

# Beckman Final Report

Nathan S. Froemming

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## 1 Introduction

I will start by saying that I am a theoretical chemist, and like all theoreticians in this area, I am fundamentally interested in the electronic structure of matter. Most theoretical chemists (myself included) will give some version of the following statement when asked what motivates their interest in this field: If the breaking and forming of bonds in any chemical reaction is governed by electrons, and if electrons are quantum-mechanical particles, then if we wish to understand and describe chemistry at the most fundamental level, we need to be able to understand and describe the quantum-mechanical behavior of electrons in such chemical reactions. But this is a very tricky business, however, because Quantum Mechanics is no easy pill to swallow; Einstein himself had serious beef with Quantum Mechanics, even though he helped invent it! Here, I don't really have the time or the space to go into any lengthy discussion of the difficulty/rigor/strangeness/beauty of the quantum theory of matter, but just know that the particular flavor of theory that I work with is called *Density Functional Theory* (DFT), and that in any of the systems I describe below, I have used DFT to investigate the electronic structure of that particular chemical system.

Specifically, my work focuses on *catalysis*, the idea that chemical reactions can be accelerated by means of a 'catalysts', which itself is not consumed in the reaction – catalysts only help to facilitate chemical reactions (by lowering the energy barrier for that particular chemical process). Again, this is an issue of how such a catalyst interacts electronically with the reactants in the chemical process, and by understanding such catalytic systems fundamentally, it is the hopes that new, more effective catalysts can be developed. The following is a brief but insightful summary of the research I have conducted during my tenure as a Beckman Scholar (2006–2007) involving three such catalytic systems, which are described in more detail below.

## 2 CO Oxidation on Au(111)

Carbon monoxide is a poison to us—it binds irreversibly to the heme in our blood and works to suffocate us upon inhalation. This is one of the reasons that catalytic converters have been mandated to be installed in all vehicles. Interestingly though, gold, which is traditionally thought of as being too inert to be a good catalyst, has shown a curious propensity for the oxidation of CO in the presence of O atoms and H<sub>2</sub>O. Here, I will discuss some of my more interesting theoretical findings as to why these reactions occur.

The oxidation of CO is a very simple chemical reaction:



First, I want to discuss why bulk Au is not reactive with respect to Equation (1). This can be traced back to the fact that at some point in the reaction path, the double bond of O<sub>2</sub> must be broken, which costs a lot of energy. This process is shown in Figure (2). Based on the barrier of this process (0.73 eV), this reaction

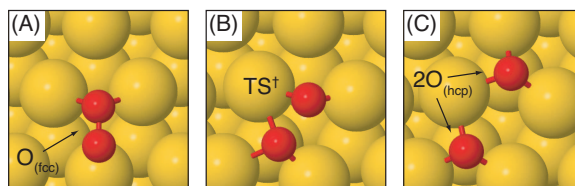


Figure 1: *The dissociation of O<sub>2</sub> on Au(111).* (A) The initial state with O<sub>2</sub> bound to the fcc site. (B) The transition state of the reaction, with both O atoms occupying two adjacent bridge sites. The barrier for this reaction is 0.73 eV. (C) The final state of the reaction with two O atoms adsorbed at two adjacent hcp sites.

should happen at temperatures of approximately 306 K (assuming a typical reaction prefactor of  $5 \times 10^{12} \text{ s}^{-1}$ ), yet it does not. Then why doesn't bulk Au catalyze this reaction? Well, the problem with bulk Au is that *it does not even bind O<sub>2</sub> to begin with*. Using DFT, I have calculated the binding energy of O<sub>2</sub> to be 0.19 eV, which corresponds to a thermal desorption temperature of approximately 76 K (about the temperature of liquid N<sub>2</sub>), meaning that O<sub>2</sub> leaves the surface long before it ever has a chance to dissociate on Au(111). Of course Au has trouble catalyzing this reaction if what it is trying to catalyze is never present on the surface to begin with!

Experimentalists have, however, figured out ways of putting single atoms of oxygen on Au(111) (for instance, by first blasting apart O<sub>2</sub> with radiofrequency pulses and then depositing these O atoms on gold). They find that these O atoms then react very easily with CO to form CO<sub>2</sub>. I have looked at this process using DFT, and my findings are summarized in Figure (2). This is a very low-energy process, corresponding to thermal activity around 98 K. Thus, both the theory and the experiment agree that once O atoms are present on the Au surface, the gold has no problem bringing the two species together and allowing them to react to form CO<sub>2</sub>.

