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# Atomic-scale Design of a New Class of Alloy Catalysts for Reactions Involving Hydrogen: A Theoretical and Experimental Approach

Manos Mavrikakis\* (Primary Contact),  
R. R. Adzic<sup>1</sup>, J. A. Dumesic\*

\*University of Wisconsin-Madison

Department of Chemical and Biological Engineering  
1415 Engineering Dr.  
Madison, WI 53706

Phone: (608) 262-9053; Fax: (608) 262-5434

E-mail: manos@engr.wisc.edu

<sup>1</sup>Materials Science Department, Brookhaven National  
Lab, Upton, NY 11973

DOE Program Officer: Dr. Raul Miranda

Phone: (301) 903-8014

E-mail: raul.miranda@science.doe.gov

Subcontractor:

Michael D. Amiridis, Department of Chemical  
Engineering, University of South Carolina, Columbia,  
SC 29208

## Objectives

Through a combination of theoretical and experimental methods, we want to identify, synthesize, and test surface-modified materials having desirable properties for hydrogen catalysis and storage. In particular we are designing and studying new materials with: (i) high catalytic activity and CO resistance for hydrogen fuel-cell anode reactions, (ii) resistance to carbon poisoning for CH<sub>4</sub> reforming, (iii) the ability to catalyze the dissociation and diffusion of hydrogen into the bulk for hydrogen purification and light metal-hydride storage, and (iv) high catalytic activity for hydrogenation/dehydrogenation of unsaturated/saturated hydrocarbons for chemical storage of hydrogen.

## Technical Barriers

Succeeding in our scientific objectives should help overcome the following “H<sub>2</sub> economy”- related technical barriers: (i) developing cheaper and more poison-resistant anode catalysts for low temperature fuel cells, (ii) improved efficiency of H<sub>2</sub> production from natural gas, (iii) improved hydrogen purification and storage materials, and (iv) efficient chemical storage of H<sub>2</sub> on chemical bonds found within appropriate “H<sub>2</sub>-carrier” molecules.

## Abstract

During this past year our research team has made significant progress in several fronts related to our scientific objectives. In particular: **(1)** Using theoretical methods we identified ternary alloys, and with electrochemical deposition methods we synthesized and tested mixed Pt+M monolayer electrocatalysts supported on appropriate late-transition metal supports, which minimize the amount of Pt used, and at the same time, show a substantially increased CO tolerance. These first-principles designed catalysts show improved CO-tolerance for the anodes of low temperature fuel cells. **(2)** With theoretical methods, we studied the effect that noble-metal deposition on late transition metals has on H<sub>2</sub> dissociation and adsorption on these non-noble metals. Our findings set the foundations for explaining the anomalous enhancement of H adsorption on non-noble metals, as induced by deposition of Au on these metals. **(3)** Using first-principles methods we identified a number of bimetallic catalysts which are capable of enhancing hydrogenation of C=C double bonds. Synthesis and experimental testing of these catalysts showed that we have indeed found bimetallic catalysts with enhanced reactivity for benzene hydrogenation, a prototype reaction for chemical storage of H<sub>2</sub>. **(4)** Using Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy, we investigated the basic chemistry taking place during the various steps involved in the preparation of supported metal catalysts from metal-dendrimer nanocomposites. These nanosynthesis techniques might provide a viable alternative to electrodeposition methods for preparing theoretically-identified promising catalytic nanostructures.

## Progress Report and Future Directions

### (1) Improved CO-tolerant ternary alloys

Capitalizing on our recent success with identifying two key reactivity descriptors for oxygen reduction reaction (ORR), we have now designed from first-principles and synthesized bimetallic and ternary alloy electrocatalysts with substantially increased CO-tolerance. Starting from first-principles, we have replaced the core of the catalytic nanoparticles with a non-Pt late transition metal, which is cheaper than Pt, and at the same time, via the strain and the ligand effect, leads to a significant destabilization of CO adsorbed on the Pt-monolayer thick shell of the nanoparticle. In a

