Theoretical Research Program on Bio-inspired Inorganic Hydrogen Generating Catalysts and Electrodes

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Objectives

Our goal is the theoretical design of a model electrocatalytic or photo-electrocatalytic system for economical production of hydrogen from water and sunlight via the hydrogen evolution reaction. The system under investigation consists of an FeS_2 (100) surface decorated with a cluster derived by design from the active site of the di-iron hydrogenase enzyme. Immersed in acidified water with the FeS_2 the source of electrons and the water of protons, the system facilely produces H_2 in simulations. Our immediate goal is to design a protective structure which inhibits the attack of the clusters and the exposed FeS_2 sites by dissolved O_2.

Technical Barriers

For economic feasibility, a system for production from sunlight and water must be made of earth abundant materials and contain a catalyst active enough to utilize efficiently electrons generated from the solar flux. The active site of the hydrogenase enzyme would meet those requirements *if* (1) it could be redesigned to retain its activity when extracted from the enzyme while stably attached to a suitable electrode and exposed to acidified water *and if* (2) it could be protected from attack by the dissolved oxygen inevitably present. Our design of the unprotected decorated pyrite surface should help overcome barrier (1). Our current research on structured overlayers should help overcome barrier (2).

Abstract

We have designed a catalytic cluster, $[FeFe]_P$, derived from the active cluster of the di-iron hydrogenase and functionalized the pyrite (100) surface with it. Remaining stable throughout, it produces hydrogen from acidified water with a free-energy barrier of less than 8.2 kcal/mol in room temperature simulations. The rate-limiting step in the cycle is the first protonation, subsequent steps are barrier free and fast. A detailed mechanistic analysis of the bond switching, oxidation-state changes, and electron flow during that step was carried out. Oxygen binding studies suggested diminished O_2 sensitivity of $[FeFe]_P$ and a need to focus on the sensitivity of the exposed pyrite Fe sites.

Progress Report

The achievements to date are: 1. design of the $[FeFe]_P$ catalytic cluster; 2. demonstration of hydrogen production from acidified water; 3. demonstration of structural stability of the functionalized surface throughout the production cycle; 4. identification of the first protonation of the catalyst as the rate-limiting step in the cycle, with an upper bound of 8.2 kcal/mol for its free-energy barrier; 5. detailed mechanistic analysis of the bond switching, oxidation-state changes, and electron flow during the first protonation; 6. finding diminished O_2 sensitivity of $[FeFe]_P$.

Design of $[FeFe]_P$

We first studied the hydrogen production cycle by the unsupported $[FeFe]_H$ cluster in vacuo[1] and in acidified water.[2] In the di-iron $[FeFe]_H$ cluster, removed from the enzyme, two iron atoms are coordinated to CO and CN ligands and bridged by a chelating group, S-CH2-X- CH2-S where X can be a NH (DTMA) or CH2 (PDT) group, Figure 1. One iron atom, Fe_p, is 6-fold coordinated, the other, Fe_d, 5-fold with a vacant coordination site V at which the reaction occurs in the active isomer, Figure 1.

We made several critical modifications to $[FeFe]_H$ (with DTMA) to obtain a stable and functional pyrite-supported catalyst.[3] We obtained a stable link by stripping off the thiol from Fe_p and connecting it directly to a pyrite surface

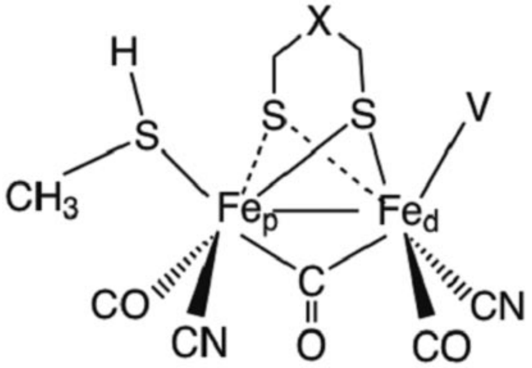

FIGURE 1. The active μ-CO isomer (after Ref. [1])

sulfur atom. Further stabilization was provided by linking a surface Fe atom to the N atom of the CN ligand of Fe$_p$. We interchanged the CO bridging group with the CN ligand of Fe$_d$ to form a third stable link between the N atom and a surface Fe atom, locking the cluster into the bridging configuration. Lastly, the outer S in the chelating group was changed to an isoelectronic PH group to stabilize the Fe$_d$-chelating group bond to form [FeFe]$_P$, Figure 2.

Demonstration of structural stability and H_2 production

Both the cluster-electrode linkage and the cluster structure remain stable throughout the H_2 production cycle,[4] which is started with the functionalized electrode in the [FeFe]$_P^{-1}$ state. Both proton additions take place entirely at the vacant coordination site V on Fe$_d$. The structural and compositional modifications leading to [FeFe]$_P$ eliminate all other protonation sites and all structural lability and greatly simplify the reaction mechanism.

