

Characterization of Structured Bimetallic Nanoparticle Catalysts

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Introduction

This article describes our recent progress in studying the structure of supported-bimetallic nanoparticle catalysts on the HXMA beamline 06ID-1. XANES (X-ray absorption near-edge structure) and XAFS (X-ray absorption fine structure) measurements of bimetallic nanoparticles allow for the determination of the internal architectures of the nanoparticles, which is used to elucidate structure-property relationships of the catalysts.

Science

Research in our group focuses on the design of nanoparticle catalysts which have enhanced activities and selectivities for specific catalytic reactions under mild conditions; such work is important in the context of “green chemistry” principles in which solvent and byproduct wastes can be eliminated from processes. One of the major thrusts of our research is to examine the design of intentional structures of bimetallic nanoparticles; in particular, we are attempting to design core-shell nanoparticle catalysts in which the more-expensive, catalytically-active metal is only present on the surface of the particles (and not buried in the core) and a second metal is present in the core of the particle. The core metal can be chosen either for economical reasons (to decrease the cost of the material) or to allow for electronic promotion of the catalytic activity of the surface metal [1]. The two major systems that will be discussed herein are nanoparticles which putatively have thin Pd shells (1-2 monolayers) on Au or Ag cores. The catalytic activities of both Ag-Pd and Au-Pd core-shell nanoparticles have been studied for hydrogenation and oxidation reactions [2, 3], respectively. In particular we have found that Ag-Pd nanoparticles can be used to hydrogenate unsaturated alcohols with much higher selectivities and activities per Pd atom than pure Pd nanoparticles.

Figure 1 shows a representative scheme on how such nanoparticles are created; typically seed nanoparticles of Au or Ag are made (ca. 2-3 nm in size), followed by deposition of the Pd shells either via the reduction of Pd salts using weak reducing agents and/or by taking advantage of spontaneous galvanic replacement reactions at the surface (for example, $2\text{Ag}^0 + \text{Pd}^{2+} \rightarrow 2\text{Ag}^+ + \text{Pd}^0$). Once the final particles are synthesized, the Ag salts are removed as AgCl and/or dialysis and the nanoparticles are then trapped in a sol-gel matrix of a metal oxide (titania, alumina, etc.) and calcined at mild temperatures in order to remove any organic stabilizers used in the synthesis of the particles. We have found that mild calcination temperatures of 300°C can often be used to

completely remove polymer stabilizers on the surface with no major changes in the average nanoparticle size or structure [3].

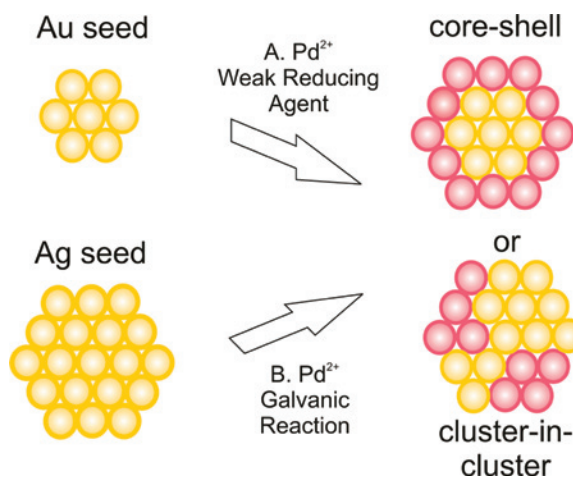


Figure 1: Representation of two routes towards synthesis of core-shell and/or cluster-in-cluster Au-Pd and Ag-Pd nanoparticles.

Discussion

To demonstrate the usefulness of XAFS spectroscopy in order to elucidate nanoparticle structures, results for Ag-Pd core-shell nanoparticles were examined on beamline 06ID-1; results obtained for AuPd alloy and core-shell materials can be found elsewhere[3]. The samples were nanoparticles dispersed in an alumina matrix such that the final amount of metal was 2.5% of the mass of the sample. XAFS spectra were collected at both the Pd and Ag -edges for both monometallic and bimetallic samples in transmission mode.

