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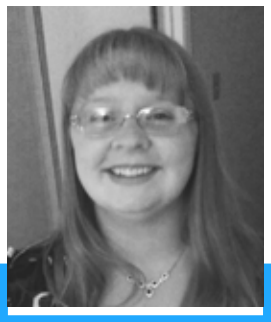
RESEARCH HIGHLIGHTS

+ From Caltech's Resnick Fellows

Mechanisms and Surface Attachment of Molecular Solar Fuels Catalysts



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Mechanisms and Surface Attachment of Molecular Solar Fuels Catalysts

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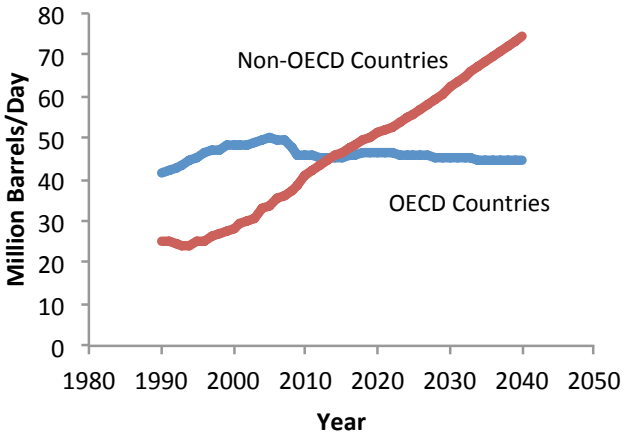
Global Significance

As earth's population grows, our energy consumption will grow with it. While consumption in developed nations may level off, as predicted by the US Department of Energy, consumption in developing nations will continue to grow.
In addition, current energy sources such as fossil fuels output CO_2 and other pollutants.
It is important to develop sustainable, clean, and economical sources of energy.

The overarching goal of this project is to make fuel from a sustainable, renewable source that does not contribute to pollution, and to make it in an inexpensive way so energy is available to everyone.



U.S. Energy Information Administration, International Energy Outlook 2014, DOE/EIA-048(2014), September 9, 2014

Figure 1: *Consumption of oil is expected to level off in developed countries (blue line), while it is expected to increase in developing countries (red line). In order to meet this demand, new energy sources must be developed.*

Figure 2: Beijing's Red Flag pollution crisis in 2015 highlights the need for clean energy sources. Much of the pollution was due to coal fired power plants north of the city.

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Project Summary

We would like to use solar energy to power the planet as it is clean and renewable. However, since the sun's daily production often does not align with energy consumption, we must find a way to store the energy so it can be accessed later. Plants store the sun's energy through photosynthesis, where sugars are made from water, CO_2 and sunlight. The chemical bonds of the sugars hold the sun's energy until the plant uses it later.

We would like to mimic plants' ability to store energy in chemical bonds, but rather than making sugars, we would like to produce a fuel like hydrogen or liquid carbon-based fuels like gasoline.

To make these fuels, a molecule called a catalyst is needed to bring down the amount of energy required to make the fuel. I use computational chemistry to look at the steps these catalysts complete in order to make fuel molecules.

Once we understand how these molecules work, we can predict new catalysts that are cheaper and more abundant. I also investigate ways to make these catalysts useful in large-scale industrial situations, such as attaching them to a surface to make it easier to separate the product fuel from the catalysts.

- This is a multi-disciplinary project that combines chemistry with materials science and computer science.
- We use the computer to model the different steps of reactions to understand what is happening to the atoms in them.

Potential Impact

If we can make hydrogen fuel from sunlight, we will be able to extend the penetration of solar into other energy markets. Instead of using batteries or capacitors to store energy, we will be able to store it in transportable fuel. If we take this project one step further and are able to create liquid carbon-based fuels from sunlight, we will be able to integrate solar fuel into the existing transportation fuel infrastructure. Currently, transportation is the second largest contributor to greenhouse gas emissions.

Converting just a tenth of current transportation fuel usage to a perfectly carbon neutral, clean source of energy would decrease CO_2 emissions by over 150 million metric tons in the US alone. According to the EPA, this is equivalent to removing approximately 30 million cars and light trucks from the road.

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The Science

Several known molecular catalysts can selectively make H_2 or carbon-based fuels, but they often involve expensive and rare metals like rhodium and iridium. We use computational chemistry to study the mechanisms compounds use to see what unique properties allow them to function. We can calculate the energy of intermediates and barriers to find the most favorable path for reactions.