In water, the first proton moves towards Fe$_d$ by a complex pathway along which there is a free-energy barrier. Because of the barrier, simulation of the reaction was carried out by constrained FPMD to prevent the proton from wandering away from the catalyst in the brief duration of the simulation. We obtained a strong upper bound of 8.2 kcal/mol (0.36 eV) for the barrier by thermodynamic integration.[4]

Electron flow and oxidation-state changes

First protonation is the rate-limiting step in hydrogen production from acidified water room-temperature simulations. Second protonation and desorption of the H_2 occur spontaneously during our picosecond-scale simulations.

We analyzed the mechanism of 1st protonation in Ref. [5] by computing densities of the maximally-localized Wannier functions (WD) and their centers of gravity (WC) for several states along the reaction pathway established in Ref. [5]. From the locations and forms of the WD and the locations and movements of the WC, we established that only the Fe$_p$, Fe$_d$, μ-C, and P atoms as well as the added H play significant roles in the reaction. We established the nature of their bonds, their oxidation states (OS), and the electron flow responsible for the OS changes and bond switching. The P atom acts as the initial proton attractor, the μC, Fe$_d$ pair act as the redox center, and the Fe$_p$ acts to facilitate bond switching from two 2-center μC-to-Fe bonds to one 3-center bond upon protonation. These features of the reaction mechanism are clearly displayed in Figure 3. This novel method of OS determination should be of broad use for the analysis of redox reactions; we illustrated it in [5] for the superoxide reductase enzyme as well.

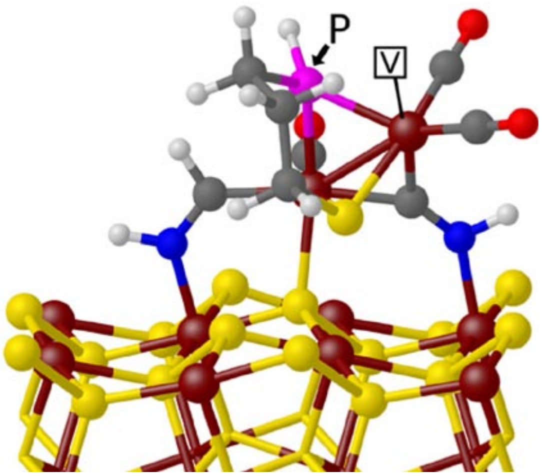

FIGURE 2. Side view of the [FeFe]$_P$ cluster linked to the FeS_2 (100) surface.

O_2 sensitivity of pyrite and the catalyst

Undesirable oxidation of catalytic active centers is a common problem in catalyst design. The active center of hydrogenase is poisoned by O_2, as modelled in Ref. [6] and could be expected for [FeFe]$_P$ as well. Moreover, the pyrite electrode reacts readily with O_2 in the presence of water.[7,8] To address these issues, we first studied the binding of O_2 on the active center in vacuo. Table 1 shows O_2 binding energies, and Fe$_d$-O and O-O distances in the optimized binding structure at different charge states. As shown in the

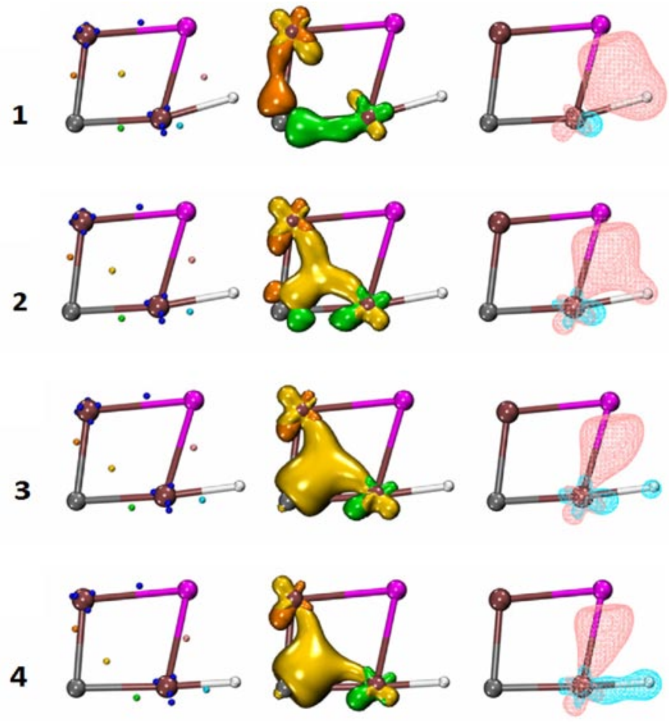

FIGURE 3. Four stages in the evolution of the relevant MLWF density and WC's as the first protonation proceeds. Fe atoms are brown; S atoms are yellow; the P atom is violet; C atoms are gray; N atoms are blue; O atoms are red; and H atoms are white. The isosurfaces are at 20% of their maximum values.

table, the neutral cluster has a small O_2 binding energy, -3.45 kcal/mol. On the other hand, the charge -1 cluster scarcely favors O_2 binding as indicated by the large Fe_d-O distance and negligible binding energy. Full-scale FPMD simulations in water are needed to confirm this weak or unfavorable binding of O_2, but these preliminary results imply that the active center could be inert to O_2 attack and focus could be placed on protecting the exposed pyrite surface.

