

V.P.21 Atomic-scale Design of a New Class of Alloy Catalysts for Reactions Involving Hydrogen: A Theoretical and Experimental Approach

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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 CH₄ 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 "H₂ economy"-related technical barriers: (i) developing cheaper and more poison-resistant anode catalysts for low temperature fuel cells, (ii) improved efficiency of H₂ production from natural gas, (iii) improved hydrogen purification and storage materials, and (iv) efficient chemical storage of H₂ on chemical bonds found within appropriate "H₂-carrier" molecules.

Abstract

The development of more efficient chemical processes through improved catalyst design has been an important goal for well over a century. Recent developments of new tools in surface science and theory can aid in achieving this goal. One such tool, Density Functional Theory (DFT), can both elucidate reaction mechanisms as well as test novel catalyst architectures for specific reactions. Using these methods, we recently identified a new class of bimetallic alloys that exhibit superior catalytic activity for hydrogen-related reactions [J. Greeley and M. Mavrikakis, *Nature Materials* 3, (2004) 810]. This class of alloys, namely Near-Surface Alloys (NSAs), is comprised of alloys wherein a solute metal is present near the surface of a host metal in concentrations differing from the bulk. The architecture of these alloys gives them remarkable properties, different from the properties of their constituent metals as well as bulk alloys of the same components. As the catalytic properties of NSAs are directly connected to the precise atomic layer-by-layer structure of their near surface region, we have also needed to develop and implement accurate nanosynthesis techniques for the preparation of the theoretically predicted optimal nanostructures. Our work has been focused in three main areas: (i) the *elucidation of fundamental principles* of industrially relevant reactions using state-of-the-art DFT, (ii) the *application* of these principles to discovering novel alloys (specifically, NSAs) with superior catalytic properties and (iii) the *synthesis and characterization* of these alloys for H-related reactions using innovative chemical and electrochemical techniques.

Over the last few years, we have made progress on these three fronts for a variety of important reactions, as follows:

- A. We have theoretically identified and experimentally synthesized and tested for their reactivity Ru-core/Pt-shell (Ru@Pt) nanoparticles that are highly active for the preferential oxidation (PROX) of CO in the presence of H₂ at room temperature. Using DFT, we elucidated the fundamental principles behind this high activity, invoking a novel H-assisted O₂ dissociation mechanism to explain this unusually high reactivity at low temperatures. Other core-shell nanoparticles are currently in the synthetic-protocol design and characterization phase.
- B. Using a combination of DFT, microkinetic modeling, and reactivity experiments, we have investigated the kinetics of the water-gas-shift (WGS) reaction on Cu and Pt catalysts; we

proposed a novel mechanism including the formation of a carboxyl (COOH^*) intermediate. Additionally, we have begun investigating the promotional effect of iron oxide (FeO) for the Pt-group catalyzed WGS reaction. We also investigated CO_2 chemistry for Cu-Pt NSA systems, relevant for the WGS and methanol synthesis reactions.

- C. We predicted the presence of subsurface H in an Au-Ir NSA system. Using electrochemical methods, we have synthesized Au^*/Ir (Au overlaid on Ir) NSA catalysts and tested their adsorption of hydrogen, validating such predictions and opening the door to new catalysts with stable subsurface hydrogen.
- D. We have begun to extend DFT calculations to electrochemical reactions and study core-shell based catalysts for these important reactions. We have focused on several reactions relevant to fuel cells, including: oxygen reduction (ORR) for fuel cell cathodes; methanol electrooxidation for direct methanol fuel cell anodes; and hydrogen electrooxidation for H_2 -PEM fuel cell anodes. In ORR, we use a new electrochemical model to understand the high activity of Pt overlayers over Pd and other surfaces for this reaction. We also use this model in methanol electrooxidation to parameterize the onset potential, allowing us to screen for better electrocatalysts.

Progress Report and Future Directions

Space limitations won't allow us to expand on any of the topics outlined in the abstract, but (A) and (C):

(A) Core-Shell Nanoparticles for preferential oxidation reactions^{1,2}

Our DFT work identified Ru-core/Pt-shell nanoparticles (Ru@Pt--see Figure 1, left panel) as a promising PROX catalyst. Our experiments showed that these catalysts indeed possess a much lower onset temperature for CO and H_2 oxidation than the constituent metals, physical mixtures or bulk alloys of Pt and Ru. Additionally, the selectivity to CO oxidation on these catalysts at low temperatures is excellent.

