Nitrogen fixation at passivated Fe nanoclusters supported by an oxide surface: Identification of viable reaction routes using density functional calculations

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Using density-functional calculations, we investigate the possibility of ammonia synthesis at supported Fe nanoclusters along catalytic routes closely resembling those in biological nitrogen fixation. To achieve similar catalytic conditions as at the active site of the enzyme nitrogenase, the clusters are passivated with either S or N atoms. From calculated potential-energy profiles for the N_2 hydrogenation, we find that low-temperature synthesis of ammonia is viable at the clusters passivated by N atoms due to the strong binding energy of the N_2 molecule in the initial adsorption step.

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I. INTRODUCTION

The conversion of atmospheric nitrogen (N_2) into the biological accessible form ammonia (NH_3), a process known as nitrogen fixation, can only proceed in the presence of catalysts because of the extraordinary strength of the dinitrogen bond. The industrial synthesis of ammonia is based on the Haber-Bosch process, in which nitrogen reacts with hydrogen over a Fe- or Ru-based catalyst at high temperatures (about 400 °C) and pressures (100 atm).[1] This reaction is characterized by the dissociation of the N_2 molecule prior to hydrogenation;[2,3] its mechanism can be regarded as known and its reaction rate can be modeled.[4] By contrast, the enzyme nitrogenase achieves the same goal of reducing N_2 to NH_3 *under ambient conditions* by what is known as the biological nitrogen fixation process.[5] Many bacteria are capable of nitrogen fixation with nitrogenase systems which appear to be remarkably similar.[6] The active site of the enzyme is a small metal-sulfur cluster denominated FeMo cofactor,[5,7] comprising one Mo, seven Fe, eight S atoms, and a light atom (most likely N) in the middle of the cluster.[8] Recent theoretical work on the reaction mechanism at the cofactor has revealed that the initial hydrogenation takes place on the N_2 bound to the cofactor in its molecular form,[9–13] a reaction mechanism noticeably different than in the Haber-Bosch process. In view of these developments, there is clear interest in realizing bioinspired nitrogen fixation on synthetically prepared surfaces. The ultimate goal is twofold. First, this would allow one to acquire a deeper understanding of the reaction steps taking benefit from the availability of highly sophisticated detection tools in surface science. Second, such a realization would pave the way toward a new route for industrial nitrogen fixation with obvious economic and ecologic advantages.

In this work, we explore through density-functional calculations the possibility of realizing ammonia synthesis in a surface-science setup following the reaction route operative in the enzyme nitrogenase. To mimic the FeMo cofactor, we consider the catalytic system consisting of passivated Fe nanoclusters dispersed on an oxide support, as can presently be realized in industrial catalytic processes. As passivating atomic species, we consider both sulfur, as found in the FeMo cofactor, and nitrogen, as recently suggested.[14] The initial binding of the N_2 molecule is identified as a critical step. For the sulfurized clusters, the relatively low desorption energy leads to a short lifetime of the N_2 adsorption state, decreasing the efficiency of the subsequent hydrogenation. However, the converse holds for the nitrogenated clusters. The latter clusters therefore constitute viable catalysts for the synthesis of ammonia at low temperatures.

The present paper is organized as follows. In Sec. II, we describe the computational method used in the calculations. In Sec. III, we present results for adsorption geometries of intermediate states during N_2 hydrogenation on sulfurized and nitrogenated Fe_7 clusters and compare the potential-energy profiles calculated for these two types of the clusters. The conclusions are given in Sec. IV.

II. COMPUTATIONAL DETAILS

We described the electronic structure within a spin-dependent generalized gradient approximation (GGA) to density-functional theory,[15] which has been shown to give an accurate description of the catalytic properties of systems involving transition metals.[16] Only valence wave functions were treated explicitly and valence-core interactions were described by ultrasoft pseudopotentials,[17,18] as implemented in the DACAPO code.[19] The effect of the Fe $3p$ semicore states was accounted for through nonlinear core corrections.[20] The electron wave functions and the augmented electron density were expanded in plane waves with cutoff energies of 25 and 140 Ry, respectively.[18] We obtained converged energies by sampling the Brillouin zone with the $2\times2\times1$ Monkhorst-Pack grid of k points.[21] We used a supercell slab geometry in which the MgO surface was modeled by two layers[22] with 26 atoms per layer, separated by at least 14 Å of vacuum. The positions of the atoms were always fully relaxed, except those of the bottom MgO layer which were held in ideal bulk positions. The N reference energy is set by the gas-phase N_2 molecule. The reference for

