Commun. Comput. Chem
doi: 10.4208/cicc.2017.v5.n3.3

Vol.5, No.3, pp.78-85
Nov 2017

Regular Article

Nitrogen and Hydrogen Adsorption on the Pyrite FeS_2 (100) surface: First-Principles Study

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Received 1 Dec. 2017; Accepted (in revised version) 25 Dec. 2017

Abstract: Based on density functional theory (DFT), the adsorption of atomic and molecular hydrogen and nitrogen on pyrite FeS_2 (100) surface was studied. Both atomic N and N_2 molecule prefer to adsorb on the top Fe site. The adsorption of atomic N on the surface of FeS_2 (100) is more stable than N_2. Adsorption energy calculation shows that the adsorption stability weakens with the increase of the N atom coverage. Hydrogen adsorption differs quite a lot with that of nitrogen adsorption. It is found that atomic H could stably adsorbs on FeS_2 (100) surface at the top Fe site, while H_2 molecule is quite difficult to adsorb on pyrite FeS_2 (100) surfaces. The adsorption stability of atomic hydrogen sharply weakens as the H coverage increases.

Key Words: FeS2; DFT study; Adsorption; Hydrogen; Nitrogen.

1. Introduction

Pyrite FeS_2 is the most abundant mineral in the Earth's crust, which is vitally important in biogeochemistry[1]. The surfaces and adsorption properties of pyrite FeS_2 play a crucial role in a large number of environmental, geochemical and industrial processes [2,3]. Since the potential of FeS_2 in the nitrogen fixation process, the FeS_2 surface has been considered as the catalyst in the synthesis of ammonia. Synthesis of ammonia by Haber-Bosch method needs high temperatures and pressures, making it an energy-intensive industrial process [4,5]. Low temperature synthesis of NH_3 from atomic nitrogen and hydrogen on (100) FeS_2 surface showed that NH_3 could be synthesized when the surface is exposed to atomic H[6]. Molecular N_2 adsorbs on FeS_2 (100) surface at 105 K, while H_2 could adsorbs under similar

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conditions [7]. Beam surface scattering demonstrated that D_2S could be produced on pyrite surface to give roughened and reduced surface[8]. Density Functional theory calculations have also been performed on the adsorption of O_2, CO, NO, NO_2, H_2O, H_2S on the (100) surface of pyrite [2,9-11]. However, to the best of our knowledge, no theoretically attempt has been reported on the reactions of FeS_2 surface with atomic or molecular nitrogen and hydrogen, which is quite important reactions in the synthesis of NH_3 on the pyrite surface.

In this work, we studied the adsorption of four adsorbates (atomic N, N_2, atomic H and H_2) on the (100) surface of pyrite FeS_2 by using first-principle calculation. We investigated the geometric structural and adsorption energetic properties of the adsorption of the four adsorbates of different coverage.

2. Computational method

All the calculations in this work were performed by VASP software[12,13] with projector-augmented wave (PAW) method[14]. The exchange-correlation potential was treated within the generalized gradient approximation (GGA) using the PW91 functional[15]. The plane wave cutoff was selected to be 500 eV. The Monkhorst-Pack k-point sampling grid 8×8×8 was used for bulk calculation. For FeS_2 (100) surface and adsorbate-surface systems, a 1×3×3 grid was adopted. Fe $3d^74s^1$, S $3s^23p^4$, N $2s^22p^3$ and H $1s^1$ were treated as valence electrons, respectively. All schematic plots of the slab structures were visualized using VESTA program[16].