TABLE 1. O_2 binding energies, and the Fe_d-O and O-O distances in the optimized binding structure at different charge states

	ΔE	$d_{Fe\text{-}O}$	$d_{O\text{-}O}$
$[FeFe]_p^{-1}$	-0.22 kcal/mol	3.64 Å	1.24 Å
$[FeFe]_p^{0}$	-3.45 kcal/mol	2.02 Å	1.29 Å

Accordingly, we studied O_2/H_2O co-absorption on the pyrite surface in vacuo We list several representative configurations in Figure 4. The corresponding absorption energies relative to an isolated O_2, an isolated H_2O, and a pristine surface are shown in Table 2. The most stable physisorption structure for O_2 is side-on where the two O atoms are linked two Fe atoms (configuration (a) and (b)). Compared to configuration (a), it is energetically less favorable for proton transfer from H_2O to the surface S, the surface Fe atoms, or O_2 in end-on binding conformation (configuration (c), (d) and (e)). A large gain in energy from configuration (a) is observed when the O-O bond breaks (configuration (f)) and the energy goes further downhill when one of the O atoms acquires a proton from H_2O (configuration (g)). This agrees with the experiments suggesting that pyrite oxidation occurs in the presence of only O_2 and that the oxidation rate is faster when water is present.

Future Directions

The calculations of O_2/H_2O absorption on pyrite in vacuo allow us to plan full-scale FPMD simulations to reveal the detailed reaction pathways and free-energy changes of pyrite oxidation. Although the active site of [FeFe]p exhibits weak or no affinity toward O_2 in vacuo, the presence of an aqueous environment could change O_2 sensitivity and initiate reactions with the water. Such detailed FPMD studies of O_2 and water interactions with both the active center and the exposed pyrite are necessary precursors to the design of structured protective overlayers. We therefore plan a systematic study of the reaction of the pristine pyrite surface and the decorated cluster with molecular oxygen in neutral water and in acidified water.

After the analysis of the sensitivity of the unprotected functionalized electrode, we plan to work on the individual design elements of a protective overlayer permitting nanochannel access of water and protons to the active sites and H_2 egress. We have already found that phosphonic acid forms a strong bidentate bond with the bare FeS_2 (100) surface after one OH is removed, making akylphosphonates promising candidates for the hydrophobic channel walls. The interaction of that end group with the decorated FeS_2 (100) surface will be studied in vacuo and in water with full quantum mechanical methods, but, when the alkyl chains are added, the increased complexity will require taking recourse to classical MD or QM/MM. The chain configuration in the protective overlayer will be studied with and without the cluster present and with and without water to build up the information needed for subsequent studies of the motion of H_2, and hydronium ions into and through the channels and the inhibition of oxygen penetration.

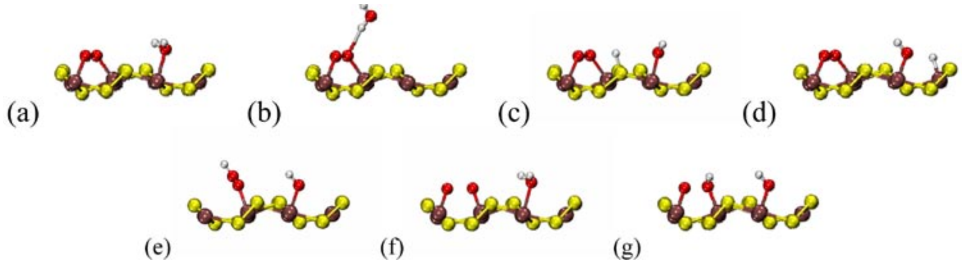

FIGURE 4. Seven representative O2/H2O co-absorption configurations. The corresponding binding energies are shown in Table 2.

TABLE 2. Binding energies of O2/H2O co-absorption configurations shown in Figure 4.

Configuration	a	b	c	d	e	f	g
Binding Energy (kcal/mol)	-29.59	-29.90	-2.32	-4.05	-20.45	-56.37	-60.65

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

1. *Simulation of Electrocatalytic Hydrogen Production by a Bio-inspired Catalyst Anchored to a Pyrite Electrode* **by F. Zipoli, R. Car, M. H. Cohen, A. Selloni,** Journal of the American Chemical Society, **2010**, 132 (25), 8593–8601

2. *Theoretical design by first principles molecular dynamics of a bio-inspired electrode-catalyst system for electrocatalytic hydrogen production from acidified water* **by F. Zipoli, R. Car, M. H. Cohen, and A. Selloni, 2010,** Journal of Chemical Theory and Computation, 2010, 6, 3490-3502

3. *Electrocatalyst design from first principles: a hydrogen-production catalyst inspired by Nature* **by F. Zipoli, R. Car, M. H. Cohen, and A. Selloni, 2010,** Catalysis Today (in press)

4. *Oxidation state changes, bond switching, and electron flow in enzymatic and electro-catalysis via Wannier function ananlysis* by **P. H.-L. Sit, F. Zipoli, J. Chen, R. Car, M. H. Cohen, and A. Selloni**, 2010, Angewandte Chemie International Edition (invited submission)