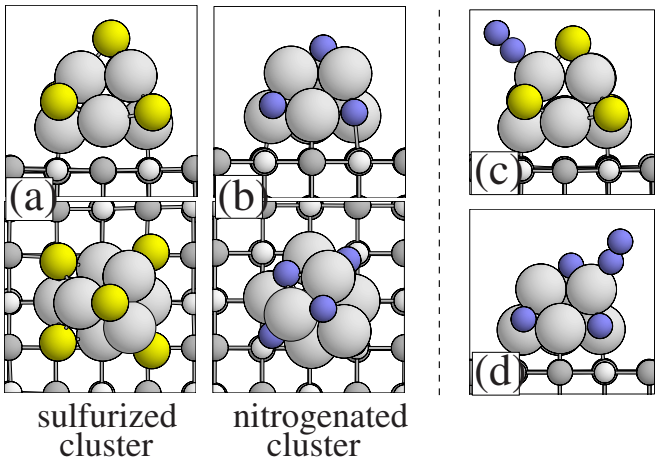

FIG. 1. (Color online) Top and side views of the structure of the Fe_7/MgO cluster with (a) five preadsorbed S atoms and (b) five preadsorbed N atoms. [(c) and (d)] Side views of the respective N_2 adsorption geometries. Code: Fe: large gray, S: yellow (light gray), Mg: white, O: small gray, and N: blue (dark gray).

S is the gas-phase H_2S molecule, a common source of S in experiments.

III. RESULTS AND DISCUSSION

As a specific model catalyst, we focused on Fe_7 clusters supported by a MgO(100) surface. The size of such clusters is comparable to that of the FeMo cofactor while the MgO substrate is taken to represent an inert oxide support.

Since at room temperature, the N_2 molecule immediately dissociates upon adsorption at *pristine* Fe_7/MgO, the catalytic properties of the clusters must be tuned in order to enable ammonia synthesis by direct hydrogenation of adsorbed dinitrogen. This can be achieved by passivating the clusters with atomic species such as S or N, as an increase in the number of preadsorbates favors the adsorption of nitrogen in its molecular state.[14] To determine the number of S and N atoms which favorably bind to the cluster, we sequentially increased the number of adsorbed atoms.[23] For both types of preadsorbed species, we found that up to five atoms strongly adsorb to the pristine cluster, with average binding energies of 2.22 and 1.03 eV/atom for S and N, respectively. Adsorption of the sixth atom is unfavorable due to strong repulsive interactions with the previously adsorbed atoms. The two Fe_7/MgO clusters, with five preadsorbed S or five preadsorbed N atoms (Fig. 1), were used here as model catalysts for ammonia synthesis along reaction routes resembling those of nitrogenase.

Next, we determined the N_2 adsorption geometries on the sulfurized or nitrogenated Fe_7/MgO clusters. The top-end configurations shown in Figs. 1(c) and 1(d) were found to be the most favorable binding geometries for both types of clusters. Calculated binding energies for N_2 attachment are 0.36 eV (sulfurized cluster) and 0.83 eV (nitrogenated cluster). The simulation of the NH_3 formation then proceeds through the addition of hydrogen atoms to the clusters with the adsorbed N_2 molecule.

The ability of the clusters to catalyze the ammonia synthesis critically depends on the hydrogen chemical potential. If gas-phase H_2 molecules are used as hydrogen source, the hydrogenation of the N_2 molecule preadsorbed on either the sulfurized or the nitrogenated Fe cluster is unlikely to occur at room temperature. Through geometry-constrained calculations, we found that the barrier for the transfer of the first H atom to the N_2 molecule is higher than 1.8 eV. Therefore, H atoms with a chemical potential higher than in H_2 are required for ammonia synthesis to proceed at room temperature. In our study, we used atomic H as the source of hydrogen. For this source, we found that hydrogenation of the cluster and of the attached N_2 molecule occurs spontaneously, i.e., without energy barriers upon H addition. Other hydrogen sources, such as NH_4^+ or H_3O^+,[10,13] give qualitatively similar results.

We sequentially added hydrogen atoms to the clusters and considered different adsorption sites for a given number of H atoms. The H atoms adsorbed on the Fe atoms are very mobile at room temperature due to the low diffusion barrier for hopping from one binding site to another. Thus, we considered only those adsorption sites where H atoms bind stronger than in the H_2 molecule. Adsorbates with weaker binding energies are expected to recombine and to desorb from the cluster in the form of H_2. The same picture also holds for H adsorption sites at the S atoms. The H atoms located on the N_2 molecules were found to be slightly weaker bound than on Fe or on S. However, they are kinetically stabilized toward recombination by large energy barriers for diffusion to other sites of the cluster. This gives metastable sites with long lifetimes, which were retained in our analysis of the reaction path.