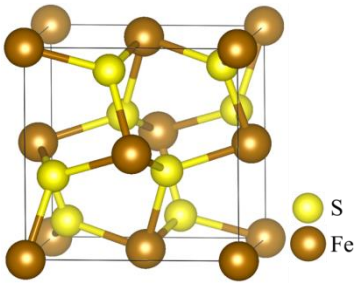

Figure 1: Unit cell of pyrite FeS_2

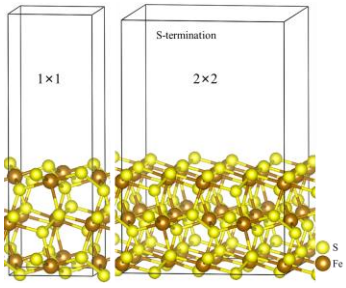

Figure 2: Slab model of FeS_2 (100) surface

The structure of pyrite FeS_2 is displayed in **Figure 1**. Pyrite FeS_2 crystallizes in simple cubic symmetry (space group *Pa*3) with 12 atoms in the unit cell. The optimized lattice constant of cubic FeS_2 in our work is a = 5.410 Å, which is in good agreement with the experimental value of 5.418 Å [17] and previous theoretical value of 5.426 Å [18]. This calculated lattice constant (5.410 Å) was applied to the adsorption calculations. The FeS_2 (100) surface (**Figure 2**.) was then constructed by vertically cleaving the FeS_2 bulk along the <100> direction. In this work, we considered two kinds of FeS_2 (100) surface with (1×1) and (2×2) surface unit cell, respectively. These surface slabs were composed by 9 atomic layers of FeS_2 with a vacuum region of 10 Å which was inserted to minimize the interaction between the neighboring layers. All he adsorbate species were fully relaxed in a large cell to simulate the gas-phase conditions.

The adsorption energy was calculated as the difference between the energy of the adsorption system ($E_{absorbate/FeS_2(100)}$) and the sum of the clean surface ($E_{FeS_2(100)}$) and gas phase adsorbate ($E_{absorbate}$), according to the following equation

$$E_{ads} = (E_{absorbate/FeS_2(100)} - E_{absorbate} - E_{FeS_2(100)}),$$

3. Results and discussion

3.1 The adsorption of nitrogen

For one atomic nitrogen adsorption on the (1×1) FeS_2 (100) surface, two possible adsorption sites (bridge site above the Fe-S bond and top Fe site) were found, as shown in **Figure 3**. The adsorption energy for the bridge and top site is –10.23 eV and –10.45 eV, respectively. The lower adsorption energy for the top Fe site indicates that the most stable site for the atomic nitrogen adsorption on the FeS_2 (100) surface is the top Fe site.

We then increased the number of the atomic nitrogen adsorbed on the (1×1) FeS_2 (100) surface from one to two, as displayed in **Figure 4**. The adsorption of a molecular N_2 is also shown in **Figure 4**. It can be seen from **Figure 4**(a) that when two atomic nitrogen adsorb on the (1×1) FeS_2 (100) surface, the most stable site is not the top site above Fe, but the bridge site above the Fe-S bond. Similarly to one atom adsorption, molecular N_2 preferentially adsorbs on the top Fe site, with the N-N-Fe chain almost arranging in a straight line. Although the top Fe site is the most stable adsorption site for both atomic nitrogen (**Figure** 3(b)) and molecular nitrogen N_2 (**Figure** 4(b)), the N-Fe bond lengths are quite different. For atomic nitrogen adsorption, a short N-Fe bond length of 1.558 Å was obtained. While for molecular nitrogen N_2, the N-Fe bond length increased to 1.834 Å, indicating weakened interaction between N_2 and FeS_2 compared with respect to that between atomic nitrogen and FeS_2. This could also be proved by the adsorption energy calculation results, as shown in Table 1. The adsorption energies for an atomic and a molecular nitrogen adsorption on (1×1) FeS_2 (100) surface are –10.45 eV and –4.98 eV, respectively. Obviously the atomic nitrogen

adsorption is highly preferred than the molecular N_2 on the FeS_2 (100) surface.

We further studied the influence of adsorbate coverage on the adsorption stability. The calculated adsorption energies for different nitrogen coverage on the (1×1) and (2×2) FeS_2 (100) surface are shown in **Table 1**. For atomic nitrogen adsorption on (1×1) surface, the adsorption energy gradually increases with the increase of the coverage from 1N, 2N to 4N. Atomic nitrogen adsorption on (2×2) surface produces same trend that with the adsorbate coverage increase from 2N, 4N to 8N, the adsorption energy increases from –14.58, –10.43 to –7.08 eV. This indicates that the interaction between atomic nitrogen and the FeS_2 (100) surface weakens with the increase of the coverage of the nitrogen. As can be seen from Table 1, the adsorption energy is –4.98 eV for one N_2 on (1×1) surface, while for two N_2 on (1×1) surface, the adsorption energy increases to –2.82 eV. Thus, similarly conclusion could also drawen to molecular N_2 that the interaction between N_2 and FeS_2 (100) surface weakens with the increase of the N_2 coverage.

Table 1. The adsorption energy of atomic N and molecular N_2 on (1×1) and (2×2) FeS_2 (100) surface with different coverge.