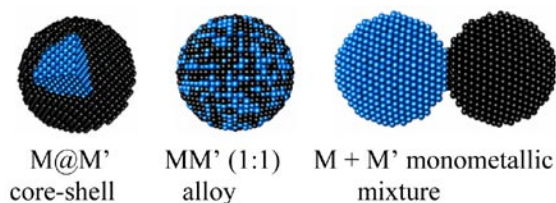


FIGURE 1. Schematic of core-shell particles, alloy particles and physical mixtures.

One thrust of our work over has been to explain this increased activity using first-principles methods. We find that a Pt skin pseudomorphically deposited on a Ru host provides a different pathway for O_2 dissociation in the presence of hydrogen (H). This novel result highlights the ability of hydrogen to assist in O_2 dissociation on Pt-Ru surface alloys (see Figure 2), thereby lowering the activation energy barrier to oxidation, thereby increasing the activity of the core-shell nanoparticles considerably.

The discovery of this H-assisted path is of interest for several reasons. First, using this new mechanism, we can identify catalysts that may show similar or even better characteristics for PROX by adding a third metal to the alloy. Second, the existence of such H-assisted dissociation may not be limited to O_2 dissociation. We have begun a study of similar dissociation pathways for other relevant intermediates, such as CO, which would allow us to better understand the surface chemistry of multiple reactions important to H_2 production and purification, but also for alkane fuels production (e.g.: Fischer-Tropsch synthesis).

(C) NSAs for Hydrogen-related reactions^{3,4}

Another focus of our research has been in synthesizing and characterizing submonolayer alloys for hydrogen-related reactions. Recently, we have deposited submonolayer amounts of Au on an Ir(111) surface and compared the uptake of hydrogen to that of a pure Ir(111) surface using electrochemical techniques. While STM demonstrates that Au is clearly deposited on the surface as a thin film, counter-intuitively, it does *not* block hydrogen adsorption. Using DFT, we analyzed the interaction of H with this NSA and showed possible reasons for this anomalous behavior. We found that hydrogen at the Au-Ir interface is stabilized as compared with hydrogen on the Au surface (see Figure 3). Such subsurface H has been implicated as

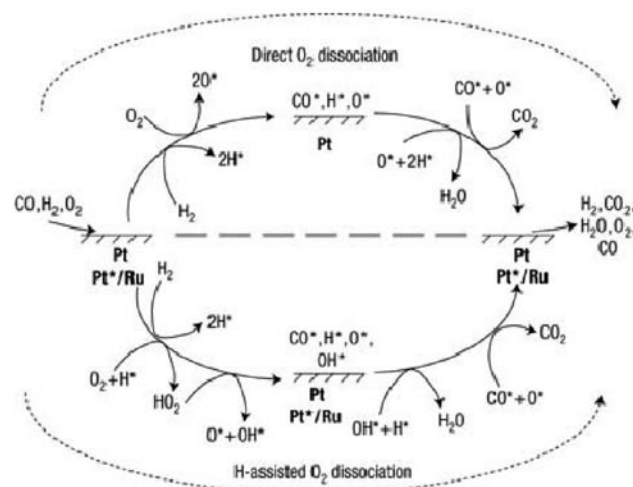


FIGURE 2. Direct and H-assisted preferential oxidation mechanisms.

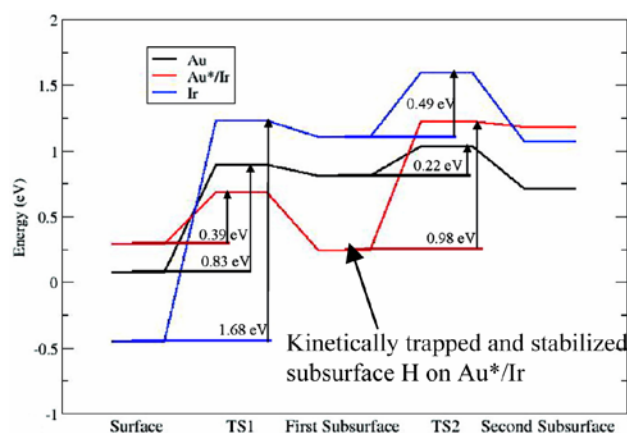


FIGURE 3. Potential Energy surface for H diffusion on Au(111), Ir(111) and Au*/Ir(111).

a reaction intermediate in hydrogenation reactions in other systems.⁵ Additionally, the subsurface hydrogen may have a promoting effect on further reaction; the presence of subsurface H in the Au-Ir system upshifts the d-band center from -4.10 to -3.02 eV, leading to a significant increase in the reactivity of the pure Au-Ir surface. We plan on continuing this analysis by looking at submonolayer Au alloys on other transition metals to see if this reactivity change is unique to Au-Ir or can be found in other NSA systems. Additionally, we have begun looking at alloy stability and formation on other than close-packed surfaces of transition metals.

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