V.N.29 Atomic-Scale Design of Metal and Alloy Catalysts: a Combined Theoretical and Experimental Approach

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Objectives

The main objective of this combined theoretical and experimental project is to: (i) *design* from first-principles, (ii) *synthesize* using advanced *nanosynthesis* techniques, and (iii) experimentally evaluate *new metal* and *alloy nanoparticles,* with unique *catalytic* properties for a number of important chemical reactions. We also want to address the fundamentals of reactivity at metal/metal oxide interfaces.

Technical Barriers

1. Low-temperature polymer electrolyte membrane (PEM) fuel cells present an attractive method of generating electricity for portable devices. However, the commercial feasibility of these systems is limited by the high cost of Pt-based catalysts. Experimental screening of catalytic materials is costly and time-consuming. From a fundamental understanding of reaction mechanisms, developed through first-principles calculations, we are able to identify promising materials using reactivity appropriate reactivity descriptors.
2. Water plays a significant role in surface reactions, even if only a spectator species, including at impurity levels. In addition, spillover of atoms from metal to metal oxide supports and the reverse has been shown to play a key role in heterogeneous catalysis. We address the role of water on hydrogen atom diffusion, and thereby spillover, at FeO/Pt interfaces.

Abstract

The catalysts designed in this project can impact a number of applications, including low temperature fuel cells, hydrogen production and purification, and liquid fuels production. The importance of the atomic-scale architecture of these new theoretically-designed catalysts to their unique properties is driving the development of *new inorganic materials synthesis* approaches, which are capable of synthesizing the theoretically determined optimal, and in some cases, metastable, nanoscale catalytic architectures.

Over the past year, we have made progress toward our objectives through a combination of theoretical and experimental studies. We have used DFT calculations to show that water is able to assist hydrogen diffusion on a FeO/Pt moire structure. This finding has substantial implications for reactions where water participates as a reactant, product, solvent, or impurity in the reaction mixture. We have also designed "onion"-structured alloy catalysts from first principles that demonstrate a high activity for the oxygen reduction reaction (ORR). These alloys, composed of a Pt monolayer deposited on a substrate metal (or alloy) with a number of 1-atom-thick Pd layers in between, have been synthesized experimentally and verified to have higher catalytic activity than pure Pt ORR catalysts.

Progress Report

***Water-Mediated Proton Hopping on an Iron Oxide Surface*[1]**
Science 2012, 336 (6083)

The diffusion of hydrogen is an important process in a number of applications, including catalytic hydrogen evolution and reforming, hydrogenation/dehydrogenation of hydrocarbons, and hydrogen storage. Hydrogen diffusion is practically important in cases where the "spillover" effect operates, where active sites for H_2 dissociation and association are spatially separated from the active sites for other reactions. Mechanisms involving hydrogen spillover have been implicated in many industrially important catalytic reactions, including methanol synthesis and hydrogenation of benzene and toluene, for example. The presence of hydrogen spillover on oxides can also affect the catalytic activity of oxide catalysts, in some cases activating an otherwise inactive catalyst.

Enhanced rates of surface reactions involving hydrogen diffusion upon addition of water have been observed in a number of cases. However, the fundamental atomistic mechanisms underlying hydrogen diffusion on solid surfaces and the factors influencing them still remain unsettled. In a recent study, we revealed the underlying mechanism of an enormous hydrogen diffusion enhancement induced by trace amounts of water on a monolayer FeO thin film deposited on a Pt surface.