A. Sulfurized cluster

The preferential binding site of atomic H at the sulfurized clusters corresponds to one of the threefold hollow Fe sites [see Fig. 2(a)], with a binding energy of 2.41 eV, only slightly higher than in the gas-phase H_2 molecule (2.29 eV). Hydrogen adsorption on top of Fe or S atoms is less favorable. The H binding energy on top of a Fe atom in contact with the MgO support is 2.05 eV and decreases by 0.1–0.3 eV at other Fe atoms. The adsorption on top of S atoms is even less favorable with binding energies ranging between 1.54 and 1.60 eV. All the considered configurations with additional H atoms adsorbed to the cluster show that the adsorption of a second or a third H atom is unstable against H_2 recombination. Therefore, we assumed that prior to hydrogen transfer to the N_2 molecule, only one H atom is chemisorbed on the sulfurized cluster at the adsorption site shown in Fig. 2(a). Upon hydrogenation of the adsorbed N_2 molecule, the transfer of the first H atom to the N_2 is accompanied with an energy gain of 1.35 eV. Diffusion to the more stable chemisorption sites on the Fe atoms is kinetically hindered due to barriers higher than 1.8 eV. Further hydrogenation of N_2 leads to stronger H chemisorption. The calculated potential energy of the N_2H_2 molecule formed on the cluster is −4.07 eV. Sequential transfer of H atoms to the N_2 further decreases the potential energy, indicating a significant weak-

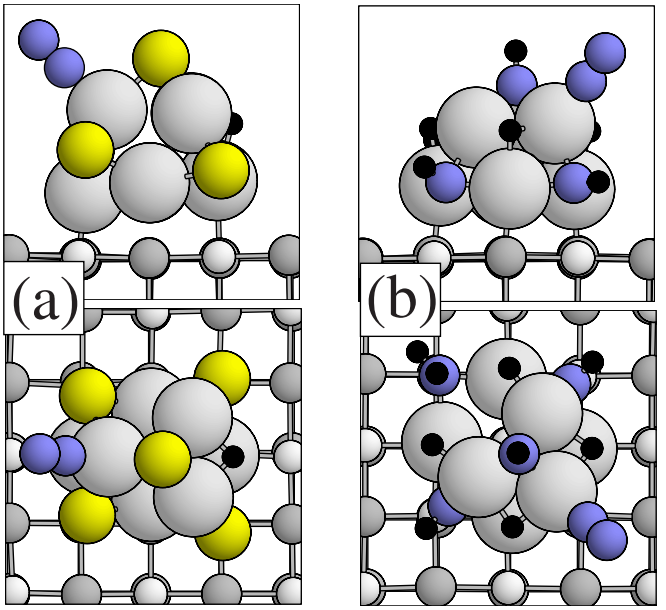

FIG. 2. (Color online) Top and side views of hydrogen structures formed on the (a) sulfurized and (b) nitrogenated clusters, prior to the hydrogenation of the adsorbed N_2 molecule. Same color code as in Fig. 1; H atoms are in black.

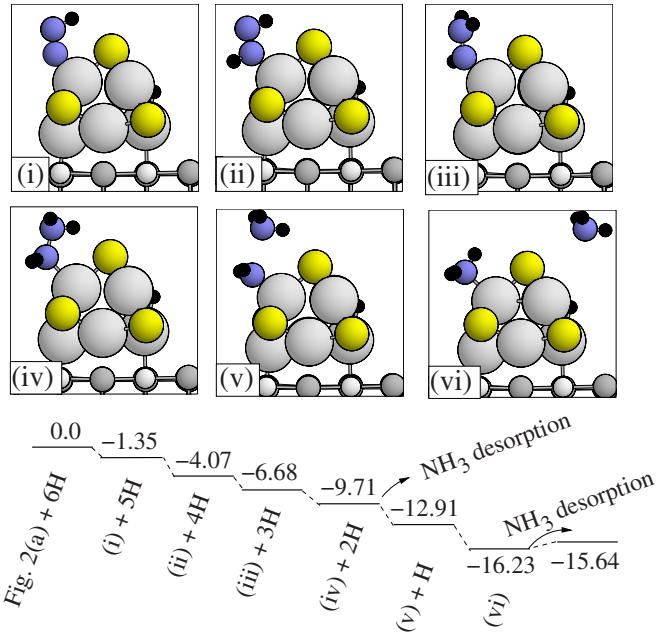

FIG. 3. (Color online) Side views of the intermediate states during hydrogenation of the N_2 molecule at the sulfurized Fe_7/MgO cluster [Fig. 2(a)] and the corresponding potential-energy profile. The indicated amounts of H correspond to atoms in the gas phase. All energies are in eV.

