II.K.16 Theoretical Research Program on Bio-inspired Inorganic Hydrogen Generating Catalysts and Electrodes

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Objectives

Our overall goal is to establish through computational studies the feasibility of efficient electrocatalytic H_2 production from water by abiotic catalysts derived from the di-iron subsite $[2Fe]_H$ of the active site of Fe-only hydrogenases and which are attached to the surface of an Fe-S electrode. More specific objectives are: to study the functionalization of an Fe-S surface with small molecular iron sulfur clusters inspired by the active site of the iron-only hydrogenase; to obtain a detailed understanding of the reactivity and catalytic properties of these systems towards H_2 production from water; and to use this understanding for the design of an efficient H_2 producing catalyst.

Technical Barriers

Electrocatalytic H_2 production in an aqueous environment by hydrogenase enzymes deposited on a graphite electrode has already been demonstrated [1]. For technical feasibility to be achieved, 1) surface coverage of the electrode must be drastically increased over that possible through use of the entire enzyme and 2) overvoltage must be reduced through linking the catalyst more directly to the electrode surface than possible with the entire enzyme. Our scientific objectives would help overcome these two barriers imposed by use of the entire enzyme: the first by stripping the protein envelope away from the $[2Fe]_H$ active site and stabilizing it in an aqueous environment through functionalization; and the second by directly linking the resultant optimized catalyst to the surface of an FeS electrode.

Abstract

We have performed an extensive Density-Functional-Theory (DFT) study of the catalytic properties of the di-iron $[FeFe]_H$ subcluster of hydrogenases in vacuo, focusing on the processes that lead to the production of H_2. Two main pathways have been examined, involving H_2 production either at the Fe_d center distal (d) to the $[4Fe\text{-}4S]_H$ cluster or at the proximal (p) Fe_p site. Our DFT calculations, carried out at the GGA level, confirm that the most efficient catalytic site in the isolated $[FeFe]_H$ subcluster is the Fe_d center. The pathway with the most favorable kinetics (lowest energy barrier to reaction) proceeds along configurations with a CO ligand in a bridging position (μ-CO) and the distal CN^- ligand in gauche position with respect to the proximal CN^- ligand, denoted *gauche-(CN)$_2$*. This isomer is slightly less stable than the non-bridging one with Fe_d-CO terminal, which has a substantially higher H_2 desorption barrier. The μ-CO, *gauche-(CN)$_2$* configuration differs from the available X-ray structures for the enzyme, in which the distal and proximal CN^- ligands are mutually *trans*. Our results suggest that catalysis of H_2 production can proceed on this stereochemically modifed $[FeFe]_H$ subcluster alone, thus offering a simpler target for functional bioinspired catalyst design. Preliminary results of studies concerning the compositional stabilization of the optimal configuration are presented.

Progress Report

We have shown that the configuration of the $[FeFe]_H$ cluster energetically stablest at each stage of the H_2 production cycle, one with a terminal CO on the Fe_d, has too large a barrier for H_2 production, 0.54 eV. The configuration equivalent to that of the $[FeFe]_H$ cluster in the enzyme (see Figure 1) is found to be unstable for the isolated subcluster (i.e. in the absence of the enzyme environment). However, with the terminal CN^- on Fe_d in the gauche position instead of the *trans-down* position of Fig.1, the CO bridging configuration is only 0.1 eV less stable that the terminal CO configuration. The H_2 desorption reaction for this *gauche-(CN)$_2$* is exothermic by 0.18 eV, and the barrier is only 0.09 eV, supporting the possibility that the enzymatic environment is not essential for efficient H_2 production. However stabilizing the CO bridging configuration is essential for obtaining favorable kinetics because it blocks the too-tightly-binding H-bridging site which is accessible in the CO terminal configuration. Moreover, the CO bridging configuration must remain delicately balanced with respect to the terminal configuration because, during

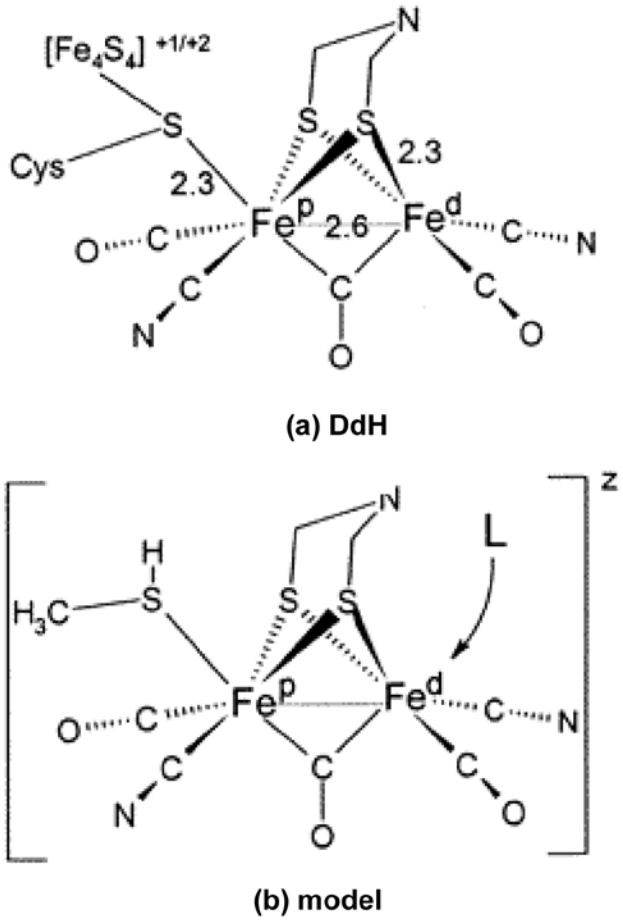

FIGURE 1. (a) Active site of the Fe-only hydrogenase, as determined experimentally for D. desulfuricans, (b) A model of the $[2Fe]_H$ subcluster used in our calculations. A DTN bridging group is assumed.

the course of the reaction, the configuration shifts subtly between more or less asymmetrical bridging of the 2 Fe's. We have already started a study of different ligands, such as CH_3O^-, NH_2CH_3, phenylthiol, etc ., at the Fe_p so as to tune the stability and catalytic efficiency of the CO bridging configuration

Future Directions

Once we will have determined the best ligand to ensure the stability of the CO bridging configuration and enhance its efficiency, we shall continue our study by linking the "optimal" catalyst via the thiol connection to the Fe_p to the surface of an Fe-S electrode. In addition, we plan to simulate the water environment of the $[2Fe]_H$ activated Fe-S surface, studying the influence of the electrode and the water on configuration stability and reaction pathway. The computational tools we employ [2] are well suited to these more complex systems.

References

1. Vincent, K. A.; Cracknell, J. A.; Lenz, O.; Zebger, I.; Friedrich, B.; Armstrong., F. A., Electrocatalytic hydrogen oxidation by an enzyme at high carbon monoxide or oxygen levels. *Proc. Natl. Acad. Sci. USA* **2005,** 102, 16951-16954.

2. Baroni, S.; Dal Corso, A.; De Gironcoli, S.; Giannozzi, P. *Quantum Espresso, http://www.democritos.it*.