

XAFS Studies of Structured Bimetallic Nanoparticle Catalysts at the CLS

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Introduction

This article describes our recent progress in studying the structure of supported-bimetallic PdAu nanoparticle catalysts on the HXMA beamline 06ID-1. XAFS (x-ray absorption fine structure) measurements of bimetallic PdAu nanoparticles allow for the determination of the internal architectures of the nanoparticles, which can then be used to elucidate structure-property relationships of the catalysts.

Science

Nanoparticles have long been used in heterogeneous catalysis in the petrochemical industry for selective hydrogenation and oxidation reactions. A long-term research objective in our research group at the University of Saskatchewan is to develop highly selective and active nanoparticle catalysts through control of the size, shape, structure, and composition of nanoparticles, as well as precisely controlling the dispersity of the nanoparticles within high-surface area solid-state supports. This work involves trapping pre-synthesized and purified nanoparticles into sol-gel matrices of oxide supports, followed by removal of organic stabilizers via calcinations or plasma treatment [1]. These studies provide an alternative method of designing industrially-relevant, supported-nanoparticle catalysts through a rational, designed chemical approach.

While the size and average composition of supported nanoparticle catalysts can be routinely characterized by methods such as transmission electron microscopy (TEM) and single-particle energy dispersive spectroscopy (EDS), information on the internal distribution of atoms within the nanoparticle is much more difficult to obtain. This information is important as the structure of a nanoparticle can have significant effects on its catalytic behaviour. While rationally-designed solution-phase nanoparticle syntheses of alloy and core-shell nanoparticles have been developed by our group, it is difficult to determine whether such structures remain intact during the synthesis of supported-nanoparticle catalysts from these precursors. XAFS spectroscopy has been a valuable tool for the examination of bimetallic nanoparticle structures by the catalyst community in the past, as it allows for determination of the chemical environment around each element [2,3]. When combined with adequate models of the nanoparticle structure and composition, XAFS measurements can be used to help shed light on possible structures of such nanoparticles. Figure 1 shows several examples of architectures of PdAu nanoparticles that have been synthesized in our laboratories.

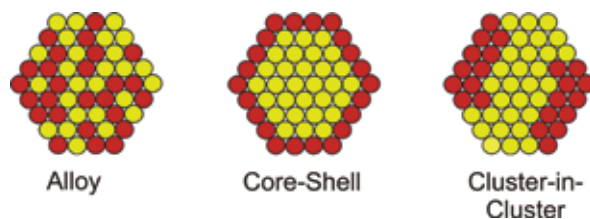


Figure 1: Examples of bimetallic architectures

Discussion

To date, our work has involved collecting XAFS spectra of well-defined alloy and core-shell PdAu particles trapped in alumina matrixes before and after calcination to remove the organic polymer stabilizers. Total metal loadings were typically 1.0 to 2.5% by mass of the catalyst sample. XAFS spectra were collected at both the Pd *K*-edge and the Au *L*₃-edge for both monometallic and bimetallic samples in transmission mode. Following this, data for both edges were simultaneously fit to single-shell and multiple-shell models in order to extract average coordination numbers (Au:Au, Pd:Au, and Pd:Pd) and bond distances from the XAFS data. Figure 2 shows representative XAFS spectra at the Au *L*₃-edge of several alloy PdAu nanoparticles prior to calcination; high quality data was collected on both edges. To date, single-shell fits of the as-synthesized supported-bimetallic nanoparticles trapped in alumina matrixes have suggested that they have approximate alloy structures initially, but that Pd surface segregation is occurring during calcination steps, which are typically done with sequential oxidizing and reducing conditions. As a result of such studies, we are pursuing low-temperature plasma treatments as alternative means of removing organic stabilizers from the as-synthesized supported-nanoparticle trapped in alumina matrixes.

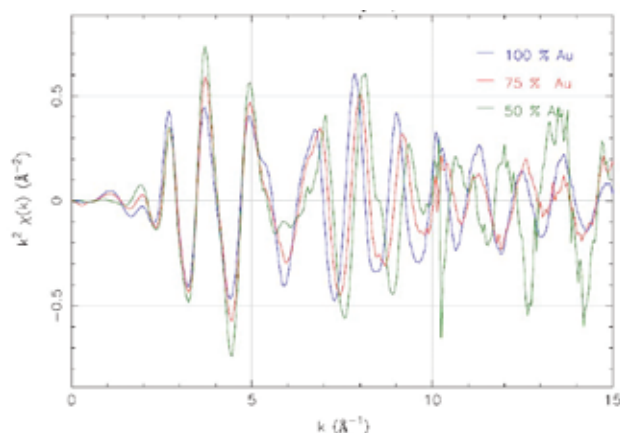
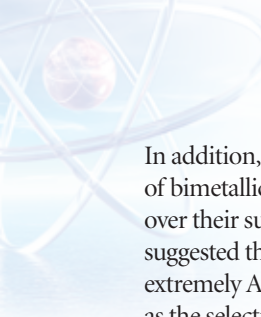


Figure 2: Background-corrected XAFS data for pure Au, 75% Au-25% Pd, and 50% Au-50% Pd supported-nanoparticle catalysts at the Au-*L*₃ edge.



In addition, we have recently begun to examine the structures of bimetallic particles after catalytic reactions have occurred over their surfaces. Recent evidence in our laboratory has suggested that the surface of PdAu nanoparticles may become extremely Au rich during the course of alcohol oxidations, as the selectivity for the oxidation of allylic alcohols changes dramatically over time [4].

Conclusion

In summary, we have shown that high-quality XAFS data can help to begin to shed light on the structure of bimetallic nanoparticles. Future work involves continuing to investigate intentionally-designed core-shell nanoparticles, and comparing XAFS data with data collected from clusters which have been used in catalysis and have shown catalytic selectivities which suggest surface enrichment of Au.

References

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Acknowledgements

The authors thank Ning Chen and Jeff Warner at the Canadian Light Source for assistance with XAFS measurements, and NSERC for financial support of the project.