By using fast scanning tunneling microscopy (STM), rapid hydrogen diffusion on a FeO/Pt moiré structure (see Figure 1) at low temperature (105 K) was observed. To understand the underlying mechanism of the fast hydrogen diffusion on this surface, we used density functional theory corrected for on-site Coulomb interaction (DFT+U) on the natural $(\sqrt{91}\times\sqrt{91})R5.2°$ (very large) unit cell. We studied intrinsic hydrogen diffusion on the FeO/Pt moire structure and found that hydrogen diffusion is highly activated, with an energy barrier of ~1 eV. By introducing a very small amount of water close to the surface, we found that a new channel for fast hydrogen diffusion opens up: this new channel goes via a proton transfer process mediated by H_2O, involving the transfer of the surface proton to the water molecule and the formation of short-lived hydronium ion (H_3O^+) species at the transition state. Subsequently, one of the original water protons is transferred to an O atom on the FeO surface. The H_2O-mediated hydrogen diffusion process needs an energy barrier of only ~0.2 eV, as shown in Figure 2. This finding, in contrast to the intrinsic H diffusion, clearly suggests that water can accelerate H diffusion by ~16 orders of magnitude at room temperature.

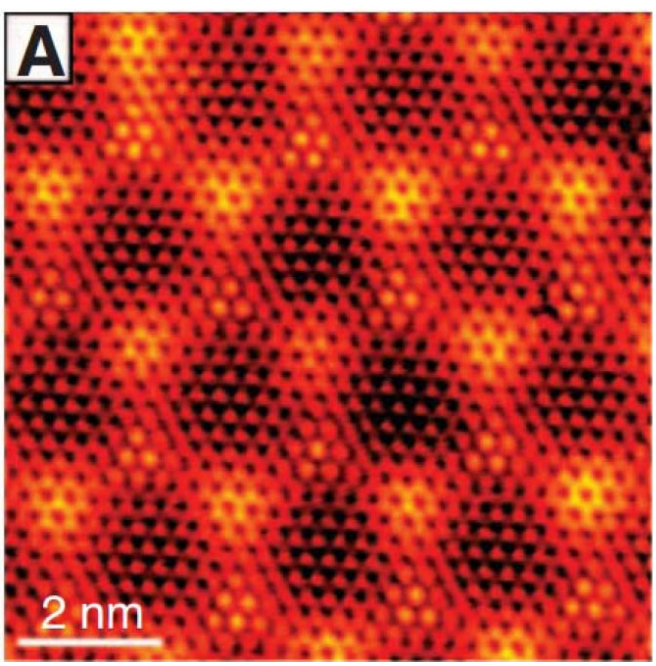

FIGURE 1. Atomically-resolved STM image of the bare FeO film on Pt(111) showing the moiré structure and protrusions due to individual Fe and O atoms. Figure from reference 1.

Oxygen Reduction on Pt-Terminated Alloy Catalysts[5] *Electrocatalysis* 2012, 3 (3-4)

Low-temperature polymer electrolyte membrane (PEM) fuel cells present an attractive method of generating electricity for portable devices. However, the commercial feasibility of these systems is limited by the high cost of Pt-based catalysts, which are necessary to catalyze the oxygen reduction reaction (ORR) at fuel cell cathodes with sufficiently low over-potentials. To overcome this materials challenge, we have been interested in developing Pt alloy catalysts that maintain or increase the high catalytic activity of Pt, while minimizing Pt-loading. Using first-principles calculations, we have identified a series of Pt-terminated alloy catalysts, which are predicted to have equal or better catalytic activity than pure Pt, while minimizing Pt-loading.

In previous work,[2] we studied a series of bimetallic catalysts featuring a Pt monolayer deposited on a substrate metal, denoted as Pt*/X (X = Au, Pd, Ru, Rh, or Ir). We found that Pt*/Pd had the highest activity, which was a 20-fold increase in Pt mass activity compared with pure Pt. In addition to their high activity, these catalysts utilized a fraction of the Pt necessary for the standard pure Pt catalyst. Our fundamental studies revealed that the activity of these catalysts was correlated with the strength of oxygen binding on the catalytic surfaces and that the optimal oxygen binding is slightly weaker than that of pure Pt. By depositing Pt on a substrate, its binding properties are modulated through electronic interactions with the substrate (referred to as the