ening of the N-N bond. Upon transfer of the fifth H atom to the N_2H_4 complex, the N-N bond breaks spontaneously and the first NH_3 molecule is released. The sixth H atom strongly binds to the amino group, forming another NH_3 molecule. The desorption of the second NH_3 molecule closes the catalytic circle. The identified hydrogenation path is shown in Fig. 3.

B. Nitrogenated cluster

For the Fe_7/MgO cluster with preadsorbed N atoms, we applied the same procedure as for the sulfurized cluster. First, we examined the binding of H atoms at different sites of the cluster. The H binding energy at preadsorbed N atoms varies between 2.8 and 3.2 eV, corresponding to noticeably higher values than for the binding at the threefold hollow Fe sites (2.4 eV) or on top of Fe atoms (~2.6 eV). Since the H atoms bind favorably at several adsorption sites, the nitrogenated Fe_7/MgO cluster is able to accommodate a substantial amount of atomic hydrogen prior to the hydrogenation of the adsorbed N_2 molecule. This is in sharp contrast to the cluster passivated with S atoms, for which we only found a single stable adsorption site for hydrogen. In our calculations, the first five H atoms adsorb at the five N atoms present on the cluster, the next four H atoms bind to the Fe atoms, and the tenth H atom finally attaches to one of the previously formed NH groups [cf. Fig. 2(b)]. Thus, the N_2 hydrogenation starts only after the adsorption of ten H atoms. From the calculated energies of the intermediate states, we found that the transfer of the first two H atoms to the N_2 is associated with H binding energies of 1.50 and 3.75 eV, respectively. Both the N_2H and N_2H_2 complexes are again kinetically stabilized due to the high energy barriers for H diffusion to the cluster. Additional hydrogenation of the N_2 further lowers the potential energy as shown in Fig. 4. After the transfer of five H atoms to the molecule, the N–N bond breaks, producing the first split-off NH_3 molecule. Further hydrogenation leads to the formation of the second NH_3 molecule (Fig. 4). The reaction pathways found at the sulfurized and nitrogenated clusters show striking similarities to those of biological ammonia synthesis.[9–12]

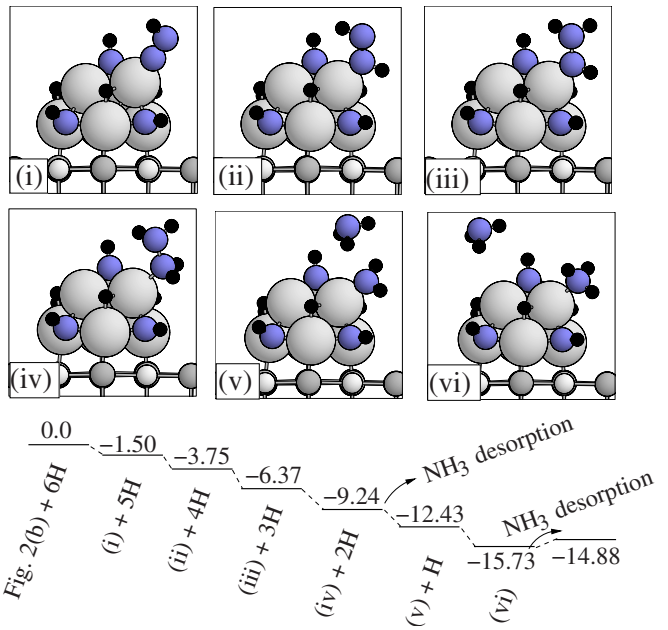

FIG. 4. (Color online) Same as in Fig. 3 but for the nitrogenated Fe_7/MgO cluster [Fig. 2(b)].

For both S- and N-passivated Fe_7/MgO clusters, the molecular adsorption state corresponds to the precursor for N_2 hydrogenation and its lifetime depends on the N_2 desorption energy. For sulfurized clusters, we found a barrier of 0.35 eV for N_2 desorption.[24] Using the Arrhenius form for the desorption frequency and assuming a typical attempt frequency of 10^{13} s^{-1}, we estimate a lifetime of 10^{-7} s for the attached configuration at room temperature. The N_2 molecule thus rapidly desorbs, making its hydrogenation very unlikely. At variance, for nitrogenated clusters, we obtained a much higher desorption energy of 1.1 eV,[24] corresponding to a lifetime of 10^5 s at room temperature. Hence, the present calculations indicate that ammonia synthesis can be realized at nitrogenated Fe_7/MgO clusters.

