Nitrogen Adsorption and Hydrogenation on a MoFe6S9 Complex

Rod, Thomas Holm; Hammer, Bjørk; Nørskov, Jens Kehlet

Published in:
Physical Review Letters

Link to article, DOI:
10.1103/PhysRevLett.82.4054

Publication date:
1999

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Nitrogen Adsorption and Hydrogenation on a MoFe$_6$S$_9$ Complex

T. H. Rod, B. Hammer, and J. K. Nørskov

Center for Atomic-scale Materials Physics, Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark

Institute of Physics, Aalborg University, Pontoppidanstrade 103, DK-9220 Aalborg Øst, Denmark

(Received 8 October 1998)

The enzyme nitrogenase catalyzes the biological nitrogen fixation where N$_2$ is reduced to NH$_3$. Density functional calculations are presented of the bonding and hydrogenation of N$_2$ on a MoFe$_6$S$_9$ complex constructed to model aspects of the active site of nitrogenase. N$_2$ is found to bind end on to one of the Fe atoms. A complete energy diagram for the addition of hydrogen to the MoFe$_6$S$_9$ complex with and without N$_2$ is given, and a mechanism for ammonia synthesis is proposed on this basis.

PACS numbers: 71.15.Nc, 82.20.Kh, 87.15.Rn

The enzyme nitrogenase catalyzes the biological nitrogen fixation, where ammonia is synthesized by the reaction N$_2$ + 8H$^+$ + 8e$^-$ → 2NH$_3$ + H$_2$. Nitrogenase consists of the Fe protein and the MoFe protein. During association of the two proteins, electrons are transferred from the Fe protein to the active site in the MoFe protein along with hydrolysis of adenosine triphosphate (ATP) [1]. The active site, where N$_2$ binds and reacts, is believed to be a metal-sulfide cluster (MoFe$_7$S$_9$) named the FeMo cofactor (FeMoco). The geometrical structure of the FeMoco [2,3] has been established recently, and a considerable amount of insight has been obtained about the overall kinetics of the hydrogenation process [4]. The binding site of N$_2$ and the atomistic mechanism of N$_2$ hydrogenation to ammonia are, however, still largely unknown. In the present Letter, we use density functional calculations to gain further insight into the interaction of nitrogen and hydrogen with the FeMoco. We study the adsorption and hydrogenation of N$_2$ on a MoFe$_6$S$_9$ complex chosen to model parts of the FeMoco. We establish the preferred binding site for N$_2$ in detail. Our study is based on fully self-consistent density functional calculations performed by expanding the wave functions in plane waves and describing the ion cores by nonlocal soft (S) and Vanderbilt ultrasoft (H, N, Fe, and Mo) pseudopotentials [9]. Plane waves with kinetic energies up to 25 Ry are used. Exchange and correlation effects are described within the generalized gradient approximation of Ref. [6]. The self-consistent electron density is determined by iterative diagonalization of the Kohn-Sham Hamiltonian, Fermi population of the Kohn-Sham states ($k_B T = 0.1$ eV), and Pulay mixing of the resulting electronic density. All total energies have been extrapolated to $k_B T = 0$ eV. Complete structural relaxation is made for each configuration studied. The same approach has proven able to describe in detail N$_2$ activation on Ru and Fe surfaces [10].

To include all the atoms of the FeMoco and its ligands (Fig. 1) in the DFT calculations requires a huge unit cell and is therefore computationally extremely demanding. This is, in particular, true when studying not only the structure, but also chemical reactions on the cluster. To make the problem tractable, we have constructed a simple model compound (Fig. 1) by removing the end Fe atom and continuing the cluster periodically. In this way we decrease the size of the problem considerably, and at the same time all the other Fe, Mo, and S atoms have the correct coordination number. The compound is periodic in one direction ($c$ axis), and in the calculations we repeat the structure periodically in the other two directions ($a$ axes). The resulting unit cell is hexagonal with side lengths $a = 9.5$ Å and $c = 7.75$ Å. The value of $c$ is chosen to minimize the total energy of the system. The first Brillouin zone is sampled with two equally spaced $k$-points along the $c^*$ axis.

We have checked that the lowest energy structure of the model compound is very similar to the one determined experimentally for the FeMoco (Fig. 1, Table I). The ground state of our model system is found to have a...
The FeMoco is the active site of nitrogenase, the enzyme that catalyzes the production of ammonia from dinitrogen.