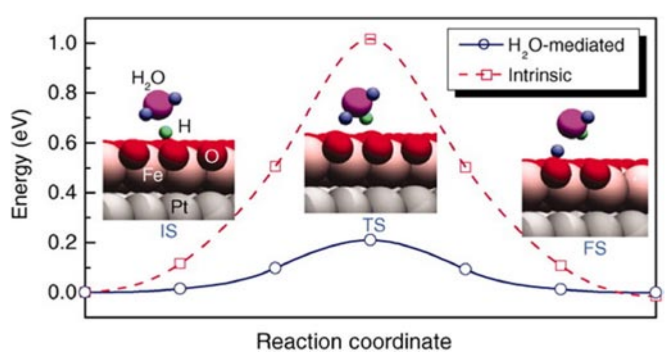

FIGURE 2. Energy profile for hydrogen atom diffusion on FeO/Pt(111): H_2O-mediated (blue solid line) and intrinsic (red dashed line); insets provide cross-sectional views of the initial (IS), transition (TS), and final state (FS) for the H_2O-mediated (fast) diffusion of H atoms. Figure from reference 1.

ligand effect[3]) and through lattice mismatch between Pt and the substrate (referred to as the strain effect[4]). In particular, for Pt*/Pd, these effects weaken oxygen binding slightly, so that Pt*/Pd gets closer to the optimal oxygen binding.

These initial studies revealed a strategy for improving the efficacy of these catalysts by taking advantage of ligand and strain effects. However, the cost of the Pd substrate was still high for commercial applications and the activity could be improved further. To address these challenges, we have now investigated a series of "onion-structured" alloys, which are composed of a Pt-monolayer deposited on a substrate with 0, 1 or 2 monolayers of Pd sandwiched between the Pt-monolayer and the substrate (denoted Pt*/M_2/M_3, see Figure 3).[5] The Pd sandwiched layers are important because they "shield" the Pt shell atoms from the ligand effect induced by the substrate material, while the substrate material was chosen to weaken the oxygen binding relative to Pt*/Pd by compressing the Pt*/Pd template slightly.

In Figure 4 we present the DFT-estimated catalytic activity (activity increases in the positive y-direction) of the onion-structured alloy catalysts, based on rigorous calculations of the reaction energetics on those surfaces, as a function of their oxygen binding affinity. This results in a "volcano curve". Additionally, we plot the theoretical activity of hypothetical catalysts over a continuum of binding properties with a purple line. This prediction is based on linear-scaling correlations[6] and Brønsted-Evans-Polanyi correlations[7], rather than through rigorous evaluations of all of the reaction energetics.

The optimal activity is found on surfaces that bind oxygen weaker (more positive in x-axis of Frig. 4) than both pure Pt and Pt*/Pd. We have found a number of candidate catalysts that are predicted to be significantly more active than Pt*/Pd (note that a change in activity of 0.06 eV corresponds to an order of magnitude change in the rate constant at room temperature). Of these active surfaces, Pt*/Pd/Pd_3Fe[8] and Pt*/PdIr[9] have now been synthesized and tested experimentally, verifying the predicted improvement in activity versus pure Pt.

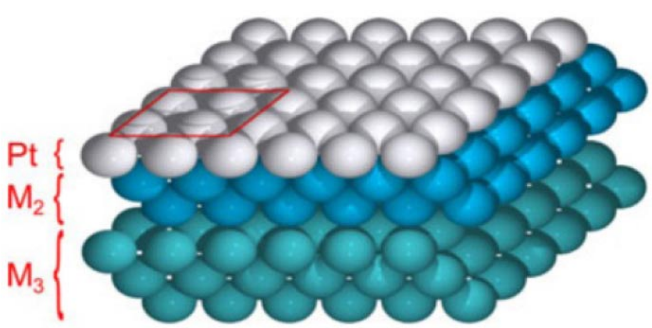

FIGURE 3. Cross-sectional view of "onion alloy" structures. M2 is typically Pd, while M_3 can be a monometallic or intermetallic alloy. Figure from reference 5.