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subsequent step, we have replaced part of the Pt-shell of the bimetallic nanoparticle with a third transition metal, which tends to adsorb CO stronger than Pt, and induces a substantial repulsion (through the substrate) to any other CO molecules, which would tend to adsorb on the Pt sites of the particle's shell. The "repulsion-by-design" has exceeded 1eV in some cases, allowing for the existence of free Pt sites, which are necessary for the robust activation of H<sub>2</sub> molecules, the prime function of the anode catalyst. We have, therefore, demonstrated that one can decrease the cost of anode catalysts and simultaneously increase the CO-tolerance of those catalysts. These catalysts have been synthesized using electrochemical methods and their catalytic performance was tested experimentally using CO-stripping voltammetry. The experimental results nicely confirmed our theoretical predictions.

These advances have been based on the effect of the electronic factor on destabilizing CO alone, without any special attention to the so-called bifunctional mechanism. Our future studies will involve that mechanism, which may allow for further improvements of CO-tolerance. In addition, we are currently working on the activation mechanism of H<sub>2</sub> on CO-saturated anode catalysts, which may open new avenues for designing even better CO-tolerant anodes.

## (2) Enhancing H<sub>2</sub> adsorption on late transition metals with noble metals

Recently a new class of metastable bimetallic alloys has been described that have superior properties for hydrogen-related reactions [1]. These 'near-surface alloys' (NSAs) have a solute metal which exists at a higher concentration near the surface of the host metal than in the bulk.

The interaction of hydrogen with several of these overlayer-NSAs has been studied in detail. Okada, et al. found that Ir(111) overlaid with 1ML of Au or Ag has the ability to dissociate H<sub>2</sub>, despite the inability of pure Au and Ag to do so [2]. Au and Ag on Pt, however, are not able to facilitate this dissociation [3]. Explaining this anomalous result forms the basis of part of our work on NSAs for hydrogen-related reactions. We find that the binding energy of hydrogen on the Au\*/Ir surface is higher in the subsurface (i.e., at the Au-Ir interface) than on the Au surface. In contrast, for pure metals, subsurface hydrogen is in general much less stable than surface hydrogen [4]. The stability of subsurface hydrogen on these NSAs has important implications in catalysis and hydrogen separation membranes. Because of these properties, we have extended our investigation of the stability of subsurface hydrogen to other NSA systems. We have investigated Au, Ag, Cu, Pt and Pd overlayers on 17 metals, focusing on the relative stability of surface and subsurface hydrogen.

Subsurface hydrogen modifies the electronic structure of the NSA. For several Au overlayer NSAs, the d-band of the surface Au layer is pushed toward the Fermi level in the presence of subsurface hydrogen, which, according to theory, will lead to increased surface reactivity [5]. We showed that the activation energy for H<sub>2</sub> dissociation in the presence of subsurface hydrogen on Au overlayers is decreased considerably.

Another property related to the relative stability of surface and subsurface H is its diffusion into the subsurface. While H diffusion into pure Au is a highly activated process, hydrogen diffusion into the subsurface of many of the Au NSAs is far easier. In fact, the energetics for diffusion into Au\*/Ir is similar to that of pure Pd, a commonly used material for hydrogen membranes. Because of the presence of surface Au, however, Au\*/Ir may have better resistance to common contaminants in H purification than Pd. One direction of our research is to identify other NSAs with similar or superior diffusion properties than the commercial Pd and Pd-Ag membranes currently in use while having superior poison resistance.

To incorporate departures from the pure overlayer structure, we have developed a new model NSA A<sub>x</sub>B<sub>1-x</sub>\*/B and we are currently studying their electronic structure and surface reactivity both with theory and experiments (cyclic voltammetry). Our preliminary results suggest that the addition of submonolayer amounts of a noble metal, e.g.: Au, actually increases the reactivity of the remaining non-noble metal, e.g.: Ir, on the surface. We plan on extending this study to better explain: (i) experimentally observed H-uptakes on bimetallics and (ii) the promoting effect of noble metals on the reactivity of non-noble transition metals in general.

