

Hydrogen Oxidation by Monometallic Nickel and Iron Catalysts

Zachary Gordon

Literature Seminar

November 12, 2013

With global energy demands rapidly increasing, many scientists are looking towards hydrogen as a sustainable alternative to fossil fuels.^{1,2} Fuel cells represent some of the most developed technology for harnessing energy stored in hydrogen. Polymer electrolyte membrane (PEM) fuel cells, among other types, can be operated using hydrogen and oxygen to produce electricity with water as the only byproduct. The utility of such devices is currently restricted by their dependence on platinum catalysts, resulting in prohibitively high costs.³ Furthermore, the vast majority of hydrogen used in these applications is currently produced from fossil fuels, preventing the development of H₂ as a truly sustainable energy source.⁴ Nature addresses both of these limitations by using hydrogenase enzymes to catalyze both hydrogen oxidation and production (Figure 1).⁵

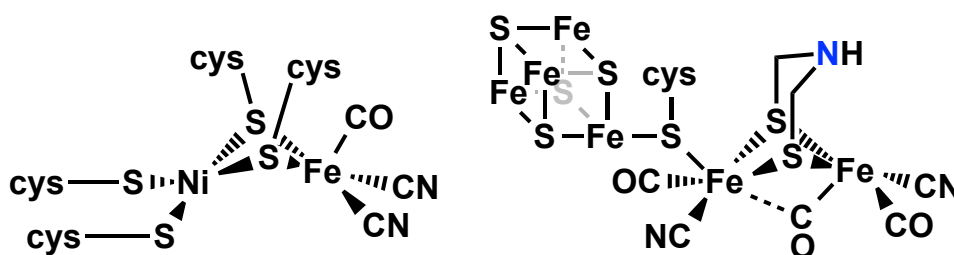


Figure 1: Active sites of [NiFe] and [FeFe] hydrogenases

Drawing inspiration from these enzymes, many researchers have developed structural⁶⁻⁹ and functional¹⁰⁻¹³ mimics. While a number of electrocatalysts for H₂ production have been reported, the chemistry of H₂ oxidation remains relatively underdeveloped. Among the most promising of these catalysts are a family of monometallic complexes developed by DuBois and coworkers at Pacific Northwest National Laboratory.

Beginning with the primary coordination sphere, a ligand framework was incrementally developed to promote similar reactivity to [FeFe]-hydrogenase. In the enzyme, strong field CO and CN ligands enforce a low spin configuration, allowing for an open coordination site capable of binding dihydrogen.¹⁴ In model nickel complexes these ligands were approximated by chelating phosphine ligands. The resulting [Ni(diphosphine)₂]²⁺ complexes were found to be electrocatalytically active for hydrogen oxidation, albeit at low rates with substantial overpotentials.¹⁵

Drawing on the role of the secondary coordination sphere at the enzyme's active site, specifically that of the amine linker in the bridging dithiolate ligand, the diphosphine framework was modified to include an analogous internal base.¹⁶ While this change decreased the operating potential for hydrogen oxidation, catalysis still proceeded slowly. A second pendant amine was then added to each diphosphine ligand to force one of the six-membered rings into a boat conformation, bringing the nitrogen atom within 3.3 Å of the metal center. This positioning further reduced the operating potential and resulted in a greater than five-fold increase in turnover frequency.¹⁷

Recently, this ^RP₂^{R'}N₂ (R=Et, Cy, Ph, ^tBu; R'=Me, ^tBu, Ph, Bn) ligand platform has been used in combination with cyclopentadienyl (Cp) derivatives to synthesize related iron complexes.¹⁸ The authors introduced Cp as an electronic mimic of hydrogenase's cyanide ligands, which also provided for facile electronic and steric modification of their molecules. Starting from the chloride precursor [C₆F₅CpFe(^tBuP₂^{Bn}N₂)Cl], hydride, dihydrogen, and coordinatively unsaturated complexes were accessible via stoichiometric reactions in good to

high yields.¹⁹ After characterizing these complexes electrochemically, the catalytic activity of the hydride derivative was examined. It was found to be an effective catalyst for electrochemical hydrogen oxidation in the presence of exogenous base, as indicated by increased peak current relative to the hydride complex in the absence of base. On the basis of these studies, the following catalytic cycle was proposed (**Figure 2**).