The last thing that I want to talk about with respect to CO oxidation on Au(111) is the role that H<sub>2</sub>O can play in the reaction. Experimentalists have noted that in the presence of O and H<sub>2</sub>O, CO oxidation on Au

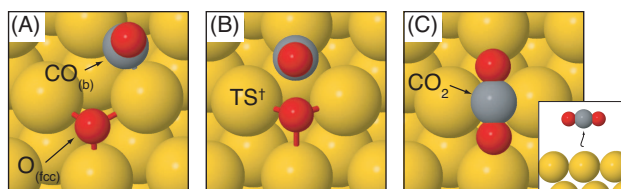


Figure 2: *The oxidation of CO on Au(111)*. (A) The initial state of the reaction. (B) The transition state of the reaction. This reaction occurs with a barrier of 0.25 eV. (C) The final state of the reaction where CO<sub>2</sub> has desorbed from the surface.

occurs more rapidly than without H<sub>2</sub>O. I've looked at this from the theoretical standpoint, and I notice some interesting things. First of all, it is actually very easy for Au to catalyze the dissociation of H<sub>2</sub>O if there are O atoms present on the Au surface. The results of some of my findings are shown in Figure (3). Based

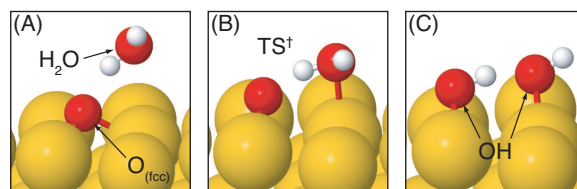


Figure 3: *The dissociation of H<sub>2</sub>O on Au(111)*. (A) The initial state of the reaction where H<sub>2</sub>O hydrogen bonds to an O atom adsorbed at the fcc site. (B) The transition state of the reaction. This reaction happens with a very low barrier, only 0.11 eV. (C) The final state of the reaction, with two hydroxyls bound to the surface and hydrogen bonding to one another. The geometry is essentially exactly the same in energy as the initial state, making it possible for hydrogen to easily transfer between H<sub>2</sub>O and O on the Au surface.

on the activation energy for this process, water dissociation occurs at temperatures around 44 K. The next interesting thing is that these hydroxyls, once formed by the dissociation of H<sub>2</sub>O, can react very easily with CO, as shown in Figure (4). Based on the activation energy for this process (0.10 eV), it is safe to say that

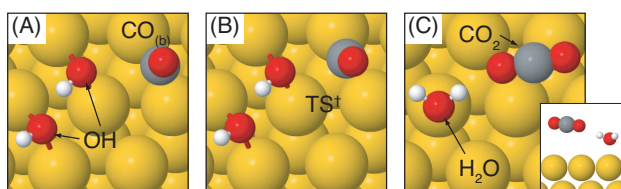


Figure 4: *Water acting as a promoter for the oxidation of CO on Au(111) via hydroxyl intermediates*. (A) The initial state of the reaction (after H<sub>2</sub>O has been dissociated) with two hydroxyls bound to the surface. (B) The TS of the reaction. The barrier for the reaction is only 0.10 eV, and depends largely on the diffusion of CO to the other reactants. (C) The final state of the reaction where H<sub>2</sub>O is still bound to the surface and CO<sub>2</sub> has essentially left.

CO oxidation in the presence of O and H<sub>2</sub>O occurs very rapidly on Au(111), somewhere around 45 K or so. This is yet again another example where the theory corresponds very nicely to the experiment. I have many other results, but these are just a few of the more interesting ones. The work I have done on this system is going to lead to a publication, but I'm not sure which journal it will be in, so I can't site that reference at the moment. On to the next system....

### **3 Methane Activation on Iridium Nanoparticles and Surfaces**

Methane, CH<sub>4</sub>, is an important compound because it is the principal chemical from which hydrogen gas, H<sub>2</sub>, is derived in the steam reforming process:



This particular reaction (called the "steam reforming process") may be of great interest in the future if hydrogen fuel cells are to replace internal combustion engines and petroleum products as the energy carrier of our future. Moreover, such catalysts may help to ease the transition to the Hydrogen Economy by facilitating the following chemical reaction (or reactions like it):



What is important in Equation (3) is that a simple hydrocarbon, methane, can be reformed into a more complex hydrocarbon (in this case ethane), while producing hydrogen gas in the process. Not only would such catalysts help to generate hydrogen to support the Hydrogen Economy, but they might also offer us a way to build higher-order hydrocarbons from simpler ones as we make the transition to the Hydrogen Economy. Iridium is a catalyst that has shown promise for catalyzing both Equations (2) and (3), and I show some of my theoretical findings that may help explain why this is so in Figure (5). I have also been compiling data for methane activation on bulk iridium surfaces, which is summed up in Figure (6). My work in this area will probably also lead to a publication eventually, but I'm not far enough along to site a specific journal article. On to the next system...