Related to hydrogen storage in metal hydrides, we have been investigating the doping of Mg with transition metals to improve H<sub>2</sub> dissociation kinetics and absorption into the bulk. Light hydrides, such as Mg, combine low cost with a high volumetric hydrogen storage capacity and a reasonable gravimetric density. However, Mg does not dissociate H<sub>2</sub> spontaneously. To improve the kinetics of H<sub>2</sub> dissociation, other metals (such as Ti and Pd) are introduced as a catalyst. The exact role played by these metals is not well understood. We are currently studying the stability of these metals incorporated into the Mg lattice and their effect on H<sub>2</sub> dissociation.

## (3) Catalytic chemical storage of H<sub>2</sub>

Identifying novel catalysts capable of catalyzing the hydrogenation/dehydrogenation of unsaturated C=C bonds holds a strong promise for storing/releasing H<sub>2</sub> at very high densities. Clearly, the pair of relevant molecules, both the one with unsaturated bonds and its hydrogenated version, is important. One needs to

choose such a pair of molecules in a way that both the thermodynamics and the kinetics of the hydrogenation/dehydrogenation steps are not very costly, so that H<sub>2</sub> storage on the chemical bonds and its release from those is relatively facile and taking place at reasonable temperatures, thereby decreasing the energy cost of the storage/release process and minimizing selectivity towards undesired side-reactions.

Using DFT, we identified bimetallic NSAs, which would bind C=C containing hydrocarbons with a modest strength, whereas at the same time would bind CCH<sub>3</sub>, a common poison of hydrogenation/dehydrogenation reactions, as weakly as possible. A number of such alloys were identified, and then synthesized. Subsequent experiments for C<sub>6</sub>H<sub>6</sub> hydrogenation (at 27C) over these bimetallic catalysts, along with chemisorption measurements used to titrate the number of sites on these catalysts, demonstrated that some of these bimetallic catalysts possess an enhanced per site hydrogenation activity (TOF), exceeding the TOF of the respective monometallic catalyst (one of the components of the bimetallic) by ca. one order of magnitude.

Future work in this direction will focus on extending our promising C<sub>6</sub>H<sub>6</sub> hydrogenation results to the catalytic hydrogenation of other molecules, which have been identified by industry as better “H<sub>2</sub> carrier molecules” (e.g.: ethyl-carbazole). The challenge ahead of us is to verify whether or not the bimetallic catalysts - we identified through theory for hydrogenation of simple unsaturated C=C bonds- work well for these more realistic (than C<sub>6</sub>H<sub>6</sub>) H<sub>2</sub>-storage molecules. If positive, we will proceed with studying the dehydrogenation reaction as well. If negative, we will have to take a step back, and theoretically identify more suitable bimetallic catalysts for these H<sub>2</sub>-storage molecules. Studies of the dehydrogenation step will follow.

#### (4) Dendrimers-based catalyst synthesis

The different steps involved in the preparation of supported metal catalysts from metal-dendrimer nanocomposites (i.e., metal-dendrimer complexation, metal reduction, nanocomposite deposition on the support and dendrimer removal) were investigated in detail by the use of *in situ* Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. The EXAFS results indicate that upon hydrolysis chlorine ligands in the H<sub>2</sub>PtCl<sub>6</sub>, K<sub>2</sub>PtCl<sub>4</sub> and RhCl<sub>3</sub> precursors were partially replaced in solution by aquo ligands.

Following treatment of the H<sub>2</sub>PtCl<sub>6</sub>/G4OH and K<sub>2</sub>PtCl<sub>4</sub>/G4OH complexes with NaBH<sub>4</sub>, no substantial changes were observed in the electronic or coordination environment of Pt, indicating that metal nanoparticles were not formed during this step. However, when the reduction treatment was performed with H<sub>2</sub>, the formation of extremely small Pt-clusters was observed. Formation of larger Pt nanoparticles, with an average diameter of approximately 1 nm, was observed after the deposition and drying of the H<sub>2</sub>PtCl<sub>6</sub>/G4OH nanocomposites on a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface.

During the third year of this project, we plan to utilize EXAFS to address questions related to the relative ease and rate of complexation and reduction of two different metals in a dendrimer solution and the resulting metal complexes/structures.

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