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Communication

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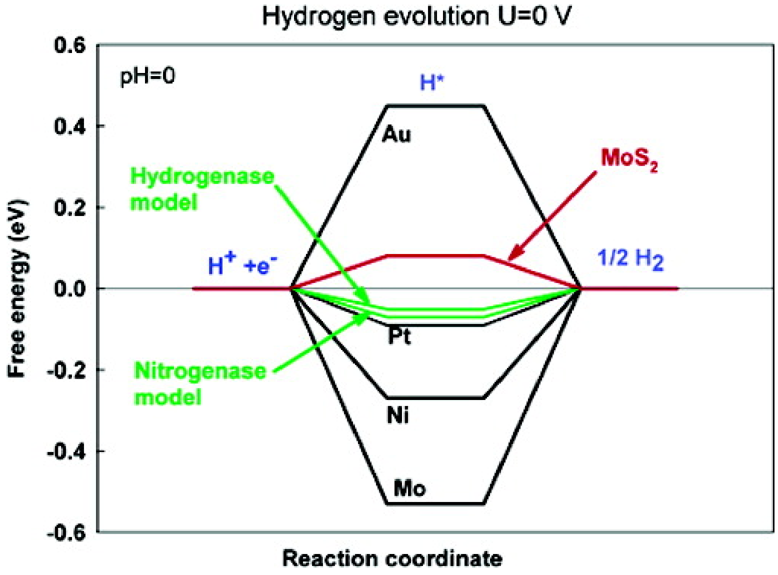

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Biomimetic Hydrogen Evolution: MoS_2 Nanoparticles as Catalyst for Hydrogen Evolution

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The electrochemical hydrogen evolution process whereby protons and electrons are combined into molecular hydrogen is catalyzed most effectively by the Pt group metals.[1] The interest in hydrogen evolution catalysts is currently increasing, as molecular hydrogen, H_2, is being considered as an energy carrier.[2] Unlike the hydrocarbon fuels used today, hydrogen produces only water during oxidation, for instance in a fuel cell. For hydrogen to be a real alternative to hydrocarbons, it must be produced in a sustainable fashion. One possibility is to use sunlight directly or indirectly (through wind power, for instance) to split water.[2] This requires an efficient catalyst for hydrogen evolution, preferably based on materials that are cheap and abundant. It is therefore important to find alternatives to the Pt group metals.

Hydrogenases and nitrogenases are also effective catalysts for the hydrogen evolution process[3,4] even though the catalytically active site of these enzymes contains the much less noble metals Fe, Ni, and Mo. Recently it has become possible to anchor hydrogenase to an electrode surface,[5] and considerable progress has been made in the synthesis of compounds in solution resembling the hydrogenase active site and showing activity for hydrogen evolution.[6]

In the present communication, we use density functional calculations to guide us to a new inorganic analogue of the other hydrogen-producing enzyme, nitrogenase. We analyze the difference between the metallic and the biological catalysts and show that in terms of being able to stabilize intermediates involving atomic hydrogen they have very similar properties. This allows us to identify a parameter determining whether a certain compound will be suitable as a catalyst in electrochemical hydrogen evolution, and it provides an efficient way to search for new systems.

Most water-splitting processes rely on electrochemical hydrogen evolution $2H^+ + 2e^- \rightarrow H_2$ in the final step. The hydrogen evolution reaction must in the first step involve bonding of hydrogen to the catalyst $H^+ + e^- + * \rightarrow H*$, where * denotes a site on the surface able to bind to hydrogen. The second step is the release of molecular hydrogen through one of the two processes:[1] $2H* \rightarrow H_2 + 2*$ or $H^+ + e^- + H* \rightarrow H_2 + *$.

