Trends in X-ray Absorption Near Edge Spectroscopy of Supported Pt Nanoparticles

Randall Meyer[1]* Yu Lei[1], and Jeffrey Miller[2]*
[1]*University of Illinois at Chicago, Chicago, IL 60607 (USA)*
[2]*Argonne National Lab, Argonne, IL 60439 (USA)*
*rjm@uic.edu *millerjt@anl.gov

Introduction

Metal clusters have been shown to demonstrate unique activity as their length scale is shrunk to the nanometer scale. However, a detailed understanding of the factors that control the reactivity of supported metal clusters has yet to be fully developed. We have undertaken an analysis of X-ray Absorption Near Edge Spectroscopy (XANES) of supported Pt catalysts to examine the change in electronic structure with particle size over varying catalytic supports (SiO_2, Al_2O_3, C, SiO_2-Al_2O_3, TiO_2). X-ray Absorption Fine Structure (XAFS) spectra were also analyzed to document the variation in Pt lattice constant with support and particle size. Density Functional Theory (DFT) calculations were performed to aid in the analysis of electronic structure and to establish relationships between the density of states and the white line intensity in the XANES spectra.

Materials and Methods

XAFS measurements were made at MRCAT-10 at the Advanced Photon Source at Argonne National Lab. The measurements were performed in flow reactor cells. All catalysts were reduced with hydrogen at 300 C (or 450 C in the case of Al_2O_3). After reduction, the cell was purged with He while holding the catalyst at high temperature. Additional measurements were made after exposure to CO at room temperature. XANES measurements were taken at the L_I (eV), L_{II} (eV) and L_{III} (eV) edges. Data analysis was performed with the WinXAS software. Fits were performed with k^2 weighting to ensure accuracy. DFT calculations were performed using the program VASP[1] with a plane wave basis set and ultrasoft pseudopotentials with periodic supercells.

Results and Discussion

In Figure 1, the lattice constant of Pt is plotted against particle size. As has previously been observed for supported Au catalysts [2], the lattice constant decreases dramatically as the particle size decreases below 4 nm. In addition, at the L_{III} and L_{II} edges, for particles smaller than 4 nm, there is a decrease in the XANES intensity (not shown) consistent with an increase in the *d*-electron density. However, since the L_I transition is an electronically forbidden transition, there is no change in the XANES intensity with particle size. DFT calculations confirm the contraction in the Pt-Pt bond distance in isolated clusters. In contradiction to anecdotal reports, neither the lattice constant nor the white line intensity were dependent upon the support. DFT calculations were used to observe changes in the density of states (DOS) as a function of particle size. As expected, the density of states shifts towards the Fermi level as the cluster size decreases as shown in Figure 2.

The white line intensity increased dramatically when CO was adsorbed on the catalyst. In fact, this increase in adsorption could be correlated with the catalyst surface area as Pt on TiO_2 did not demonstrate any CO adsorption after annealing at elevated temperature due to encapsulation of Pt by the reduced support. DFT calculations were used to analyze the perturbation in the density of states in the valence region upon CO adsorption. The increase in white line intensity is ascribed to hybridization of *d*-orbitals involved in back donation to the CO pi-bond. Unfortunately, a lack of accounting of spin orbit coupling do not allow us to distinguish between spin symmetry effects when comparing the white line intensity increases in the L_{II} vs. the L_{III} edge when CO is adsorbed.

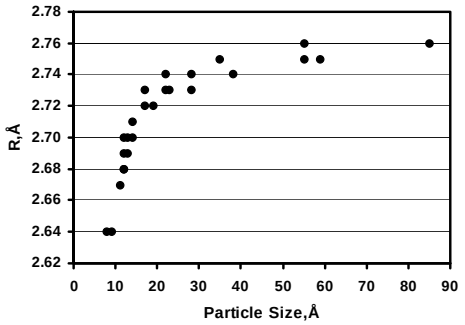

Figure 1. Lattice constant of Pt clusters as a function of particle diameter.

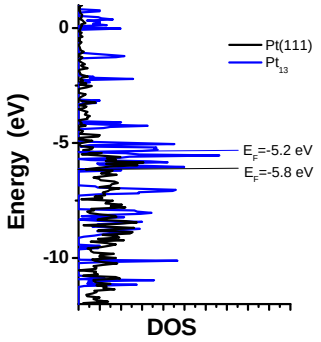

Figure 2. Comparison of DOS of Pt_{13} with Pt(111). The DOS shifts towards the Fermi level (and the work function is simultaneously reduced).

Significance

The use of XANES in concert with DFT calculations has been applied to develop an understanding of reactivity in supported Pt clusters. Support effects both with respect to lattice parameters and white line intensities were found to be minimal when cluster size was held constant. As expected, the lattice constant of Pt decreased with particle size. In addition, the white line intensity in both the L_{III} and L_{II} edges decreased as the particle size decreased, mirroring a shift in the density of states toward the Fermi level. When CO was adsorbed, the white line intensity jumped dramatically as bonds formed between CO and the metal cluster.

References

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