Biomimetic Hydrogen Evolution: MoS_2 nanoparticles on graphite as catalyst for hydrogen evolution

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Computational Methods

All density functional calculations have been carried out with the plane-wave pseudopotential code dacapo[1], which uses a plane-wave basis and ultra soft pseudopotentials[2, 3, 4]. All energies have been calculated self-consistently with the RPBE functional[5]. For the calculations of the MoS_2 system, plane waves up to an energy of 30Ry have been included, and the cut-off in the electron density has been set to 180Ry. The standard choice is to take the density cutoff as four times the wavefunction cutoff (120Ry in the present case), but increasing the cutoff even further improves the accuracy for contributions from the pseudopotentials and the nonlinear core correction (double grid technique as described in Ref.4) The hydrogen adsorption energies have been calculated with a slab, which are four Mo atoms wide in x-direction and six Mo atoms wide in y-direction. The lattice constant of MoS_2 has been determined to be 3.235Å and compares well with the experimental lattice constant of 3.16Å. The unit cell dimension in x-direction is 12.94 Å, in y-direction 25Å and in z-direction 18Å. Electrostatic decoupling of the slabs is used. The Brillouin zone is sampled by a Monkhorst-Pack 4x1x1 k-point grid[6], i.e. 4 k-points in the x-direction, and one k-point in the y- and z-direction. The separation between neighboring k-points is 0.12Å^{-1}. The slab exposes two edges simultaneously, the $\left(10\bar{1}0\right)$ Mo-edge, which is the edge present in the catalytic particles, and the $\left(\bar{1}010\right)$ S-edge. Under the employed reaction conditions, the nanoparticles are terminated by the Mo-edge with sulfur monomers[7]. The S-edge is not present in the catalytic particles, and the exact termination is irrelevant in the calculations, as long as the same termination is used throughout. The DFT binding energies do not contain contributions from zero-point energies and entropy, and we have added these contributions separately in order to obtain the Gibbs free energy.

We describe the stability of hydrogen by the differential hydrogen chemisorption energy ΔE_H, which is calculated as follows

$$\Delta E_H = E(MoS_2+nH) - E(MoS_2+(n-1)H) - n/2\, E(H_2) \qquad (1)$$

where $E(MoS_2+nH)$ is the total DFT energy for the MoS_2 system with n hydrogen atoms adsorbed on the edge, $E(MoS_2+(n-1)H)$ is the total DFT energy for (n-1) hydrogen atoms adsorbed on the edge and $E(H_2)$ is the DFT energy for a hydrogen molecule in the gas phase. The differential hydrogen binding energy describes the energy needed to increase the coverage by one hydrogen atom. Our model slab is four rows of Mo wide and therefore we have four hydrogen binding sites and can describe the coverages 25%, 50%, 75% and 100%. The differential binding energy is defined such that the value for 25% indicates, how much energy is required for increasing the coverage from 0% to 25%, the value for 50% indicates, how much energy is required to increase the coverage from 25% to 50%, and similar for the other coverages. From the DFT results we obtain the differential binding energies -0.62eV for 25%, -0.21eV for 50%, 0.48eV for 75% and 0.50eV for 100%. From these energies we calculate the Gibbs free energy for hydrogen adsorption as

$$\Delta G_H^0 = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H \qquad (2)$$

where ΔE_H is the differential hydrogen chemisorption energy from the DFT calculations, ΔE_{ZPE} is the difference in zero point energy between the adsorbed state and the gas phase and ΔS_H is the entropy difference between the adsorbed state and the gas phase. The energy contribution from the configurational entropy in the adsorbed state is small (<0.04eV) and is therefore neglected. Likewise, as the vibrational entropy in the adsorbed state is small (<0.005eV), we can take the entropy of hydrogen adsorption as $\Delta S_H \cong \frac{1}{2} S_{H_2}^0$ where $S_{H_2}^0$ is the entropy of H_2 in the gas phase at standard conditions. The gas phase values are all taken from Ref. 8. We have calculated the vibrational frequencies of H adsorbed on MoS_2 with 50% coverage and found them to be 2535cm^{-1}, 594cm^{-1} and 474cm^{-1}. This means that for the MoS_2 structures $\Delta G_H^0 = \Delta E_H^{diff} + 0.29$eV. As the vibrational frequencies do not differ notably for different coverages, we use this correction for all coverages. This results in the differential binding free energies of -0.33eV for 25%, 0.08eV for 50%, 0.76eV for 75% and 0.79eV for 100%. The only free energy close to thermoneutral is 0.08eV, which describes the change in coverage from 25% to 50%. Therefore, it is most likely that the hydrogen evolution is mainly driven by hydrogen adsorption at these two coverages.

The methodology of the calculations for the nitrogenase active site is specified in Ref.9. To obtain the Gibbs free energy for hydrogen adsorption, we have calculated the vibrational frequencies for H adsorbed on the FeMoco (see Figure 2) and find them to be 2547cm^{-1}, 541cm^{-1} and 440cm^{-1}, which leads to $\Delta G_H^0 = \Delta E_H + 0.29$eV and a free energy of hydrogen binding of -0.07eV. The hydrogen binding energy for hydrogenase has been taken from Ref.10 for the model with a charged His77, which presumably is the most realistic one. The binding energy is the energy of structure 6 (specified in Fig. 9 and 10 of Ref.10). To estimate the zero-point energy, we use the frequencies of adsorbed H on Cu(111) calculated by Gokhale *et al.*[11] as an estimate. This leads to $\Delta G_H^0 = \Delta E_H + 0.24$eV and to a free energy of hydrogen binding of -0.05eV.

