Hydrogen Adsorption on Shape-Shifting Platinum Nanoparticles

he adsorption of hydrogen gas onto a solid material is a technologically-important phenomenon, showing promise, for instance, as a safe and efficient means of hydrogen storage. In the case of platinum, the adsorbed hydrogen resides in a thin layer on its surface. Considerable attention has been devoted to increasing the efficiency of hydrogen adsorption, including the use of solid nanoparticles (typically 1 nm to 100 nm across). Recent theoretical and experimental results indicate that decreasing nanoparticle size below the nanometer level enhances adsorption. Now, research carried out at the APS by scientists from the University of Central Florida, UOP LLC (Honeywell), and Ruhr-University Bochum (Germany) confirms earlier theoretical work linking nanoparticle morphology with hydrogen coverage. Since the pressures and temperatures used in this research mimic industrial conditions, these results may well lead to improvements in hydrogen storage, hydrogenation reactions, and electrocatalysis.



Fig. 1. The number of hydrogen atoms per surface Pt atom (H/Pt) determined from XANES measurements on 22 atom Pt/ γ -Al₂O₃ nanoparticles in H₂ pressures from 1-21 bar. The inset shows the initial biplanar 2-D shape of the Pt22 particles and a possible model 3-D shape at higher pressures after a shape transformation.

10-ID-B • MR-CAT • Materials science, environmental science, chemistry • X-ray absorption fine structure, time-resolved x-ray absorption fine structure, micro x-ray absorption fine structure, microfluorescence (hard x-ray) • 4.3-27 keV, 4.3-32 keV, 15-90 keV • On-site • Accepting general users •

In this research, the degree of hydrogen adsorption on sub-nanometersized platinum (Pt) particles deposited on aluminum oxide (Al₂O₃) was measured at room temperature as hydrogen pressure ranged from one to twentyone bar. X-ray absorption measurements performed at MR-CAT beamline 10-ID-B of the APS showed that the hydrogen to platinum ratio (H/Pt) increased with increasing pressure, which was accompanied by a change in nanoparticle shape from a raft-like two-dimensional (2-D) structure into a three-dimensional (3-D) form.

The platinum nanoparticles used here were both shape- and size-se-lected, with an average diameter of 0.8 nm (± 0.2 nm). The nanoparticles were deposited onto a high-surface-area aluminum oxide support (Pt/ γ -Al₂O₃, where γ denotes the crystalline phase of the Al₂O₃). The supported platinum nanoparticles possessed a raft-like shape (see 2-D inset, Fig. 1).

Two x-ray absorption techniques were used to probe the $Pt/\gamma - Al_2O_3$ sample: x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS). In both techniques, x-rays were used to excite core electrons in the platinum atoms. The XANES technique was used to determine the sample's hydrogen to platinum ratio (H/Pt) as the pressure of the hydrogen gas was steadily increased. The XANES measurements showed that as H₂ pressure increased, the adsorption of hydrogen onto the surface of the platinum nanoparticles also increased. The average H/Pt ratio rose from ~1.9 at a pressure of 1 bar, to a maximum ratio of ~2.5 at 21 bar. However, this rise in the H/Pt ratio as a function of pressure was non-linear, as indicated by Fig. 1.

The other x-ray technique, EXAFS, was employed to determine any structural changes in the platinum nanoparticles as hydrogen gas pressure rose. These structural changes were deduced from two parameters: the first nearest neighbor (NN) coordination number, and the atomic bond lengths. The platinum-to-platinum (Pt-Pt) coordination number indicates the average number of neighboring platinum atoms forming a Pt-Pt bond within the nanoparticles. On the other hand, the Pt-O coordination number indicates the average number of oxygen atoms neighboring a platinum atom, representing the Pt-O bonds formed between a platinum atom at the nanoparticle-support interface and oxygen atoms in the support material.

Figure 2a shows how the first NN coordination number for the platinum atoms rose with increasing hydrogen adsorption (due to increasing H₂ pressure). By contrast, the coordination number for Pt-O pairs (not shown) decreased as the hydrogen pressure and coverage grew larger, indicating a rupture of the interfacial connection between the platinum nanoparticles and their Al₂O₃ support.

Figure 2b shows a gradual increase in the Pt-Pt bond lengths with increasing hydrogen coverage (due to increased pressure) from 1 through 16 bar, with a sudden decrease at 21 bar, likely associated with the decrease in the contact area of the nanoparticles with the support. All these EXAFS results - the increase in platinum coordination number and bond length, along with the separation of the platinum nanoparticles from the Al₂O₃ support — indicate a transition in nanoparticle structure from a two-dimensional biplanar form into a three-dimensional configuration. Figure 2a indicates one possible scenario (shown in red) for this 2-D-to-3-D transition based upon theoretical considerations. However, further research will be required to determine the actual three-dimensional shape of these platinum nanoparticles.

These findings confirm the results of other studies involving platinum nanoparticles, namely that the use of smaller-sized particles (in this case, sub-nanometer particles) leads to an increase in hydrogen adsorption.

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Fig. 2. EXAFS data revealing structural changes in Pt₂₂ nanoparticles supported on γ -Al₂O₃ with increasing surface hydrogen coverage. a) Average Pt-Pt 1st nearest neighbor coordination number acquired from EXAFS data of Pt₂₂ nanoparticles (black triangles) as a function of the H/Pt ratio at the particle surface. Blue circles show theoretical predictions for Pt₁₃ nanoparticles from Mager-Maurey et al. b) Average Pt-Pt bond length in Pt₂₂ nanoparticles as a function of H/Pt.

Cuenya^{1,3*}, "Pressure-Dependent Effect of Hydrogen Adsorption on Structural and Electronic Properties of Pt/γ-Al₂O₃ Nanoparticles," Chem. Cat. Chem. **6**, 348 (2014). DOI: 10.1002/cctc.201300783 *Author affiliations:* ¹University of Central Florida, ²UOP LLC (Honeywell), ³Ruhr-University Bochum

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