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First principles study on adsorption for different concentration of H_2S on Fe(100)

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Abstract. Using the first principles method, which is based on the density function theory (DFT), the structures and electronic properties for different concentration of H_2S are adsorbed on the Fe (100) surface, and their molecular orbital and absorption energies were calculated with the generalized gradient approximation. The results show that, whether one or two molecules of H_2S adsorpted Fe (100) surface, adsorption of single molecules Fe (100) surface partial density of states between pure Fe (100) and two molecules, and the total density of states is mainly composed of 3d electronic contribution.

Introduction

Hydrogen sulfide is often produced by sour gas wells and carried by the sour gas during the production and transportation. When temperatures and pressures change, sulfur may first precipitate out from the sour gas and then deposit on the production tubing or pipeline wall. Hydrogen sulfide deposition can significantly affect the production by blocking the production tubing. In the presence of water, hydrogen sulfide can also lead to a catastrophic corrosion problem. Applying the combination of hydrogen sulfide solvent and corrosion inhibitor to the gas production is the most common way to mitigate the blockage and corrosion problems caused by hydrogen sulfide deposition [1].Corrosion of steel is a considerable burden on the economy due to steel's ubiquitous use in industry. The main stainless groups are austenitic and ferritic steels. Today a third important group is developing around the so-called duplex grades. These steels offer a unique combination of outstanding mechanical performance and appropriate corrosion resistance and present promising alternative materials for various technological applications[2-6].

Most experimental studies of H_2S interaction with iron have employed polycrystalline iron films. Using X-ray photoelectron spectroscopy (XPS), Narayan[7] et al. studied iron sulfidation by hydrogen sulfide from 100 to 773 K. On the basis of binding energy shifts of the S 2p level, they concluded that hydrogen sulfide adsorption is molecular at 100 K, but dissociative from 190 K up to ambient temperatures. At T >423 K, they found formation of FeS, where the initial nonstoichiometric form converts to the stoichiometric form with increased hydrogen sulfide dosing. No direct evidence was presented to confirm the molecular adsorption of hydrogen sulfide at100 K.High-sulphur nature gas dissolves out mass elemental sulfur grains can retain in wellbore and continual depositing it. If these grains can't transport out of the hole by gas finally it will plug the wellbore. In this work, we characterize the hydrogen sulfide adsorption sites and different concentration of H_2S adsorbed on the Fe (100) surface with periodic density functional theory (DFT)[8-9].

Calculational Details

We perform first-principles calculations based on spin-polarized density functional theory (DFT). The Cambridge Sequential Total Energy Package(CASTEP) is used to solve the Kohn-Sham equations with periodic boundary conditions and a plane-wave basis set. Here, we employ Blöchl's all-electron (with frozen core) projector augmented wave (PAW) method [10] as implemented by Kresse and Joubert [11]. We use the generalized gradient approximation (GGA) of PBE for the treatment of electron exchange and correlation [12].

We use a kinetic energy cutoff of 400 eV for all of the calculations, which converges the total energy to ~1 meV/atom for the primitive cell of bulk Fe. The Monkhorst-Pack scheme is used for the k-point sampling [13]. The first-order Methfessel-Paxton method is used for the Fermi surface smearing [14], with a width of 0.1eV to obtain accurate forces. An equilibrium lattice constant of 2.75Å is used for ferromagnetic bcc Fe, as we obtained earlier with a converged k-mesh of 15×15×15 [15].

To model for molecule of H_2S, we place a molecule or atom in a 17 Å cubic box. We perform spin-polarized calculation for openshell H_2S, where the valence electron configuration used for S atom is triplet (3p), approximately the 3p ground state and for H is 1s. This lattice constant for optimized structure of Bcc Fe is 2.75 Å agrees well with the experimental value of 2.86 Å [16]. The optimized structure of Bcc Fe displayed in figure 1.

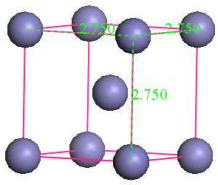

Fig.1. The Optimized Structure of Bcc Fe

We chose a three-layer slab to model Fe(100) and put adsorbates on one side of the slab, this produces a small dipole due to the dipole of the molecular adsorbate itself and to charge transfer between the adsorbate and the metal surface. However, we did not bother with a dipole correction to the total energy because it was generally small (<0.03 eV/cell). Only the top two layers of the three substrate layers are allowed to relax, together with the adsorbate layer [17,18]. The bottom three layers are kept fixed in bulk positions to represent the semi-infinite bulk crystal beneath the surface. In our work, we have constrained the atoms except first substrate layer's and hydrogen sulfide. When the maximum force acting on each of the relaxed atoms drops below 0.01 eV/Å, the structural relaxation is stopped. We use a k-mesh of 9×9×2 for the p(2×2) Fe(100) cell, which converges the adsorption energy of H_2S to within 0.02 eV.

In this work, we study different concentration of H_2S adsorbed on the Fe (100) a c(1×2) superstructure surface displayed in Figure 2. Single H_2S molecule adsorbed on the Fe (100) for H-site is the most stable[19].