Using density functional theory (DFT) calculations, we can elucidate the thermochemistry (which is independent on the precise mechanism of the second step) of the reaction; see Figure 1.[7] By calculating the free energy of atomic hydrogen bonding to the catalyst, one can compare different metal surfaces as catalysts. For a chemical process to proceed at or around room temperature, no reaction step can be associated with large changes in the free energy. This immediately excludes the metals that form strong bonds to atomic hydrogen (Ni and Mo in Figure 1) as good catalysts because the hydrogen release step will be slow. Metals that do not bind to atomic hydrogen (Au in Figure 1) are also excluded because here the proton/electron-transfer step will be thermodynamically uphill and therefore slow. There could be extra energy barriers associated with the proton-transfer steps or H_2 recombination, but independent of this it is a necessary, but not sufficient, criterion for a material to be a good catalyst that the free energy of adsorbed H is close to that of the reactant or product (i.e., $\Delta G^\circ_H \cong 0$). This principle can explain available experimental observations regarding metals as catalysts and electrode materials for hydrogen evolution.[7]

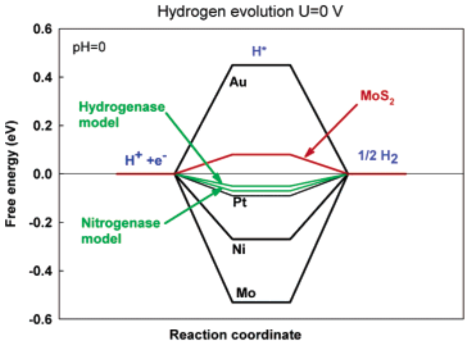

Figure 1. Calculated free energy diagram for hydrogen evolution at a potential $U = 0$ relative to the standard hydrogen electrode at pH = 0. The free energy of $H^+ + e^-$ is by definition the same as that of $^1/_2$ H_2 at standard conditions. The free energy of H atoms bound to different catalysts is then found by calculating the free energy with respect to molecular hydrogen including zero-point energies and entropy terms. The comparison of different elemental metals is taken from ref 7. The results for hydrogenase are from ref 11. The included result for MoS_2 is the free energy required to increase the hydrogen coverage from 25 to 50%; see Figure 2.

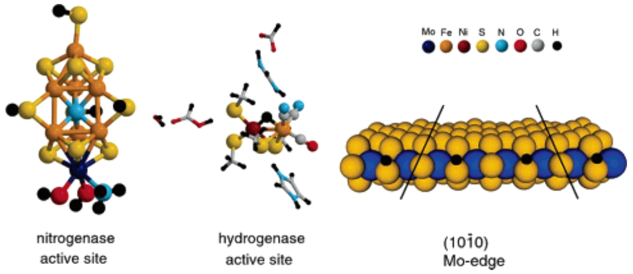

Figure 2. (Left) Nitrogenase FeMo cofactor (FeMoco) with three hydrogen atoms bound at the equatorial μ_2S sulfur atoms. (Middle) Hydrogenase active site with one hydrogen atom bound. The structure is taken from ref 11. (Right) MoS_2 slab with sulfur monomers present at the Mo edge. The coverage is 50%, i.e., hydrogen is bound at every second sulfur atom. The lines mark the dimension of the unit cell in the *x*-direction.

It is interesting to apply the same analysis to the active sites in nitrogenases and hydrogenases. For nitrogenase we have considered the model of the active site, the FeMo cofactor (FeMoco) shown in Figure 2.[8] We find that hydrogen atoms can only bind exothermically to the three equatorial sulfur ligands (μ_2S ligands) on the FeMoco. When the free energy of hydrogen atoms bound to the equatorial sulfur of the FeMoco is included in Figure 1, it

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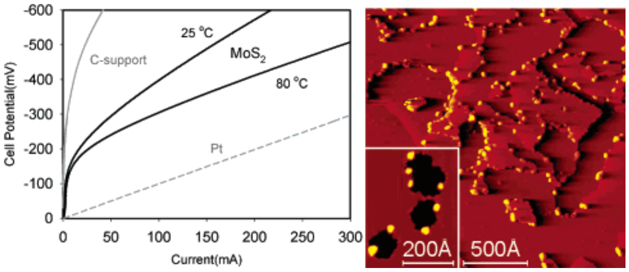

