

REFINING THE WAY CATALYSTS ARE MADE

Platinum supported on alumina catalysts are important for production of high-octane gasoline in the petroleum industry and exhaust gas abatement in the automotive industry. A better understanding of how these catalysts are produced is crucial for the preparation of more effective catalysts in the future. The Revised Physical Adsorption (RPA) model simulates the uptake of Pt versus pH onto alumina but is simplistic in that only the doubly valent $[\text{PtCl}_6]^{2-}$ complex is considered. Because previous studies suggested that other Pt complexes might be present in the preparative solutions, investigators from the University of Illinois at Chicago, BP Research Center in Naperville, Illinois, and Argonne National Laboratory collaborated to refine the RPA model. By characterizing the molecular changes that occur when Pt complexes are adsorbed onto alumina, a better understanding of Pt adsorption is expected to lead to better control of the composition and performance of these catalysts.

The high sensitivity of the undulator beamline at MR-CAT, APS sector 10, was used to determine, via extended x-ray adsorption fine structure (EXAFS) measurements, the structures of Pt complexes in dilute solution and adsorbed on alumina. The exact structures of the aqueous Pt species were highly dependent on the Pt and Cl concentration, pH, and age of the solutions. For example, aqueous solutions of H_2PtCl_6 , which are commonly used to prepare catalysts, were observed to undergo rapid hydrolysis, giving Pt (IV) complexes with 3 Cl and 3 O ligands (Fig. 1). Although EXAFS cannot distinguish between OH and H_2O ligands, a proton balance indicated that the initial O ligands were H_2O . After about 24 h, as the solutions age, the H_2O ligands are exchanged by OH ions. The number of hydroxide ligands also increases as the pH increases.

In aqueous solution, γ -alumina with a surface area of about $200 \text{ m}^2/\text{g}$ becomes positively charged. A "double layer" theory is the kernel of the RPA model, which predicts that there is a Coulombic attraction between the negatively charged Pt complexes and the positive surface charge on alumina. Pt complexes, which initially contain H_2O ligands, are positively charged and not readily adsorbed. Aged solutions with hydroxide ligands, however, are readily adsorbed and lead to the formation of small particles upon reduction. EXAFS analysis (Fig. 1) also indicates that the Pt species undergo additional changes upon adsorption. These structural changes are due to the influence of the surface pH of the alumina. Proper control of the support, pH of the preparative solutions, and the charge on the metal complex, leads to monolayer coverage of the support and smaller metal particles upon reduction.

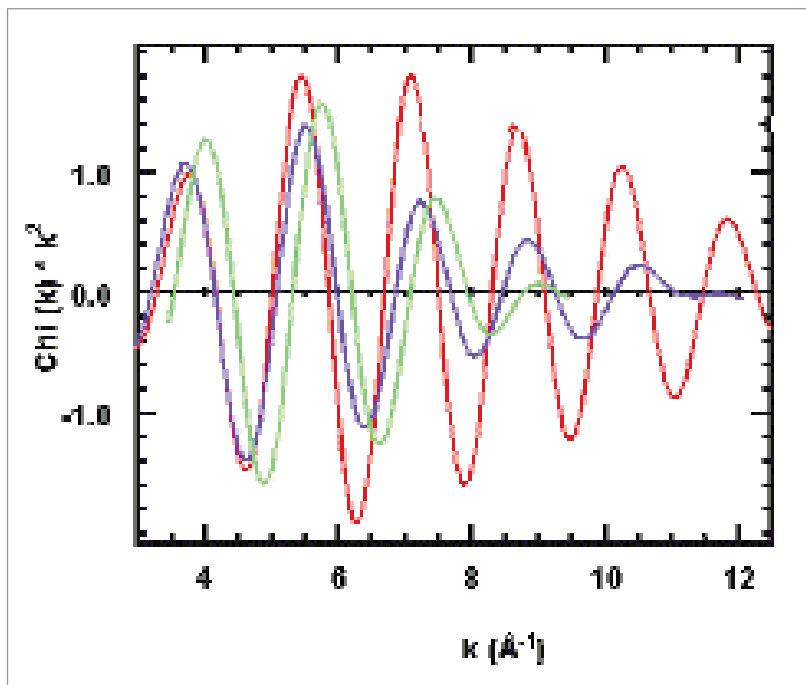


Fig. 1. k^2 -weighted EXAFS of solid H_2PtCl_6 (6 Pt-Cl at 2.32 \AA in red); 200 ppm H_2PtCl_6 at pH = 2.5 (2.7 Pt-Cl at 2.32 \AA and 3.3 Pt-O at 2.05 \AA) in blue; 200 ppm H_2PtCl_6 at pH = 2.5 adsorbed on alumina (1.7 Pt-Cl at 2.32 \AA and 4.3 Pt-O at 2.05 \AA) in green.

From this and similar studies, a general understanding has been developed that makes it possible to make superior catalysts with nearly any metal on any support. By using these advances, a simple method for production of a new generation of fuel cell electrodes, which has a very high Pt loading and very small metallic particles, has been recently developed. This work has attracted the interest of several catalyst manufacturers and is currently under development. ^m

See: W.A. Spieker¹, J. Liu¹, X. Hao¹, J.T. Miller², A.J. Kropf³, and J.R. Regalbuto¹, "An EXAFS study of the coordination chemistry of hydrogen hexachloroplatinate (IV) 2. Speciation of complexes adsorbed onto alumina," *Appl. Catal. A* **243**, 53-66, (2003).

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