To understand the significant difference between the N_2 binding energies at nitrogenated and sulfurized clusters, we considered their electronic structure and the effect of the preadsorbates. In particular, we focused on the electronic density of states projected onto the Fe $3d$ orbitals at the N_2 bonding site, prior to N_2 adsorption [Fig. 5]. As seen in Figs. 5(a) and 5(b), the Fe $3d$ majority-spin states are located well below the Fermi energy and are therefore filled for both clusters. Their attractive interaction with the lowest unoccupied molecular orbital (LUMO) of the N_2 molecule contributes to the binding of the molecule at the clusters. However, the partially filled Fe $3d$ minority-spin states, positioned at higher energies, are chemically more active. Upon adsorption of the N_2 molecule, the empty Fe $3d$ states hybridize with the highest occupied molecular orbital (HOMO) of the N_2 molecule resulting in a bonding state which is pushed below the Fermi energy and contributes considerably to the lowering of the total energy. The lowest unoccupied states of the nitrogenated clusters carry substantial Fe $3d_{z^2}$ character [cf. Fig. 5(c)], favoring a large overlap with the HOMO of the N_2 molecule and the creation of a strong bonding state. The local electronic properties of the corresponding Fe atom at the sulfurized cluster are different. The states of dominant Fe $3d_{z^2}$ character are already occupied [cf. Fig. 5(d)] and their interaction with the HOMO of the N_2 molecule is repulsive. Furthermore, the lowest unoccupied states of the sulfurized cluster, marked by an asterisk in Fig. 5(b), are mainly of Fe $3d_{xy}$, Fe $3d_{xz}$, and Fe $3d_{yz}$ characters. Since these orbitals do not form favorable bonding configurations with the HOMO of the N_2 molecule, the binding of the N_2 molecule at sulfurized Fe_7/MgO cluster is weak.

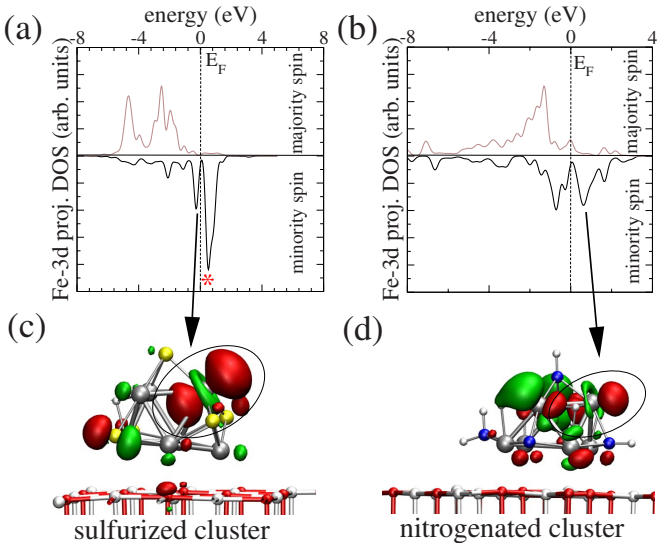

FIG. 5. (Color online) Electron density of states (DOS) projected onto the Fe $3d$ orbitals at the binding site for the (a) sulfurized and (b) nitrogenated clusters prior to N_2 adsorption. The asterisk in (a) marks empty states of mainly Fe $3d_{xy}$, Fe $3d_{xz}$, and Fe $3d_{yz}$ character. Contour plots of (c) the HOMO of the sulfurized cluster with one H atom and of (d) the LUMO of nitrogenated cluster with ten H atoms are also given. The Fe $3d_{z^2}$ orbitals are encircled.

IV. CONCLUSION

By means of DFT calculations, we investigated the possibility of achieving ammonia synthesis in a surface-science setup following reaction pathways which are inspired by the nitrogen fixation in the biological enzyme nitrogenase. As a model catalyst, we used Fe_7 clusters supported by a MgO(100) surface. We studied the sequential hydrogenation of the N_2 molecule at both sulfurized and nitrogenated Fe_7 clusters supported by MgO substrates. The calculated energetics suggests that the nitrogenated cluster carries a promising potential as catalyst for the synthesis of ammonia at low temperature.

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