Following this, the Ag and Pd XAFS data was fit to single-shell models in order to determine average coordination numbers of metals around both Ag and Pd ($N_{\text{Ag-M}}$ and $N_{\text{Pd-M}}$), average first-shell distances ($R_{\text{Ag-M}}$ and $R_{\text{Pd-M}}$) as well as Debye-Waller XAFS terms (σ^2). It should be noted that because Pd and Ag have nearly the same atomic number, it is not possible to distinguish Pd from Ag neighbours in the first coordination shell. Figure 2 shows representative fits of XAFS data in R-space for both the Ag and Pd edges for 5:1 Ag:Pd nanoparticles; excellent fits were obtained for both edges. Results support the growth of partial Pd shells on the Ag nanoparticle seeds as the average first shell coordination numbers around Pd ($N_{\text{Pd-M}} = 7.8(1.0)$) were significantly lower than those around Ag ($N_{\text{Ag-M}} = 10.6(5)$); in addition, there was a significant Pd-N coordination at lower R-values

in the Pd edge data which could be fit using appropriate Pd tetraamine models to yield $N_{\text{Pd-N}}$ values of ca. 2. The $N_{\text{Pd-N}}$ first shell likely represents the coordination of amido groups from the poly(vinylpyrrolidone) polymer stabilizer onto the Pd shell surface. While these results are highly suggestive of core-shell structures being formed, we do note that the fact that $N_{\text{Ag-M}}$ values are significantly below 12 and that the $N_{\text{Pd-M}}$ values are higher than expected which indicates that a more appropriate model for the final nanoparticle structure may be a cluster-in-cluster model. More work is continuing on these systems to try to understand why perfect core-shell materials do not form under galvanic conditions.

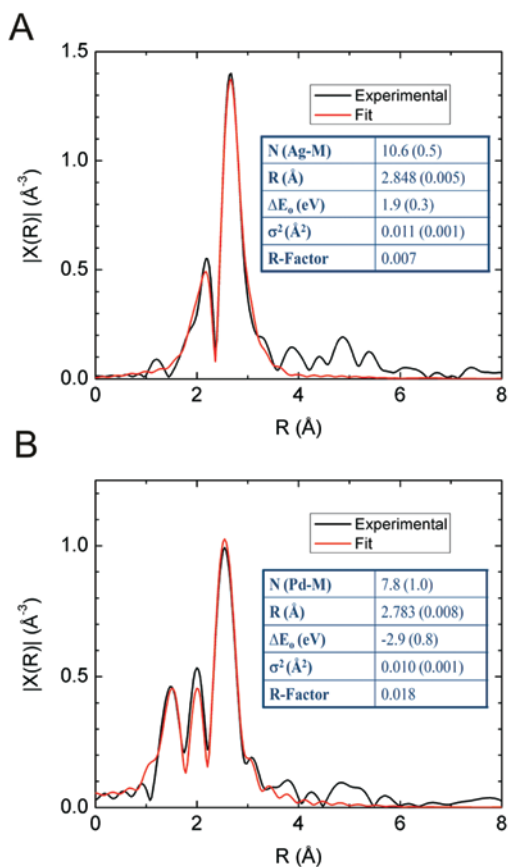


Figure 2: XAFS fit in R space for 5:1 Ag:Pd nanoparticles (A) Ag K-edge, and (B) Pd K-edge.

We are continuing to investigate the electronic interactions that take place in core-shell nanoparticles via examinations of their L-edges on the SXRMB beamline at the CLS[4]. These studies will allow us to precisely study how the electronic interactions of the core metal with the catalytically-active shell metal can influence the activity and selectivity of reactions on the surface of the particle. We plan to examine the effect of the thickness of the Pd shell layer, i.e. how thick can the Pd shell be before it is no longer influenced by the underlying core.

Conclusion

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 to investigate whether core-shell structures remain intact after catalytic reactions.

References

1. Toshima, N., Yonezawa, T. 1998. *New Journal of Chemistry*. 22, 1179-1201. DOI: 10.1039/a805753b.
2. Hou, W., Dehm, N.A., Scott, R.W.J. 2008. *Journal of Catalysis*. 253, 1, 22-27. DOI:10.1016/j.jcat.2007.10.025
3. Dash, P., Bond, T., Fowler, C., Hou, W., Coombs, N., Scott, R. W. J., *Journal of Physical Chemistry C*, 2009, 113, 12719-12730. DOI: 10.1021/jp9037182
4. Coulthard, I., and Sham, T.K., *Physical Review Letters*, 1996, 77, 4824-4827. DOI: 10.1103/PhysRevLett.77.4824

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