**Fig. 1** (color). The FeMoco with ligands (to the left) and the minimum energy structure of the one-dimensional model (MoFe₆S₉)ₙ complex (to the right). Ligands are illustrated by balls and sticks while the FeMoco and model are illustrated by space-filling spheres. For the continuing model only one unit cell is colored. Color key: Fe: brown; Mo: dark blue; S: yellow; C: gray; O: red; and N: light blue.

**Table I.** Comparison of experimental and calculated bond lengths. The Fe–Fe' bond length is the distance between opposite atoms in the two iron triangles and the Fe-Fe bond length is the distance between atoms in the same iron triangle (Fig. 1). The experimental bond lengths are extracted from crystallographic data, and except for the Fe–Fe' bond length only the three Fe and six S atoms closest to Mo are taken into account in order to compare with the model (Fig. 1). Both the experimentally determined and the calculated structure has a range of bond lengths, and we indicate that by giving the minimum and maximum values. The crystallographic coordinates are taken from Brookhaven Protein Data Bank (ID code 3min), published in Ref. [3].

<table>
<thead>
<tr>
<th>Bond</th>
<th>Experiment</th>
<th>DFT calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–Fe'</td>
<td>2.48–2.60</td>
<td>2.56–2.58</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>2.45–2.61</td>
<td>2.46–2.54</td>
</tr>
<tr>
<td>Fe–μS</td>
<td>2.06–2.20</td>
<td>2.10–2.13</td>
</tr>
<tr>
<td>Fe-S</td>
<td>2.10–2.23</td>
<td>2.15–2.18</td>
</tr>
<tr>
<td>Mo-S</td>
<td>2.16–2.34</td>
<td>2.48–2.52</td>
</tr>
</tbody>
</table>

The model cannot be expected to describe the FeMoco in detail. It is, for instance, known that small changes in the ligands or the exchange of Mo for V or Fe can change the selectivity (the ratio of H₂ to NH₃ formation) of the FeMoco significantly [1,12]. Combined with the limited accuracy of the DFT calculations, this means that we concentrate on establishing a possible reaction pathway and on the general energetics of the reactions rather than on quantitative details.

We now continue with a discussion of the adsorption and reaction properties of the model compound. In the present Letter we consider only the stability of intermediates, not reaction barriers separating them. First, consider the adsorption of N₂ on the neutral MoFe₆S₉ complex. We will later consider complexes where the oxidation number has been reduced by adding hydrogen. We tried several adsorption sites, and the only one which gave a bond which is stable relative to N₂ far from the complex is the one shown in Fig. 2(b). N₂ adsorption strongly distorts...
the complex, presumably in order to diminish the overlap between N₂ and the S atoms. Changing the boundary conditions by varying c by 6% changes N₂ adsorption energy by less than 30 meV indicating that the chemical reactivity does not depend on the boundary conditions. Ongoing molecular mechanics calculations also show that the structure in Fig. 2(b) is compatible with the rest of the protein [13].

We then added H atoms to the adsorbed N₂ one by one. Addition of an H atom is a simple way of simultaneously adding an electron and a proton to the complex. Each time an H atom is added, several possible configurations were tried and the lowest energy structure was identified. We define the binding energy of the system by

$$\Delta E = E(X) - E(\text{MoFe}_6\text{S}_9) - n_H E(\text{H}) - n_{N_2} E(N_2),$$

(1)

where E is the calculated total energy of its argument, and n_H is the total number of adsorbed H atoms. \(X = \text{MoFe}_6\text{S}_9\text{H}_{n_H}\) when no N₂ is added (\(n_{N_2} = 0\)), and \(X = \text{MoFe}_6\text{S}_9\text{N}_2\text{H}_{n_H}\) when N₂ is adsorbed (\(n_{N_2} = 1\)).

Each of the hydrogenation steps for N₂ on the MoFe₆S₉ complex is strongly exothermic (Fig. 3). This is in contrast to the hydrogenation of gas phase N₂, where the addition of an H atom is thermoneutral or endothermic [14]. This shows an important role of the MoFe₆S₉ complex in activating the N₂ bond in analogy to other metal complexes [15]. Similar energetics has been obtained for the H addition to N₂ interacting with a Fe₂ dimer sulfide [8] indicating that this is a general phenomena for iron sulfides.