Figure 3. (Left) Polarization curve for hydrogen evolution on Pt, daihope C-support, and MoS_2 cathodes. The polarization curves for Pt and C support are made at 25 °C. The potentials are measured with respect to a carbon-supported Pt anode in a proton exchange membrane electrode assembly. (Right) STM images of MoS_2 nanoparticles on modified graphite.

results in a binding energy close to that of Pt. The FeMoco thus complies with the $\Delta G_{\mathrm{H}}^{\circ} \cong 0$ requirement.[9] A number of researchers have performed computational studies of hydrogenase,[10,11] and the results obtained by Siegbahn[11] allow us to calculate the atomic hydrogen adsorption free energy for a [NiFe]-hydrogenase system. The Siegbahn model for the hydrogenase active site is shown in Figure 2. When the free energy is included in Figure 1, one can see that hydrogenase also fulfils the $\Delta G_{\mathrm{H}}^{\circ} \cong 0$ requirement and fulfils it best for all considered systems.[9]

We therefore conclude that $\Delta G_{\mathrm{H}}^{\circ}$ is a good descriptor of materials that can catalyze hydrogen evolution and applies to a broad range of systems, both metals and enzymes. This means that we can use the same calculations to search for other systems, which could be candidates as catalysts for hydrogen evolution. One compound we have found computationally to obey the criterion is MoS_2; see Figure 1. Comparing the nitrogenase active site and the MoS_2 edge structure, we see that they bear a close resemblance, as shown in Figure 2. In both structures, the sulfur atom, which binds the hydrogen, is 2-fold coordinated to metal atoms, either to molybdenum or to iron. Only the edges of MoS_2 are interesting in this context, as the basal plane of MoS_2 is catalytically inactive.[12] The first H that bonds to the edge is strongly bound, but at an H coverage above 0.25, the differential free energy of adsorption is 0.1 eV. According to the calculations, additional H atoms should then be able to adsorb with a low barrier or, equivalently, a low overpotential of the order 0.1 V. A good material would be nanometer-large MoS_2 crystallites supported on, for example, graphite, which is conducting but otherwise inert. Such materials are used as catalysts for hydrotreating (hydrogenation of sulfur compounds in crude oil[13]), and methods for their preparation can be found in the literature.[14] It is indeed possible to prepare nanosized MoS_2 clusters on a graphite support, as can be seen in the scanning tunnel microscope (STM) image shown in Figure 3. The MoS_2 nanoparticles are approximately 4 nm in diameter and 1 nm in apparent height, and nucleate along the graphitic steps.

We have tested experimentally whether MoS_2 nanoparticles supported on carbon can be used as catalyst for electrochemical hydrogen evolution. This was done by preparing a membrane electrode assembly (MEA), based on a Nafion proton exchange membrane, with a standard platinum electrode on one side and a MoS_2/graphite electrode on the other side. By having the same hydrogen pressure on both sides, we could make the electrochemical measurements using a Parstat 2273 potentiostat resulting in the $I-V$ curve shown in Figure 3. The experimental approach has been used successfully in other studies.[15] The conditions of the experiment correspond to pH $= 0$ as in the calculations. As shown in Figure 3, MoS_2/graphite is a quite reasonable material for hydrogen evolution with an overpotential in the range 0.1−0.2 V.

We note that MoS_2 has been found to be a promoter for the hydrogen evolution activity of NiS_x electrodes,[16] which can be understood from our findings. Furthermore, MoS_2 has been tested for photocatalytic hydrogen evolution and shows activity but with significantly lower currents.[17]

Our findings suggest that we can begin searching for new catalytic materials using quantum chemical methods. The MoS_2 nanoparticles supported on graphite may be an example of a new class of electrode materials.

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Supporting Information Available: Details of the DFT calculations, experimental setup, and obtained data. This material is available free of charge via the Internet at http://pubs.acs.org.

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