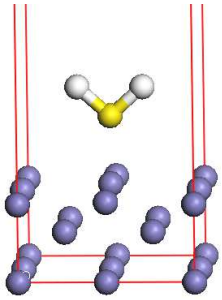

Fig.2. The Optimized Structure of Single H_2S molecule adsorbed on the Fe (100) for c(2×2) superstructure surface

Results and Discussion

Optimized Structure of H_2S molecule adsorbed on Fe(100) with the Different concentration. When a molecule adsorbed on the Fe (100), the distance S atom of H_2S to Fe (100) is 2.67 Å, and for two molecules are 1.59Å and 2.70 Å. From this perspective, we can think that the higher concentration, the stronger adsorption.The structue for two molecules of hydrogen sulfide on Fe(100) are displayed in Figure 3.

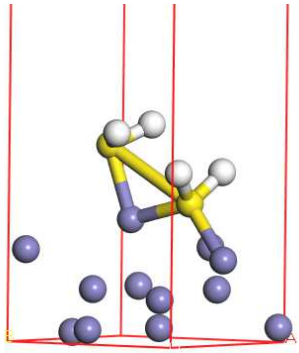

Fig.3. The Optimized Structure Two molecules of hydrogen sulfide on Fe(100)

Partial Density of States of H_2S molecule on Fe(100) with the Different concentration. By analyzing partial density of the state (PDOS) of the adsorbed H_2S, further insight into the adsorption can be obtained. The Partial Density of states(PDOS) plots for pure Fe (100) are shown in Figure 4.

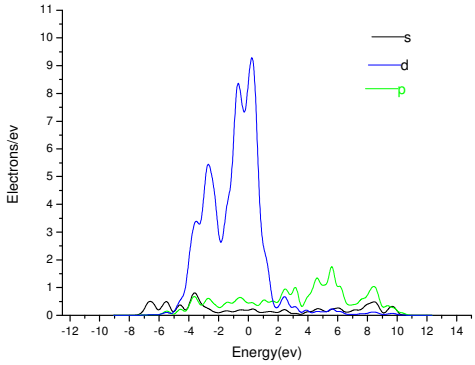

Fig.4. Partial Density of states (PDOS) of pure Fe (100)

For pure Fe (100), the 4s states expand into a rather wide energy region from -7.5 to +10 eV with respect to Fermi energy and 3d form -6 to +10eV and for 3p is -6 to +11 eV. For the adsorbed two molecules of H_2S are shown in Figure 5, the energy of the 3s states and 3p states have been some decrease. It mainly consists of 3d orbitswith energy region from -8 to +1.5 eV.

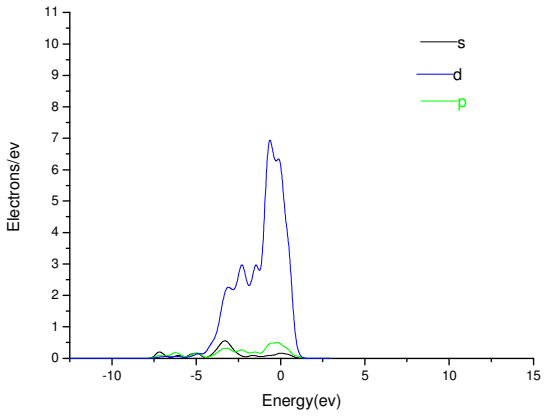

Fig.5. Partial Density of states for two molecules of H_2S adsorbed on the Fe (100)

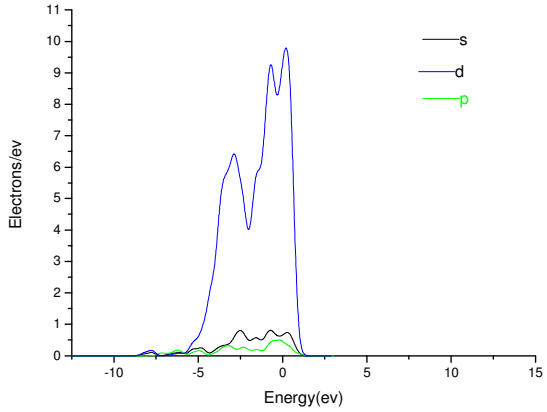

Fig.6. Partial Density of states of Single H_2S molecule adsorbed on the Fe (100)

Figure 6 shows the PDOS of one H_2S molecule absorbed by Fe (100),similar to the pattern of two molecules absorbde by Fe (100). Two patterns have the characteristics of energy decrease . For the 4s states, the energy of the former is higher than the latter one.For the 3p states, their energy is so approximate. The 3d states show the twin peaks with similar to pure Fe (100),and PDOS of a H_2S molecule adsorption on Fe (100) as shown in figure 6, similar to two H_2S molecules, are characterized by energy reduction.Total density of states for single H2S molecule adsorbed on the Fe (100) is between pure Fe (100) and two H2S molecule and mainly composed of 3D electronic contribution.

Conclusions

Using periodic density functional theory within the generalized-gradient approximation to electron exchange and correlation, we have studied different concentration of H_2S adsorbed on the Fe (100) surface. The results show that, whether one or two molecules of H_2S adsorpted Fe (100) surface, adsorption of single molecules Fe (100) surface partial density of states between pure Fe (100) and two molecules, and the total density of states is mainly composed of 3d electronic contribution.

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