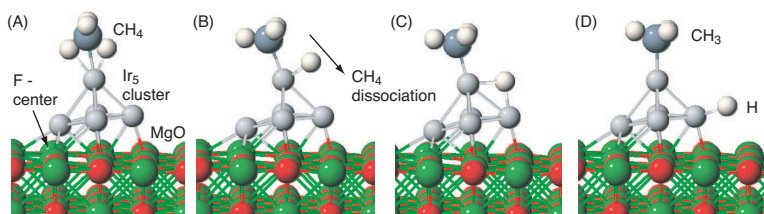


Figure 5: Dissociation of  $\text{CH}_4$  on an  $\text{Ir}_5$  cluster supported at an O-vacancy on  $\text{MgO}(100)$ . This reaction occurs spontaneously. Such iridium nanoparticles may work to perform the elementary steps necessary to catalyze Equation (2) as well as to recombine methyl substituents in order to catalyze Equation (3). Theoretical treatment of such systems is essential in accurately describing these complex catalytic processes as well as understanding the electronic properties of the catalysts that leads to their efficacy.

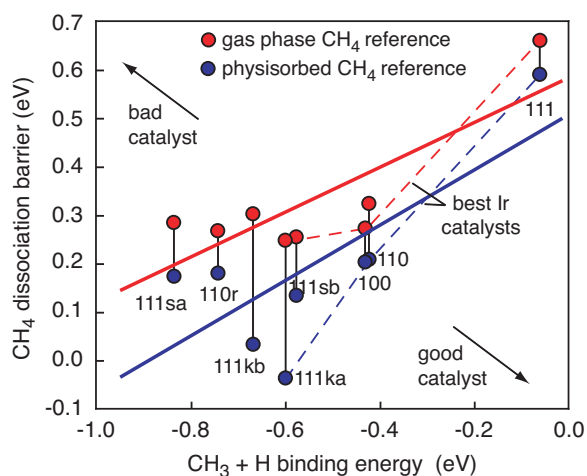


Figure 6: Activation energies and binding energies for methane activation on various iridium surfaces. It is important to note that an ideal catalyst would make the chemical reaction happen with a little or no energy barrier and would bind the products of the reaction with little or no energy (such that the overall reaction would proceed at the maximum rate), which is denoted in the lower right-hand corner of the graph.

## 4 Survival of the Fittest: Using a Genetic Evolutionary Algorithm to Design Better Fuel Cell Catalysts

(This is the research that I gave my talk on at the Beckman Scholars Symposium just a few days ago. It may very well lead to a publication in a research journal (especially after some of these catalysts are investigated experimentally), but it's really too early to say.) Platinum-based fuel cells offer an attractive alternative to internal combustion engines as a future means of utilizing chemical energy, however, severe shortcomings of such technologies must be resolved if they are to become practical and widespread. Some of these difficulties include a disparity between the reaction rates at the anode and cathode, the short lifetime

of electrodes in acidic environments, the energy loss due to a kinetic overpotential, and the high material cost and limited supply of Pt itself. Better catalysts need to be developed, yet the task of discovering cheaper, more effective platinum alternatives has proven to be extremely challenging. In my current work, I am investigating the catalytic properties of a large number of candidate bimetallic catalysts using a genetic evolutionary algorithm. Specifically, I apply the algorithm to bimetallic nanoparticles in which the core atom type differs from the shell atom type. In the algorithm, a chromosome that takes into account the identities of the core and shell represents each system, and each system's fitness is its ability to catalyze the oxygen reduction reaction, the so-called bottleneck of present fuel cell technologies. I evaluate the fitness of each system by using density functional and transition state theories (theoretical chemistry) to calculate the electronic structure of the nanoparticle and to determine activation and reaction energies for the oxygen reduction reaction. At each step in the algorithm, the best catalysts in the population are selected for based on their fitness and bred by crossing their chromosomes, and the worst catalysts in the population are replaced with the offspring of the best catalysts. With time, subsequent generations evolve toward the best fitness, and I show how the energy of the electrons in the shell can be optimized for the oxygen reduction reaction by varying the core and shell metal types in the bimetallic nanoparticles. Promising platinum alternatives revealed by such a theoretically based search-and-screen approach can then be tested experimentally, helping to avoid the costly trial-and-error processes commonly used to optimize catalysts.