Both nitrogenase and hydrogenase work at pH=7 instead of pH=0. The change from pH=0 to pH=7 introduces a shift in redox potential of -414mV[8], which corresponds to an energy shift of -0.41eV. This means that the hydrogen adsorption energies for nitrogenase and hydrogenase are decreased by -0.41eV. The second correction results from the redox potential, with which the electrons are transferred to the active site. In nitrogenase, the electrons are provided by the [4S-4Fe]$^{1+/2+}$ redox pair, whose redox potential has been measured to be -430mV/SHE for Azotobacter vinelandii in the presence of bound MgATP[12]. This means that the electrons are provided to the FeMoco with an extra chemical potential of 430mV which corresponds to an energy shift of

0.43eV. Thus for nitrogenase, the energy corrections from pH=7 and from the electron transfer redox potential compensate each other to a large degree, so that the net correction will be small. For hydrogenase, the redox potential of the proximal [4Fe-4S] cluster is -340mV and the redox potential of the distal [4Fe-4S] cluster is -290mV[13]. Thus also in this case the energy shifts introduced by the pH=7 correction and by the redox potential for the electron transfer compensate each other to a large degree. Therefore, we can neglect these contributions in the present study.

Figure 2 has been prepared with Molscript and Raster3D[14,15].

Experiments

The catalyst used as electrode materials are hydrodesulphurization catalysts consisting of pure MoS_2 supported on active carbon. The catalyst was made by standard incipient wetness impregnation of active carbon (Mitsubishi active carbon Daihope008) with a solution of the active metals. The catalyst was then dried at 110°C and subsequently activated by treatment sulfidation in gaseous H_2S at 450°C. The metal loads obtained depended on the concentration of the impregnation liquid and the pore volume of the carbon and was in this case found to be 9.7% Mo.

The supported MoS_2 catalyst was then used to make one of the electrodes in a membrane electrode assembly (MEA). The MEA was made by a thin layer deposition technique described by Litster and McLean[16], where one side was prepared with Pt and the other side with a MoS_2 based electrode catalyst. The Pt side of the MEA was made using commercially available E-TEK 20 % Pt/C. Approximately 40 mg of the E-TEK powder was mixed with 0.1mL of a 5 wt% Nafion solution and diluted with methanol until an ideal viscosity was reached. When good suspension was reached, the solution was painted onto a 3.14 cm^2 torray carbon sheet, by fine paint brush. By weighing the carbon sheet before and after deposition it was found that this recipe enabled the deposition of approximately 1 mg Pt pr. cm^2. The MoS_2 electrodes were prepared in a similar manner except that the deposition was performed in a glove bag filled with nitrogen in order to reduce oxidation. Approximately 1mg of MoS_2 pr. cm^2 was deposited. After the catalyst was deposited on the carbon sheets, the sheets were bonded to a Nafion 117 membrane. The carbon sheets with catalyst, was positioned on both sides of the Nafion membrane and then pressed together with 150 bars of pressure at 120 °C for 5 minutes. Pressing under lower temperatures, was found to give poor bonding. The final MEAs containing MoS_2, thus consisted of one side with E-TEK Pt and one side with MoS_2 both supported on carbon.

The MEAs were tested in an experimental setup described elsewhere in detail[17] and pure hydrogen (99.9999%) was used in all experiments. First the MEA was inserted under an argon flow, then the gas flow was switched to hydrogen flow on the Pt side. A mass spectrometer probing the gas on the MoS_2 side was then used to determine if there was any hydrogen leaking through the membrane. If no leak was detected H_2 was also flowed over the MoS_2 side. During measurements the H_2 flow is 25 mL/min on both sides.

The electrochemical measurements were made with a Parstat 2273, where the working electrode and the reference electrode were connected to the Pt side of the MEA, while the counter electrode was connected to the MoS_2 side of the MEA. Thus the potential is measured with respect to the platinum side of the MEA.

The MEA was activated by cycling the cell through potentials between 0 and -1000mV for approximately 24 hours. After the catalysts were activated, polarization curves were measured, see Figure 4, by ramping the cell potential with 30mV/min while recording the corresponding current. The applied cell potential was usually varied between 0 and -1000 mV as higher cell potentials could damage the catalyst.

The MoS_2 MEA has also been tested in a simple electrolysis setup, where MoS_2 was used as the cathode, and no significant loss in activity was measured during 60 hours of operation.

The MoS_2 particles on a graphite support were investigated in a stardard ultra-high vacuum (UHV) system with a scanning tunneling microscope (STM) of the Århus type[18]. The STM images were measured in a constant current mode (scanning parameters for the 2000 Å x 2000 Å image were 1V and 0.5 nA, for the smaller image of 360 Å x 460 Å, 1 V and 0.2 nA were used, see Figure 3).

The graphite surface (highly oriented pyrolytic graphite, HOPG) was cleaved in air, transported into the UHV chamber via a loadlock, and then activated by ion sputtering with 160 eV He^+ ions for 30 s under UHV to create defects on the surface. The sputtered surface was then heated in atmospheric air to 900K for 5 min[19]. After re-introduction into UHV, the sample was again sputtered (160 eV, 120 s). The MoS_2 structures were then synthesized on to the modified and activated graphite surface under UHV, following the procedure of Ref. 20, where a Au(111) surface was used as a substrate. Before imaging with STM, the samples were annealed at 1000K for 20 min.

References

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