiments may help in designing better catalysts.

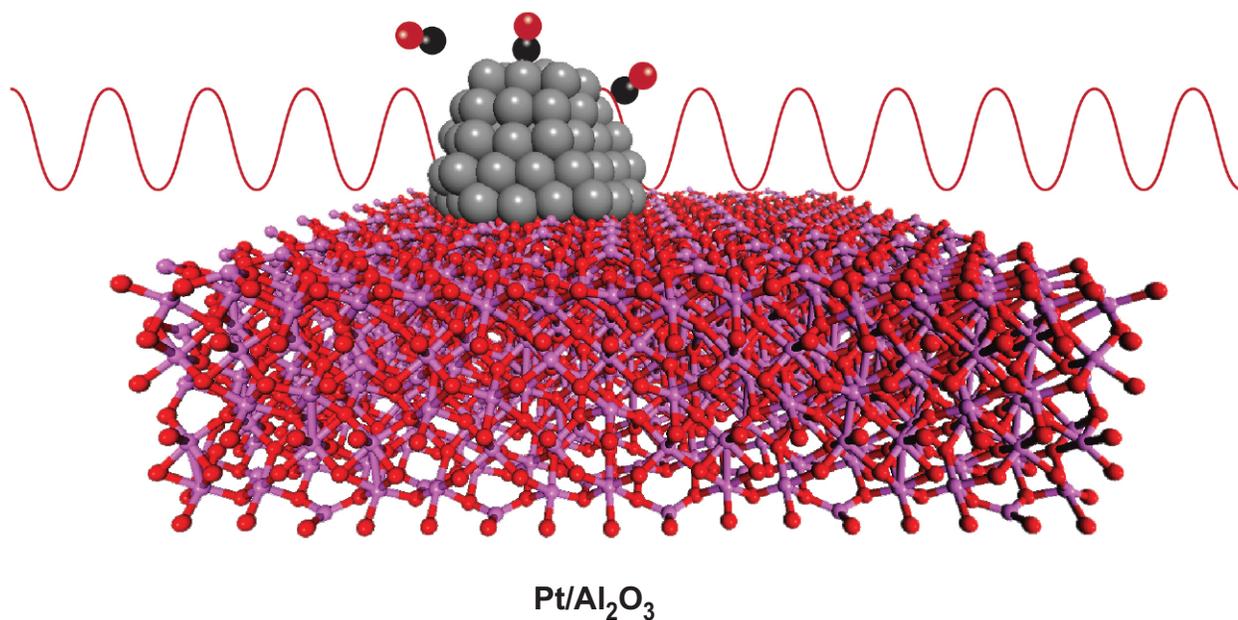


Fig. 1. Combined experimental and theoretical studies of Pt nanoparticles on alumina (Al_2O_3) characterize precisely the contract and expansion of the lattice parameter caused by different chemical environments.

Platinum, nickel, palladium, and similar metals are used as catalysts in the petroleum and pharmaceutical industries to accelerate organic synthesis, as well as in car exhaust systems to remove toxic fumes. These metals are able to drive reactions by trapping reactants on their surface. Therefore, for a given amount of metal, reaction rates can be increased if the material is divided up into nanoparticles that have a high surface-to-volume ratio.

Earlier x-ray studies suggested that metal nanoparticles are slightly

smaller in size than one would expect from the atom-spacing found in normal chunks of metal. One possible explanation for this contraction is that atoms forming the outer surface are pulled inward because they have no neighbors pulling from the other side. Previous experiments have found evidence for this model, but scientists would still like to understand precisely how the surface atoms behave in different circumstances.

Scientists from the Argonne and Brookhaven national laboratories, the

University of Alabama in Huntsville, Kansas State University, and Purdue University performed both x-ray scattering and spectroscopy measurements on Pt nanoparticles.

The team began by growing Pt nanoparticles on powder grains of alumina (Al_2O_3). A powder substrate like this is often used for industrial catalysts. However, the researchers used a special atomic layer deposition process that controlled the size of the Pt nanoparticles by varying the number of deposition cycles. Three separate sam-

ples were produced with nanoparticle widths of 1, 2, and 3 nm, as measured through small-angle x-ray scattering (SAXS) at the XSD 12-ID-B x-ray beamline at the APS.

The prepared samples were next placed in the XSD beamline 11-ID-B, where total scattering measurements revealed typical atom separations as represented by the pair distribution function (PDF, Fig. 2, left).

The sample chamber was initially filled with helium gas, which doesn't absorb on platinum. In this "bare surface" case, the atomic separations for 1-nm wide Pt particles were on average 1.4% smaller than those in normal bulk metal. Similar contraction was observed — but to a lesser degree — for the bigger nanoparticles in the other two samples.

However, during catalysis, the nanoparticle surfaces will not be bare. To explore this, the team first injected hydrogen gas (H_2) into the sample chamber. The hydrogen adsorbed on the platinum, exemplifying the typical reduction step in a catalytic cycle. Afterwards, the team purged the system and introduced carbon monoxide (CO), which represents the complementary oxidation step in a catalytic cycle.

