Nitrogen Adsorption and Hydrogenation on a MoFe6S9 Complex

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The enzyme nitrogenase catalyzes the biological nitrogen fixation where N\textsubscript{2} is reduced to NH\textsubscript{3}. Density functional calculations are presented of the bonding and hydrogenation of N\textsubscript{2} on a MoFe\textsubscript{6}S\textsubscript{9} complex constructed to model aspects of the active site of nitrogenase. N\textsubscript{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\textsubscript{6}S\textsubscript{9} complex with and without N\textsubscript{2} is given, and a mechanism for ammonia synthesis is proposed on this basis.

In the present Letter we go one step further and consider a large FeMoco model and the complete hydrogenation of N\textsubscript{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\textsubscript{B}T = 0.1 eV), and Pulay mixing of the resulting electronic density. All total energies have been extrapolated to k\textsubscript{B}T = 0 eV. Complete structural relaxation is made for each configuration studied. The same approach has proven able to describe in detail N\textsubscript{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\textsuperscript{e} 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
FIG. 1(color). The FeMoco with ligands (to the left) and the minimum energy structure of the one-dimensional model (MoFe$_6$S$_9$)$_n$ 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.

total spin density of zero—all the Fe-Fe interactions are antiferromagnetic, consistent with experiment [11].

The model is best suited to study the chemistry associated with the six central Fe atoms, since all their nearest and next nearest neighbors are identical to those of the true FeMoco. The Mo atom, on the other hand, has sufficiently different surroundings that its chemistry may be somewhat different. We therefore concentrate in the present study on adsorption and reactions associated with the central Fe atoms. This does not exclude that reactions associated with the Mo atoms can be important in connection with the FeMoco, but we note that Mo can be exchanged for V or Fe in the enzyme without loss of the ability to produce ammonia [1,12] suggesting that Mo may not be the active site.

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 H$_2$ to NH$_3$ 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 N$_2$ on the neutral MoFe$_6$S$_9$ 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 N$_2$ far from the complex is the one shown in Fig. 2(b). N$_2$ adsorption strongly distorts

FIG. 2(color). Calculated structures of the lowest energy configuration of the MoFe$_6$S$_9$ (a), with N$_2$ adsorbed (b), with 1–3 H atoms [(c)–(e)], 4 H atoms [(f)–(i)], and with 5 and 6 H atoms [(j), (k)]. Also shown is the N$_2$-free complex with 1–4 H atoms [(l)–(o)] and with 2 H atoms and molecular H$_2$ adsorbed (p). In case of the structures [(e), (f)] and [(o), (p)] the unseen H is bound to the hidden twofold coordinated S. All the structures are rotated 60° relative to Fig. 1 and only one unit cell is shown for each structure. All degrees of freedom of the system have been allowed to relax to minimize the energy of the system. In each case several different configurations have been considered, but we cannot exclude that configurations may exist that are not found by our energy minimization routine. The scenario presented is therefore a possible one, but not necessarily the only one. Same color key as in Fig. 1 and H atoms are black.
the complex, presumably in order to diminish the overlap
between N$_2$ and the S atoms. Changing the boundary
conditions by varying $c$ by 6% changes N$_2$ 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 N$_2$ 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

$$\Delta E = E(X) - E(\text{MoFe}_6S_9) - n_H E(H) - n_{N_2} E(N_2),$$

where $E$ is the calculated total energy of its argument,
and $n_H$ is the total number of adsorbed H atoms. $X = \text{MoFe}_6S_9H_n$ when no N$_2$ is added ($n_{N_2} = 0$), and $X = \text{MoFe}_6S_9N_2H_n$ when N$_2$ is adsorbed ($n_{N_2} = 1$).

Each of the hydrogenation steps for N$_2$ on the MoFe$_6$S$_9$
complex is strongly exothermic (Fig. 3). This is in contrast
to the hydrogenation of gas phase N$_2$, where the addition
of an H atom is thermoneutral or endothermic [14].
This shows an important role of the MoFe$_6$S$_9$ complex in
activating the N$_2$ bond in analogy to other metal complexes
[15]. Similar energetics has been obtained for the H
addition to N$_2$ interacting with a Fe$_2$ dimer sulfide [8]
indicating that this is a general phenomena for iron sulfides.

In addition, we have added H atoms to the MoFe$_6$S$_9$ part
of the complex rather than to the adsorbed N$_2$. This does
not change the overall energetics of subsequently adding H
atoms to the N$_2$ molecule (Fig. 3). By exploring all possi-
ble configurations with H atoms on the MoFe$_6$S$_9$ com-
plex and on the adsorbed N$_2$ we construct the complete
energy diagram, Fig. 3. For a given total number of H
atoms, the lowest energy configuration gives the stabllest
intermediate, and by following these as the total number
of H atoms is increased, the energetically preferred reac-
tion path for the N$_2$ hydrogenation can be deduced. After
N$_2$ has been adsorbed, the first three H atoms are stabllest
on the complex and not on the N$_2$ molecule. But with the
addition of the fourth, it becomes most favorable for all
the H atoms to bind to the N$_2$ molecule to form adsorbed
hydrazine Fig. 2(i). This is then further hydrogenated to
split off first one NH$_3$ and then the next. Only the de-
sorption of the last NH$_3$ is endothermic. In principle we
should include the possibility of adding another proton to
form NH$_4^+$. This would make the final step more exother-
mic. 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 $n_H [E(H) - E^{\text{bio}}(H)]$, where
$E^{\text{bio}}(H)$ 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. $E^{\text{bio}}(H)$ will
typically be higher than $\frac{1}{2} E(H_2)$ by an energy $\Delta E_H^{\text{bio}} =
E^{\text{bio}}(H) - \frac{1}{2} E(H_2)$ which is given by the reduction ener-
gy of the $[4\text{Fe-4S}]^{+/2+}$ cluster at synthesis conditions
and the energy funneled into the reaction during ATP
hydrolysis.

In Fig. 4 we show the energy of the stabllest intermedi-
dates from Fig. 3 using the energy $E(H_2)$ per atom in H$_2$
as the reference state. This corresponds to $\Delta E_H^{\text{bio}} = 0$. It
can be seen that as long as the sum of the reduction energy
and the energy from hydrolysis of ATP is moderately nega-
tive 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 pro-
cesses to be facile [16].

Figure 4 shows that with up to three H atoms on the
cluster, N$_2$ adsorption is reversible. With the N$_2$
adsorption energy from the calculation, the N$_2$ coverage
will actually be quite small at room temperature and 1 bar
of N$_2$ in the gas phase. Transfer of the fourth H atom

\begin{figure} [h]
\centering
\includegraphics[width=0.8\textwidth]{fig3.png}
\caption{The calculated binding energy $\Delta E$ [Eq. (1)] of N$_2$ and H to the MoFe$_6$S$_9$ complex ($X$). Along the horizontal axis we show whether N$_2$ is adsorbed and how many H atoms are bound to the adsorbed N$_2$. Going down from one structure to the next in the vertical direction corresponds to the addition of hydrogen to the body of the complex. Energy bars for systems with the same total number of H atoms, $n_H$ (on the N$_2$ and on the body of the complex), are connected by dashed lines, and $n_H$ is shown to the left of the leftmost bar. The arrows connect the stabllest intermediates as N$_2$ is adsorbed and H atoms are added one by one. The labels [(a)–(p)] refer to the corresponding structures in Fig. 2.}
\end{figure}
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