Adsorbate	E_{ads} (eV)
(1×1) 1N	-10.45
(1×1) 2N	-7.49
(1×1) 4N	-5.87
(1×1) N_2	-4.98
(1×1) $2N_2$	-2.82
(2×2) 2N	-14.58
(2×2) 4N	-10.43
(2×2) 8N	-7.08
(2×2) N_2	-8.78

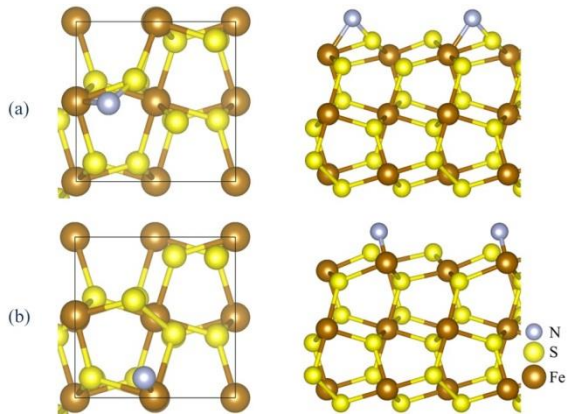

Figure 3: Structures of one atomic N adsorption on the (1×1) FeS_2 (100) surface: (a) bridge site and (b) Fe top site

3.2 The adsorption of hydrogen

In the atomic hydrogen adsorption case, two stable adsorption site on the (1×1) FeS_2 (100) surface were found, as depicted in **Figure 5**. Atomic hydrogen could adsorb on the top S site (**Figure 5**(a)) with the adsorption energy of –2.75 eV. However, the top Fe site (**Figure 5**(b)) gives a smaller adsorption energy of –3.04 eV. The lower adsorption energy for the top Fe site implies that the atomic hydrogen prefers to stay at the top Fe site while adsorbing on the FeS_2 (100) surface, which is similar to the adsorption of atomic nitrogen process. Comparing the adsorption energy of atomic nitrogen and hydrogen on FeS_2 (100) surface, however, one could find that the hydrogen has much higher adsorption energy (–3.04 eV) than that of the nitrogen (–10.45 eV). This suggests that atomic nitrogen could more easily and stably adsorb on the FeS_2 (100) surface than the atomic hydrogen.

The geometric structure of the adsorption of molecular H_2 on the (1×1) FeS_2 (100) surface is shown in **Figure 6**, where the adsorption of the atomic H case is also given for comparison. One can see from **Figure 6**(a) that atomic H could stably adsorb on the FeS_2 (100) surface with H-Fe bond length of 1.517 Å. However, the distance between H_2 and the surface is quite large (4.346 Å, **Figure 6**(b)), and such a large interval implies that it is very hard for H_2 to adsorb on the FeS_2 (100) surface. This is accord with the experimental finding[6] that atomic H readily adsorbs on FeS_2 (100) surface, while H_2 does not.

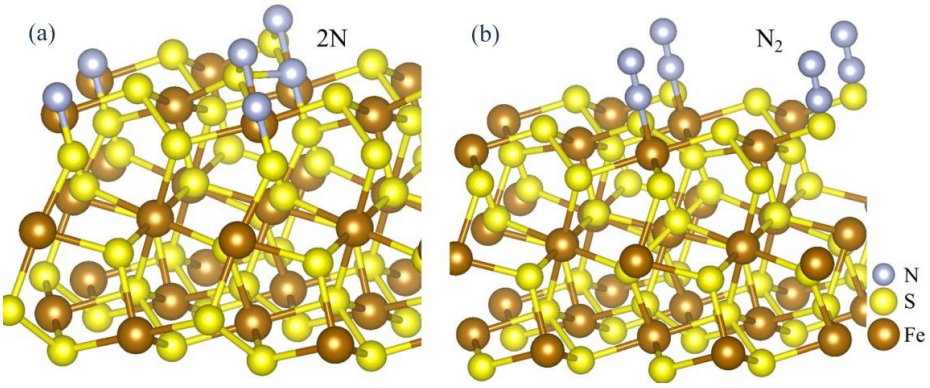

Figure 4: Structures of the adsorption of: (a) two atomic N and (b) a molecular N_2 on the (1×1) FeS_2 (100) surface