For both gas exposures, x-ray scattering measurements showed that the adsorption caused the nanoparticles to expand from their contracted bare surface state. However, the amount of expansion was not the same in the two cases. Nanoparticles with CO on their surfaces had slightly larger interatomic separations than nanoparticles with H_2 adsorption.

To understand the chemical bond behavior during this contraction and expansion, the researchers performed x-ray absorption spectroscopy (XAS) at the 10-BM-A,B beamline of the MR-CAT at the APS (Fig. 2, right).

The nanoparticles exhibited different absorption spectra, depending on whether the surrounding gas was helium, hydrogen or carbon monoxide. The largest spectral differences occurred for the 1-nm wide sample, which suggests that smaller nanoparticles form stronger bonds with the adsorbed gas molecules.

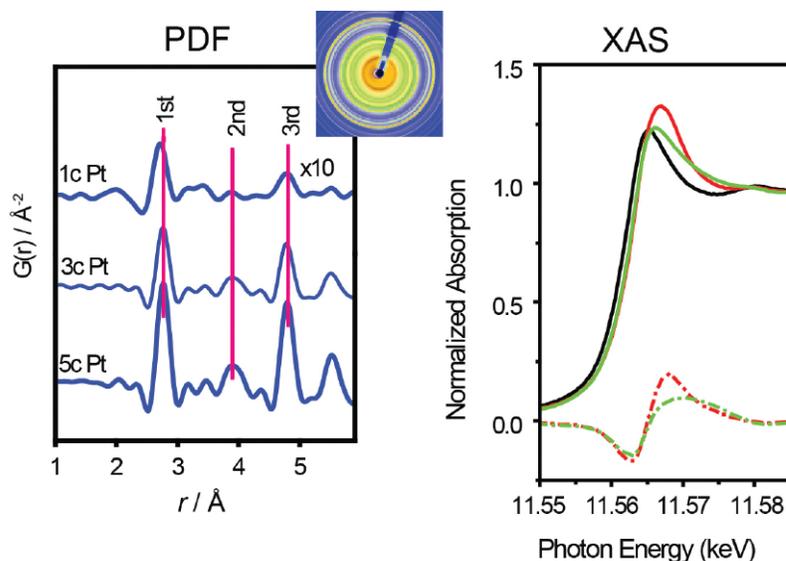


Fig. 2. *Left:* The PDF, which is derived from x-ray scattering data, has peaks that correspond to atomic separations in Pt nanoparticles that are 1-nm wide (labeled 1c Pt), 2-nm wide (labeled 3c Pt) and 3-nm wide (labeled 5c Pt). The two-dimensional diffraction image (upper right inset) represents the data used to construct the PDF. *Right:* X-ray absorption spectroscopy measurements show differences in the chemical bond structure when 1-nm-wide Pt nanoparticles are exposed to the following gases: helium (black), hydrogen (solid green), and carbon monoxide (solid red). Also displayed are the spectral differences between hydrogen-helium (dashed green) and carbon monoxide-helium (dashed red).

Such quantitative information could be useful in designing catalysts, since engineers want a material that can hold reactants on its surface, but not too strongly. Finding the right balance may simply be a question of sizing up nanoparticles. — *Michael Schirber*

See: Yu Lei², Haiyan Zhao¹, Rosa Diaz Rivas³, Sungsik Lee¹, Bin Liu⁴, Junling Lu¹, Eric Stach³, Randall E. Winans¹, Karena W. Chapman¹, Jeffrey P. Greeley⁵, Jeffrey T. Miller¹, Peter J. Chupas¹, and Jeffrey W. Elam^{1*}, "Adsorbate-Induced Structural Changes in 1–3 nm Platinum Nanoparticles," *J. Am. Chem. Soc.* **136**, 9320 (2014).

DOI: 10.1021/ja4126998

Author affiliations: ¹Argonne National Laboratory, ²University of Alabama in Huntsville, ³Brookhaven National Laboratory, ⁴Kansas State University, ⁵Purdue University

Correspondence: * jelam@anl.gov

This material is based upon work supported as part of the Institute for Atom-efficient Chemical Transformations, an Energy Frontier Research Center funded by the U.S. De-

partment of Energy (DOE) Office of Science-Basic Energy Sciences. MR-CAT operations are supported by the DOE and the MR-CAT member institutions. Y.L. gratefully acknowledges the start-up support by the University of Alabama in Huntsville. B.L. also thanks the start-up support by the Kansas State University. This research used resources of the Advanced Photon Source, a U.S. DOE Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

10-BM-A,B • MR-CAT • Materials science, chemistry, environmental science, physics • X-ray absorption fine structure, x-ray lithography, tomography • 3-200 keV, 4-32 keV • On-site •

11-ID-B • XSD • Chemistry, environmental science, materials science • Pair distribution function • 58.66 keV, 86.7 keV • On-site • Accepting general users •

12-ID-B • XSD • Chemistry, materials science, life sciences, polymer science, physics • Small-angle x-ray scattering, grazing incidence small-angle scattering, wide-angle x-ray scattering, grazing incidence diffraction • 7.9-14 keV • On-site • Accepting general users •