

Structural Characterization and Phase Behavior in Supported Metallic Nanoparticles

Charles W. Hills

Final Seminar

July 24, 2001

Nanoscale materials have received increasing attention due to the unique chemical and physical properties they exhibit.¹⁻⁵ These properties, which arise from perturbations caused by the finite size of these systems, often are radically different than those characterizing the bulk.^{1,2,4,5} For example, extensive studies have probed the intriguing optical and electronic properties which arise from quantum confinement;^{1,4,5} however, the structural habits of these systems, which prove critical for many of their proposed technological applications, have only recently become the subject of detailed studies.^{1,3,5}

Supported Pt nanoparticles are of great interest due to their enhanced catalytic ability.^{1,6-10} Unfortunately, a detailed understanding of the nanoparticle structure has yet to be achieved. To accomplish this fact, three different Pt samples, with catalyst weight loadings of 10, 40, and 60 %, were studied. Analyzing these particles by electron microscopy and microdiffraction probes their size and microstructure. In this case, the particles had average diameters of ca. 20, 40, and 80 Å respectively, and assumed close-packed structures that were indexed as face-centered cubic (fcc).

X-ray absorption spectroscopy (XAS), namely extended X-ray absorption fine structure (EXAFS), is a powerful analytical technique for studying the shape and morphology of these nanoclusters. This technique probes the local coordination environment (8-10 Å) around an absorbing atom.^{11,12} This environment is extremely sensitive to the size and shape of the nanoclusters. For this system, three possible models are considered, a spherical cuboctahedron, and two hemispherical cuboctahedron (truncated either along the [111] and [001] basal planes). The experimental results show that the nanoparticles form hemispherical cuboctahedrons along the [111] basal plane, similar to the model shown in Figure 1. To expand on the versatility of the EXAFS technique, a comparison of the experimental static disorder data with a simple molecular modeling study of structural relaxation phenomenon is also presented. The results from a relaxation of only surface atoms are more consistent with the experimental values.



Figure 1.

Supported alloy nanoparticles are of great interest in the development of Direct Methanol Fuel Cells (DMFCs).^{13,14} Supported Pt-Ru nanoparticles show enhanced activity towards methanol electrooxidation while exhibiting increased resistance towards poisoning, relative to supported Pt particles.^{13,14} The phase behavior of these supported nanoscale alloys has only recently received increasing attention. While the phase

behavior of bulk materials is well characterized, the structural properties of nanoscale materials often are dramatically different. In the case of Pt-Ru, three main regions characterize the bulk phase diagram.¹⁵ At concentrations below 62 % Ru, Pt-like fcc structures are expected, while at concentrations above 80 % Ru, Ru-like hcp structures are expected.¹⁵ A miscibility gap is found in the region between these two concentrations, in which structures of both types would coexist.¹⁵ Binary alloys are formed using a seeded reductive condensation, in which pre-supported nanoparticles of one metal are used as nucleating sites for the reduction of a precursor of a second metal. The alloys formed are fully reduced and display broad size and compositional distributions. A correlation of these distributions with the close-packed structures of the nanoclusters, probed by electron microdiffraction, creates an apparent phase diagram, as seen in Figure 2.

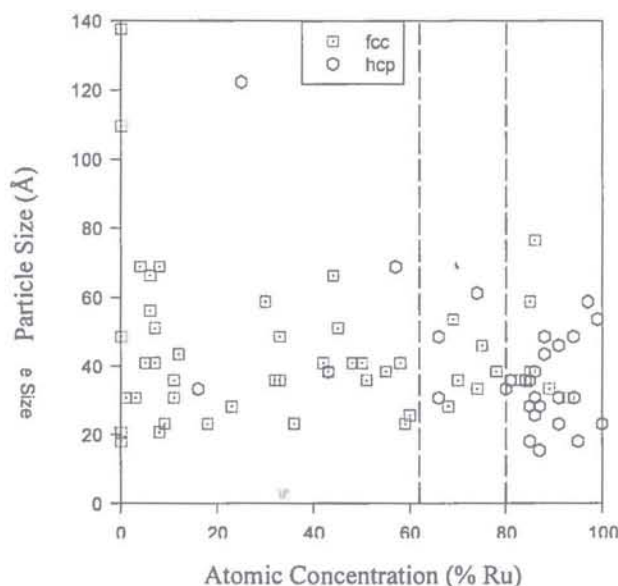


Figure 2.

Inspecting the phase diagram provides intriguing insights into the structural behavior of these nanoalloys. Persistent metastable structures are apparent, with hcp structures at concentrations as low as 17 % Ru and fcc structures at concentrations as high as 90 % Ru. A general trend towards fcc structures is seen, as more fcc structures penetrate the gap and hcp region than vice versa. A definite template effect is also evident for nanoalloys grown on pre-supported Pt clusters. In this case, the fcc structure is dominant to Ru concentration above 90 %. The same is not true for the particles grown using Ru/C as a “substrate.” Increasing the reduction temperature has only a limited effect on this templating. In a sample reduced at elevated temperatures (823 K), the template effect is only slightly mediated, as fcc structures are still dominant at concentrations above 85 % Ru.

References:

1. Bradley, J. S. *The Chemistry of Transition Metal Colloids*; VCH: Weinheim, 1994.
2. Moriarty, P. *Rep. Prog. Phys.* **2001**, *64*, 297.
3. Nashner, M. S.; Frenkel, A. I.; Adler, D. A.; Shapley, J. R.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 7760-7771.
4. Rao, R. C. N.; Giridhar, U.; Thomas, P. J.; Edwards, P. P. *Chem. Soc. Rev.* **2000**, *29*, 27.
5. Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.
6. Briot, P.; P., G.; Leclercq, C.; Primet, C. *Microsc. Microanal. Microstruct.* **1990**, *1*, 149-157.
7. Collier, P. J.; Iggo, J. A.; Whyman, R. *J. Mol. Catal. A* **1999**, *146*, 149.
8. Johnson, B. F. G. *Coordin. Chem. Rev.* **1999**, *192*, 1269.
9. Lange, C.; De Caro, D.; Gamez, A.; Storck, S.; Bradley, J. S.; Maier, W. F. *Langmuir* **1999**, *15*, 5333.
10. Meuterties, E. L.; Krause, M. J. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 135.
11. Teo, B. K. *EXAFS: Basic Principles and Data Analysis*; Springer-Verlag: Berlin, 1986.
12. Koningsberger, D. C.; Prins, R. Eds.; *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*; Wiley: New York, 1988.
13. Gottesfeld, S.; Zawodzinski, T. A. *Polymer Electrolyte Fuel Cells*; Wiley-VCH: Weinheim, 1997; Vol. 5.
14. Landgrebe, A. R.; Sen, R. K.; Wheeler, D. J. *Proceedings of the Workshop on Direct Methanol-Air Fuel Cells*; The Electrochemical Society: Pennington, NJ, 1992; Vol. 92-14.
15. Hutchinson, J. M. *Platinum Met. Rev.* 1972, *16*, 88.