The $R^2P_2R^1N_2$ ligand framework has displayed the ability of hydrogenase-inspired complexes to efficiently oxidize H_2 . Ni^{2+} and Fe^{2+} complexes based on this design have achieved record high turnover frequencies (58 s^{-1} and 2.0 s^{-1} respectively).^{20,19} While further improvements are still required for this technology to achieve widespread use in alternative energy applications, this work demonstrates the potential of monometallic nickel and iron-based complexes as fast, cost-effective electrocatalysts for hydrogen oxidation.

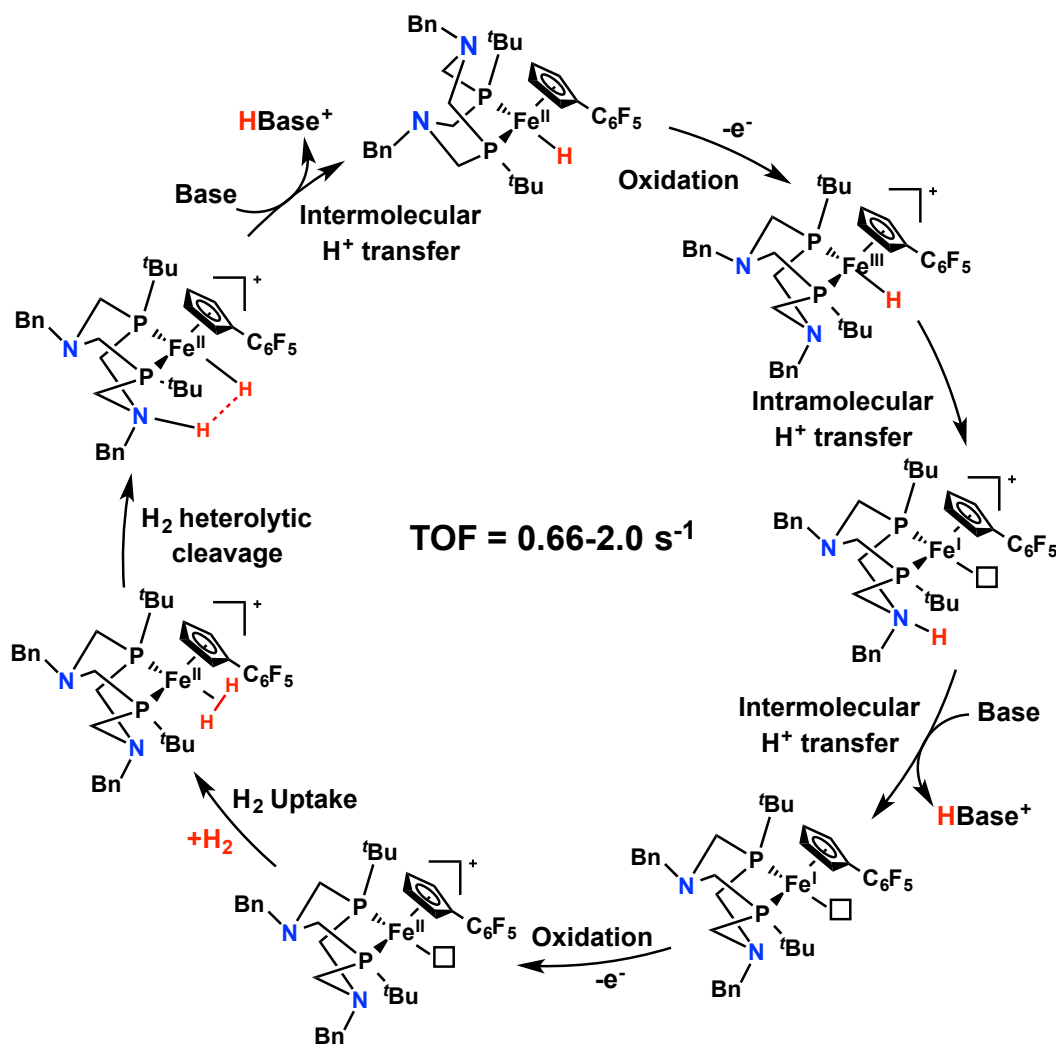


Figure 2: Proposed catalytic cycle for electrochemical H_2 oxidation (base = N -methylpyrrolidine, Et_3N , or iPr_2EtN)

References:

1. Crabtree, G. W.; Dresselhaus, M. S.; Buchanan, M. V. "The hydrogen economy," *Phys. Today* **2004**, *57*, 39-44.
2. Dunn, S. "Hydrogen futures: toward a sustainable energy system," *Int. J. Hydrogen Energy* **2002**, *27*, 235-264.
3. Di Noto, V. et al. "Polymer electrolytes for a hydrogen economy," *Int. J. Hydrogen Energy* **2012**, *37*, 6120-6131.
4. Armaroli, N.; Balzani, V. "The Hydrogen Issue," *ChemSusChem* **2011**, *4*, 21-36.
5. Frey, M. "Hydrogenases: hydrogen-activating enzymes," *ChemBioChem* **2002**, *3*, 153-160.
6. Camara, J.; Rauchfuss, T. B. "Mild redox complementation enables H₂ activation by [FeFe]-hydrogenase models," *J. Am. Chem. Soc.* **2011**, *133*, 8098-8101.
7. Camara, J.; Rauchfuss, T. B. "Combining acid-base, redox and substrate binding functionalities to give a complete model for the [FeFe]-hydrogenase," *Nature Chem.* **2012**, *4*, 26-30.
8. Hsieh, C. H., et al. "Structural and Spectroscopic Features of Mixed Valent Fe^{II}Fe^I Complexes and Factors Related to the Rotated Configuration of Diiron Hydrogenase," *J. Am. Chem. Soc.* **2012**, *134*, 13089-13102.
9. Harb, M. K., et al. "Comparison of S and Se dichalcogenolato [FeFe]-hydrogenase models with central S and Se atoms in the bridgehead chain," *Tetrahedron* **2012**, *68*, 10592-10599.
10. Sun, Y., et al. "Molecular Cobalt Pentapyridine Catalysts for Generating Hydrogen from Water," *J. Am. Chem. Soc.* **2011**, *133*, 9212-9215.
11. Lee, C. H.; Dogutan, D. K.; Nocera, D. G. "Hydrogen Generation by Hangman Metalloporphyrins," *J. Am. Chem. Soc.* **2011**, *133*, 8775-8777.
12. McNamara, W. R., et al. "A Cobalt-Dithiolene Complex for the Photocatalytic and Electrocatalytic Reduction of Protons," *J. Am. Chem. Soc.* **2011**, *133*, 15368-15371.
13. Bhattacharjee, A. et al. "A Computational Study of the Mechanism of Hydrogen Evolution by Cobalt(Diimine-Dioxime) Catalysts," *Chem. Eur. J.* **2013**, *19*, 15166-15174.
14. Shaw, W. J.; Helm, M. L.; DuBois, D. L. "A modular, energy-based approach to the development of nickel containing molecular electrocatalysts for hydrogen production and oxidation," *Biochim. Biophys. Acta.* **2013**, *1827*, 1123-1139.
15. Curtis, C. J.; Miedaner, A.; Ellis, W. W.; DuBois, D. L. "Measurement of the hydride donor abilities of [HM(diphosphine)₂]⁺ complexes (M=Ni, Pt) by heterolytic activation of hydrogen," *J. Am. Chem. Soc.* **2002**, *124*, 1918-1925.
16. Curtis, C. J., et al. "[Ni(Et₂PCH₂NMeCH₂PEt₂)₂]²⁺ as a Functional Model for Hydrogenases," *Inorg. Chem.* **2003**, *42*, 216-227.
17. Wilson, A. D., et al. "Hydrogen oxidation and production using nickel-based molecular catalysts with positioned proton relays," *J. Am. Chem. Soc.* **2006**, *128*, 358-366.
18. Liu, T., et al. "Synthesis, characterization, and reactivity of Fe complexes containing cyclic diazadiphosphine ligands: the role of the pendant base in heterolytic cleavage of H₂," *J. Am. Chem. Soc.* **2012**, *134*, 6257-6272.
19. Liu, T.; DuBois, D. L.; Bullock, R. M. "An iron complex with pendent amines as a molecular electrocatalyst for oxidation of hydrogen," *Nature Chem.* **2013**, *5*, 228-233.
20. Yang, J. Y., et al. "Two Pathways for Electrocatalytic Oxidation of Hydrogen by a Nickel Bis(diphosphine) Complex with Pendant Amines in the Second Coordination Sphere," *J. Am. Chem. Soc.* **2013**, *135*, 9700-9712.