The influence of the coverage of hydrogen on the adsorption stability has been studied. In **Table 2**, we show the adsorption energies for different hydrogen coverage on the (1×1) and (2×2) FeS_2 (100) surface. For atomic hydrogen adsorption on (1×1) surface, three different coverage of 1H, 2H and 4H were studied. For atomic hydrogen adsorption on (2×2) surface, three different coverage of 2H, 4H and 8H were compared. For both (1×1) and (2×2) surfaces, the adsorption energy gradually increases with the increase of the atomic H coverage. When the number of the atomic nitrogen on (1×1) surface increases from 2H to 4H, the adsorption

energy sharply increases from –2.19 to –0.97 eV, suggesting the nearly adsorption saturation situation of the atomic 4H adsorption. The adsorption energies of molecular H_2 adsorption on the (1×1) and (2×2) surface are also given in **Table 2**. It is clearly seen that H_2 adsorption gives a very large energetic value (–0.01 eV), indicating the impossible H_2 adsorption on FeS_2 (100) surface, which is in accord with the large H_2-surface distance found.

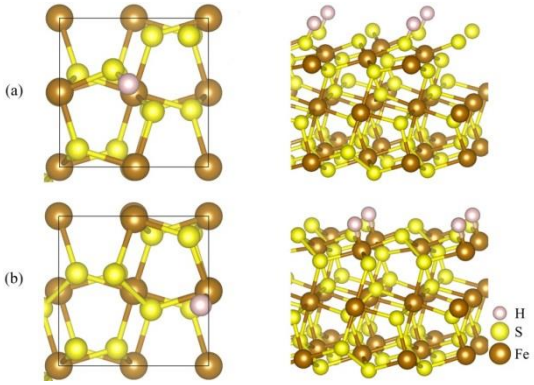

Figure 5: Structures of one atomic hH adsorption on the (1×1) FeS_2 (100) surface: (a) top S site and (b) top Fe site.

Table 2. The adsorption energy of atomic H and molecular H_2 on (1×1) and (2×2) FeS_2 (100) surface with different coverge

Adsorbate	E_{ads} (eV)
(1×1) 1H	-3.04
(1×1) 2H	-2.19
(1×1) 4H	-0.97
(1×1) H_2	-0.01
(2×2) 2H	-3.08
(2×2) 4H	-2.94
(2×2) 8H	-2.68
(2×2) H_2	-0.01

4. Conclusion

The present work provides insights into the adsorption of atomic and molecular nitrogen and hydrogen on the pyrite FeS_2 (100) surface by using the first-principles calculation. Similar to H_2O and H_2S, atomic N atom and molecular N_2 prefer to adsorb on the top Fe site. Calculation of the adsorption energy shows that the stability gradually decreases with the increase of the N atom coverage. Compared to molecular N_2, the adsorption of atomic N on the surface of FeS_2 (100) is more stable. Adsorption of atomic H and molecular H_2 at FeS_2

(100) surface calculations suggest that atomic H could stably adsorbs on FeS_2 (100) surface at the top Fe site. However, from both H_2-surface distance and adsorption energy points of views, H_2 molecule is quite difficult to adsorb on pyrite FeS_2 (100) surfaces, in agreement with experimental results.

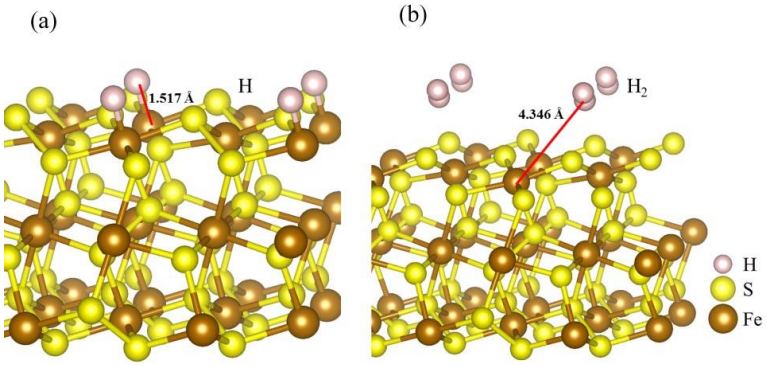

Figure 6: Structures of the adsorption of: (a) atomic H and (b) molecular H_2 on the (1×1) FeS_2 (100) surface

Acknowledgment

This work is supported by the National Natural Science Foundation of China (11304028, 21473015, and 21203016) and the Fundamental Research Funds for the Central Universities (3132016124).

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