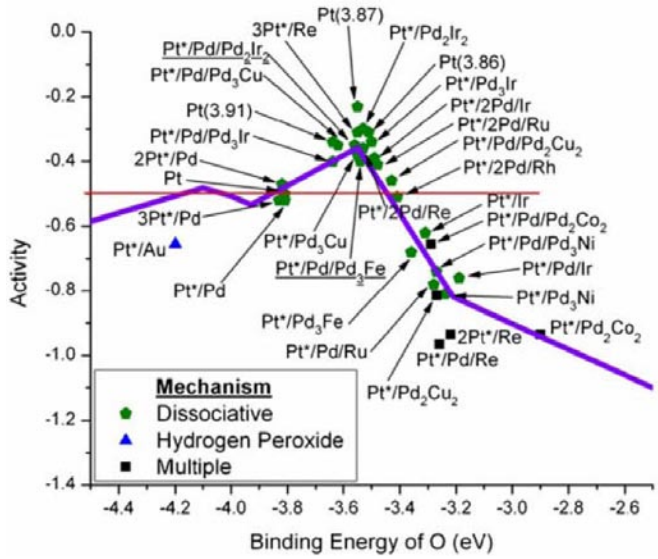

FIGURE 4. DFT-derived "volcano curve" for ORR activity (in eV) of close-packed surfaces versus oxygen binding energy. Activity of pure Pt is shown with the red horizontal line. Purple line represents the theoretical prediction of activity as a function of binding energy of oxygen. Figure from reference 5.

Future Directions

Our research plans for this coming year of the project have not changed from those described in detail in the most recent renewal proposal. In addition to furthering the work described here, we continue to pursue experimental and theoretical studies to test surface alloys for the vapor phase NO reduction by H_2. We also continue to investigate shape-selective nanoparticle synthesis, particularly through the variation of Br- ion concentration in the synthesis process, to yield nanocubes, truncated cubes, or cubotachedrons.

References

1. L.R. Merte, G.W. Peng, R. Bechstein, F. Rieboldt, C.A. Farberow, L.C. Grabow, W. Kudernatsch, S. Wendt, E. Laegsgaard, M. Mavrikakis, F. Besenbacher, "Water-Mediated Proton Hopping on an Iron Oxide Surface," *Science* **336**, 889-893 (2012).

2. J.L. Zhang, M.B. Vukmirovic, Y. Xu, M. Mavrikakis, R.R. Adzic, "Controlling the catalytic activity of platinum-monolayer electrocatalysts for oxygen reduction with different substrates," *Angewandte Chemie-International Edition* **44**, 2132-2135 (2005).

3. J.R. Kitchin, J.K. Norskov, M.A. Barteau, J.G. Chen, "Role of strain and ligand effects in the modification of the electronic and chemical properties of bimetallic surfaces," *Physical Review Letters* **93**, (2004).

4. M. Mavrikakis, B. Hammer, J.K. Norskov, "Effect of strain on the reactivity of metal surfaces," *Physical Review Letters* **81**, 2819-2822 (1998).

5. J.A. Herron, J. Jiao, K. Hahn, G. W. Peng, R.R. Adzic, M. Mavrikakis, "Oxygen Reduction Reaction on Platinum-Terminated "Onion-structured" Alloy Catalysts," *Electrocatalysis* **3**, 192-202 (2012).

6. F. Abild-Pedersen, J. Greeley, F. Studt, J. Rossmeisl, T.R. Munter, P.G. Moses, E. Skulason, T. Bligaard, J.K. Norskov, "Scaling properties of adsorption energies for hydrogen-containing molecules on transition-metal surfaces," *Physical Review Letters* **99**, (2007).

7. S.G. Wang, B. Temel, J.A. Shen, G. Jones, L.C. Grabow, F. Studt, T. Bligaard, F. Abild-Pedersen, C.H. Christensen, J.K. Norskov, "Universal Bronsted-Evans-Polanyi Relations for C-C, C-O, C-N, N-O, N-N, and O-O Dissociation Reactions," *Catalysis Letters* **141**, 370-373 (2011).

8. W.P. Zhou, X.F. Yang, M.B. Vukmirovic, B.E. Koel, J. Jiao, G.W. Peng, M. Mavrikakis, R.R. Adzic, "Improving Electrocatalysts for O-2 Reduction by Fine-Tuning the Pt-Support Interaction: Pt Monolayer on the Surfaces of a Pd3Fe(111) Single-Crystal Alloy," *Journal of the American Chemical Society* **131**, 12755-12762 (2009).