In addition, we have added H atoms to the MoFe₆S₉ part of the complex rather than to the adsorbed N₂. This does not change the overall energetics of subsequently adding H atoms to the N₂ molecule (Fig. 3). By exploring all possible configurations with H atoms on the MoFe₆S₉ complex and on the adsorbed N₂ we construct the complete energy diagram, Fig. 3. For a given total number of H atoms, the lowest energy configuration gives the stables intermediate, and by following these as the total number of H atoms is increased, the energetically preferred reaction path for the N₂ hydrogenation can be deduced. After N₂ has been adsorbed, the first three H atoms are stables on the complex and not on the N₂ molecule. But with the addition of the fourth, it becomes most favorable for all the H atoms to bind to the N₂ molecule to form adsorbed hydrazine Fig. 2(i). This is then further hydrogenated to split off first NH₃ and then the next. Only the desorption of the last NH₃ is endothermic. In principle we should include the possibility of adding another proton to form NH₄⁺. This would make the final step more exothermic. We could also include solvent effects. This would again make desorption of ammonia more exothermic. The calculated structures of the reaction path suggested by the energy diagram are shown in Figs. 2(a)–2(k).

Using atomic H as the reference state in Fig. 3 is a matter of choice. Under “biological” turnover conditions, the H atom enters as a proton and an electron, which is transferred from the 4Fe-4S cluster in the Fe protein. The energy of each state with n_H H atoms in Fig. 3 should therefore be shifted by \(n_H [E(H) - E^{\text{bio}}(\text{H})]\), where \(E^{\text{bio}}(\text{H})\) is the energy of the electron and proton added to the FeMoco during synthesis, and \(E(H)\) is the atomic H energy used as reference in Eq. (1) and Fig. 3. \(E^{\text{bio}}(\text{H})\) will typically be higher than \(\frac{1}{2} E(H_2)\) by an energy \(\Delta E^{\text{bio}}_H = E^{\text{bio}}(\text{H}) - \frac{1}{2} E(H_2)\) which is given by the reduction energy of the [4Fe-4S]^{1+/2+} cluster at synthesis conditions and the energy funneled into the reaction during ATP hydrolysis.

In Fig. 4 we show the energy of the stablest intermediates from Fig. 3 using the energy \(E(H_2)\) per atom in H₂ as the reference state. This corresponds to \(\Delta E^{\text{bio}}_H = 0\). It can be seen that as long as the sum of the reduction energy and the energy from hydrolysis of ATP is moderately negative there is no state of the reaction path which is higher in energy than the reactants. This means that every state is thermodynamically accessible. Whether it is kinetically accessible depends on barriers which we do not consider here. We will, however, expect the proton transfer processes to be facile [16].

Figure 4 shows that with up to three H atoms on the cluster, N₂ adsorption is reversible. With the N₂ adsorption energy from the calculation, the N₂ coverage will actually be quite small at room temperature and 1 bar of N₂ in the gas phase. Transfer of the fourth H atom
(electron and proton) will, however, transfer the whole system irreversibly to the much more stable state \( i \), where hydrazine is formed. This is in good qualitative agreement with the kinetic model of Thorneley and Lowe [4].

Figure 4 also shows that \( H_2 \) evolution is a competing reaction, and, in fact, may be as fast for the system considered here, since the first step with four \( H \) atoms is as stable without \( N_2 \) adsorbed as with \( N_2 \) adsorbed.

It is interesting to compare the proposed reaction on the model enzyme to the reaction taking place on Fe surfaces. Here it is known that the ammonia synthesis proceeds via \( N_2 \) dissociation and subsequent hydrogenation of the adsorbed \( N \) atoms [17]. This is very different from the reaction studied in the present paper. We have found no tendency for \( N_2 \) dissociation on the MoFe\(_9\)S\(_9\) complex. This, we suggest is the reason that the enzyme can function at room temperature, whereas the metallic Fe based catalysts have to function at about 700 K. The high temperature is primarily needed to keep the surface from being blocked by strongly bound atomic nitrogen [18]. The prize may be that molecular \( H_2 \) is not quite energetic enough to make the reaction go, cf. Fig. 4.

We gratefully acknowledge many stimulating discussions with J. Ulstrup, C. J. Pickett, and M. Durrant, and help with the pseudopotentials from L. B. Hansen. The present work was financed in part by The Danish Research Councils through Grant No. 9501775. The Center for Atomic-scale Materials Physics (CAMP) is sponsored by the Danish National Research Foundation.