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Regular Article

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

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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].

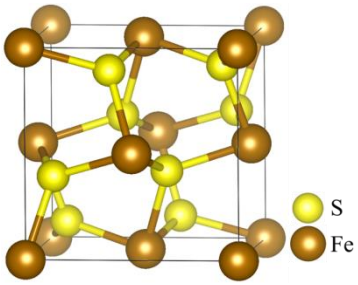

Figure 1: Unit cell of pyrite FeS_2

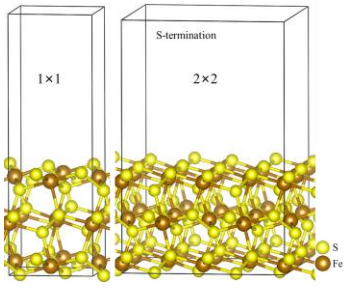

Figure 2: Slab model of FeS_2 (100) surface