From our deeper understanding of the mechanism, we predict and test new catalysts, some of which have yet to be made. Additionally, we can look computationally at methods of attaching these catalysts to electrodes to aid in transporting electrons to the catalyst and in separating the product fuels from the catalyst.

One catalyst of note is Cp*Rh(bpy) [Cp* = pentamethylcyclopentadienyl, bpy = bipyridine], which is shown below. Upon reduction and presence of an acid, this catalyst can produce hydrogen. It can also be attached to a silicon surface via excitation of chlorine bonds, but once electrons are added, it dissociates from the surface.

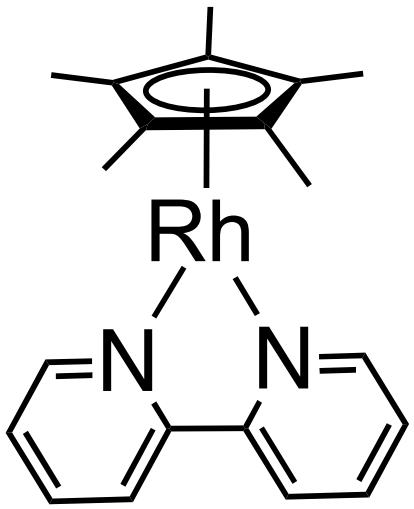

Figure 3: *Cp*Rh(bpy)*

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Key Results

Contrary to previously held assumptions, upon protonation, the proton can migrate from the metal to the Cp* ligand. This ligand is widely thought to not participate in many reactions and the metal is thought to do all the significant work. However, in the Rh system, the Cp* ligand serves as a "parking spot" for the proton. Transfer of the proton back to the metal may be the rate limiting step for this catalyst. This result is significant because it shows a unique and previously undiscovered case where an "innocent" ligand participates in a catalytic reaction.

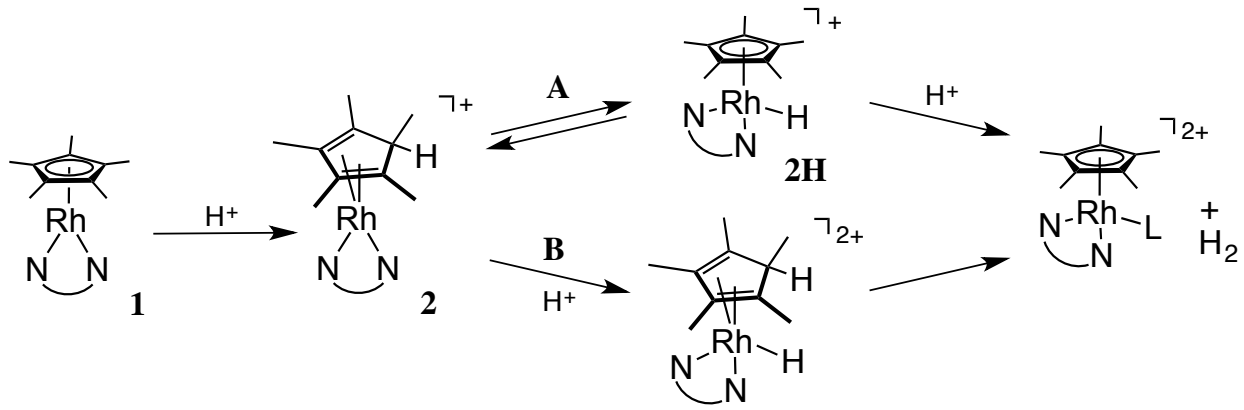

Figure 4. *The Rh catalyst can take one of two pathways: One through pathway A where the proton transfers back to the metal center and then is pronated, or B where the second protonation occurs at the metal and then the two protons are combined.*

Future Steps

We are computing the rest of the mechanism for hydrogen evolution in this catalyst. The key is to find the barrier by which a second proton is added to the system to make H_2. Finally, we are testing a variety of dissociation pathways in surface attached catalysts.

Publications

- Quintana, L. M. A.; Johnson, S. I.; Corona, S. L.; Villatoro, W.; Goddard, W. A.; Takase, M. K.; VanderVelde, D. G.; Winkler, J. R.; Gray, H. B.; Blakemore, J. D., Proton–hydride tautomerism in hydrogen evolution catalysis. Proceedings of the National Academy of Sciences 2016, 113 (23), 6409-6414.
- Samantha I. Johnson, James D. Blakemore, Robert J. Nielsen, Bruce S. Brunschwig, Nathan S. Lewis, Petter Persson, William A. Goddard III. "Design of robust attachment of bipyridine ligands and metal complexes to Si for heterogeneous catalysis". In preparation.