

Catalysis and Corrosion on Transition Metal Nanoclusters

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Scientific Thrust Area

Nanoscale Theory and Modeling

Research Achievement

This effort involves comprehensive Density Functional Theory (DFT) simulations of a range of phenomena involving heterogeneous catalysis and corrosion on metal nanoparticles and clusters. It complements experimental catalysis and corrosion efforts at the Center for Nanoscale Materials, Argonne National Laboratory, and elsewhere.

Catalysis is the study and control of chemical transformations; a good catalyst will permit a given chemical reaction to proceed at high rates at modest temperatures (“activity”) and will, at the same time, prevent the formation of unwanted byproducts (“selectivity”) [1]. Typical catalysts are composed of either metal alloy or metal oxide nanoparticles and have been developed primarily by trial and error-based approaches. To fully optimize their properties, however, it is essential to develop fundamental understanding of the molecular-level properties that govern their operation. DFT analyses play an essential role in developing such understanding and will, ultimately, also facilitate the design and discovery of novel catalytic materials [2].

An emerging area of importance in theoretical nanocatalysis is the study of electrocatalytic systems [3]. Such systems, which are of first-order importance in the operation of fuel cells, batteries, and other electrochemical devices, are susceptible to all of the activity and selectivity-related problems of heterogeneous nanocatalysts, but they additionally suffer from significant corrosion and stability problems. Again, theory is poised to make an important contribution to the understanding, and ultimately suppression, of such nanocorrosive effects.

One application area in which we have been recently working is the use of subnanometer platinum clusters to catalyze chemical transformations in molecules needed for petrochemical processing. For example, we have recently completed a study of the properties of Pt₈₋₁₀ nanoclusters for the oxidative dehydrogenation of propane to propylene (an important precursor for the production of polypropylene)[4]. Experimental results (S. Vadja et al., ANL/CNM-CSE) indicate that the nanoclusters catalyze this reaction with high selectivity and with an activity 40-100 times that of any existing catalyst. Our DFT-based investigations, in turn, provide a compelling explanation for this observation. The highly undercoordinated nature of the atoms in the Pt clusters permits them to rapidly cleave C-H bonds in propane, yielding propylene; the barriers for these critical steps are reduced by several tenths of an electron volt compared to the more

extended single-crystal surfaces that would be found on larger nanoparticles, resulting in substantially enhanced activity for the subnanometer catalysts.

A second thrust area that we have been studying is the catalytic activity and stability of metal nanoclusters supported on metal substrates in electrochemical environments. In collaboration with Nenad Markovic (ANL/MSD), we have found that Pt nanoparticles (0.5 -3 nm diameter) supported on Pt(111) or Pt(100) single crystal substrates have CO electrooxidation activities at least as high as that of the best known Pt-based alloy catalysts. Using extensive DFT calculations, we have traced the origin of this high activity to an enhanced competition of OH groups for highly undercoordinated sites on the particles' surfaces [5]. In addition, given the likelihood of corrosion of these small nanoparticles in electrochemical environments, we have studied the clusters' stability as a function of the electrode potential. We have found, among other results, that the stability of atoms in the clusters is directly proportional to their coordination number and that water dissociation, with concomitant oxide deposition, facilitates their dissolution.

Future Work

We will explore the catalytic properties of a broad array of subnanometer metal clusters for key heterogeneous catalytic reactions, including methanol dehydrogenation and propylene epoxidation. We will develop a database of key reactivity properties on these clusters that will ultimately permit us to make predictions about which clusters are likely to have promising properties for these reactions. In tandem, we will continue to explore the relationship between the oxidation state and the stability of metal clusters in electrochemical environments; our ultimate goal in this case will be to identify key features that will promote the stability of these clusters under realistic, fuel cell-like conditions.

References

- [1] Somorjai, G. A., *Introduction to Surface Chemistry and Catalysis*. Wiley: New York, 1994.
- [2] Hammer, B., Nørskov, J. K., *Adv. Catal.* **45**, 71 (2000).
- [3] J. Rossmeisl et al., in *Fuel Cell Catalysis*. Wiley: New York, 2009.
- [4] S. Vajda et al., *Nature Materials*. **8**, 213 (2009).
- [5] D. Strmcnik et al., *J. Am. Chem. Soc.* **130**, 15332 (2008).

Publications

C. Lucas et al., "Temperature-induced ordering and phase transitions in metal/adsorbate structures at electrochemical interfaces," *J. Am. Chem. Soc.*, *in press*.

S. Vajda et al., "Subnanometre platinum clusters as highly active and selective catalysts for the oxidative dehydrogenation of propane," *Nature Materials*. **8**, 213 (2009).

D. Strmcnik et al., "Unique activity of platinum ad-islands in the CO electrooxidation reaction," *J. Am. Chem. Soc.* **130**, 15332 (2008).

P. Strasser et al., "Voltammetric surface dealloying of Pt bimetallic nanoparticles: an experimental and DFT computational analysis," *Phys. Chem. Chem. Phys.* **10**, 3670 (2008).