9. S.L. Knupp, M.B. Vukmirovic, P. Haldar, J.A. Herron, M. Mavrikakis, R.R. Adzic, "Platinum Monolayer Electrocatalysts for O-2 Reduction: Pt Monolayer on Carbon-Supported PdIr Nanoparticles," *Electrocatalysis* **1**, 213-223 (2010).

Publication list (including patents) acknowledging the DOE grant or contract:

1. Yang, L., Vukmirovic, M.B., Su, D., Sasaki, K., Herron, J.A., Mavrikakis, M., Liao, S., Adzic, R.R., Tuning the Catalytic Activity of Ru@Pt Core–Shell Nanoparticles for the Oxygen Reduction Reaction by Varying the Shell Thickness. *Journal of Physical Chemistry C* **2013**, *117* (4)

2. Merte, L.R., Peng, G., Bechstein, R., Rieboldt, F., Farberow, C.A., Grabow, L.C., Kudernatsch, W., Wendt, S., Lægsgaard, E., Mavrikakis, M., Besenbacher, F., Water-Mediated Proton Hopping on an Iron Oxide Surface. *Science* **2012,** *336* (6083)

3. Herron, J.A., Jiao, J., Hahn, K., Peng, G., Adzic, R.R., Mavrikakis, M., Oxygen Reduction Reaction on Platinum-Terminated "Onion-structured" Alloy Catalysts. *Electrocatalysis* **2012,** *3* (3-4)

4. Jewell, A.D., Peng, G., Mattera, M.F.G., Lewis, E.A., Murphy, C.J., Kyriakou, G., Mavrikakis, M., Sykes, E.C.H., Quantum Tunneling Enabled Self-Assembly of Hydrogen Atoms on Cu(111). *ACS Nano* **2012,** *6* (11)

5. Svenum, I.-H., Herron, J.A., Mavrikakis, M., Venvik, H.J., Adsorbate-Induced Segregation in a PdAg Membrane Model System: $Pd_3Ag(111)$. *Catalysis Today* **2012,** *193* (1)

6. Herron, J.A., Tonelli, S., Mavrikakis, M., Atomic and Molecular Adsorption on Pd(111). *Surface Science* **2012,** *606* (21-22)

7. Rossmeisl, J., Ferrin, P., Tritsaris, G.A., Nilekar, A.U., Koh, S., Bae, S.E., Brankovic, S.R., Strasser, P., Mavrikakis, M., Bifunctional Anode Catalysts for Direct Methanol Fuel Cells. *Energy & Environmental Science* **2012,** *5* (8)

8. Karan, H.I., Sasaki, K., Kuttiyiel, K., Farberow, C.A., Mavrikakis, M., Adzic, R.R., Catalytic Activity of Platinum Monolayer on Iridium and Rhenium Alloy Nanoparticles for the Oxygen Reduction Reaction. *ACS Catalysis* **2012,** *2* (5)

9. Peng, H.-C., Xie, S., Park, J., Xia, X., Xia, Y., Quantitative analysis of the coverage density of Br^- ions on Pd{100} facets and its role in controlling the shape of Pd nanocrystals. *Journal of the American Chemical Society* **2012,** *135* (10)

10. Xie, S., Choi, S.-I., Xia, X., Xia, Y., Catalysis on faceted noble-metal nanocrystals: both shape and size matter. *Current Opinion in Chemical Engineering* **2013,** *2*

11. Xia, Y., Xia, X., Wang, Y., Xie, S., Shape-controlled synthesis of metal nanocrystals. *MRS Bulletin* **2013**, in press

12. Patent Application: P120136US01 Mixed-metal platinum catalysts with improved carbon monoxide tolerance, Filed Date: Sept. 21, 2012; M. Mavrikakis, A.U. Nilekar, R.R. Adzic, K. Sasaki