First-principle calculations of interaction of O_2 with pyrite, marcasite and pyrrhotite surfaces

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Abstract: The interaction of O_2 with pyrite, marcasite and pyrrhotite surfaces was studied using first-principle calculations to obtain the oxidization mechanisms of these minerals. The results show that the adsorption energy of O_2 on pyrrhotite surface is the largest, followed by that on marcasite surface and then pyrite surface. O_2 molecules adsorbed on pyrite, marcasite and pyrrhotite surfaces are all dissociated. The oxygen atoms and surface atoms of pyrite, marcasite and pyrrhotite surfaces have different bonding structures. Due to more atoms on pyrrhotite and marcasite surfaces interaction with oxygen atoms, the adsorption energies of O_2 on pyrrhotite and marcasite surfaces are larger than that on pyrite surface. Larger values of Mulliken populations for O−Fe bond of pyrrhotite surface result in relative larger adsorption energy compared with that on marcasite surface.
Key words: iron sulfide; O_2 adsorption; surface oxidation; first-principle

1 Introduction

Iron sulfide is a chemical compound with the formula of FeS, and exists in several distinct forms, which differs in the ratio of sulfur to iron and properties. Common iron sulfides include pyrite (FeS_2), marcasite (FeS_2), pyrrhotite (Fe_xS_{1-x}) and so on. The structures of pyrite and marcasite have been well characterized and described in detail elsewhere, and the structural relationships between pyrite and marcasite were also studied [1−3]. According to BROSTIGEN and KIEKSHUS [3], the pyrite (001) and the marcasite (101) planes show the same atomic arrangement. Pyrrhotite is an unusual iron sulfide mineral with a variable iron content. Pyrrhotite is also called magnetic pyrite because the color is similar to that of pyrite and it is weakly magnetic. Pyrrhotite exists in a hexagonal or monoclinic form. The iron content ranges from 46.5% to 46.8% (mole fraction) in monoclinic pyrrhotite and from 47.4% to 48.3% in hexagonal forms [4]. The formula of pyrrhotite minerals can also be expressed as $Fe_{n-1}S_n$ with $n{\geq}8$ to give structures from Fe_7S_8 to $Fe_{11}S_{12}$. The most

Fe-deficient end member, Fe_7S_8, has a monoclinic symmetry, whereas the intermediate ($Fe_{1-x}S$) and equimolar (FeS) members have hexagonal and orthorhombic structures, respectively [5,6]. The bulk sulfides have been well studied and displayed different electronic structures and properties [7−10].

The surface chemistry of sulfides plays a large role in the commercially important processes of mineral benefaction and the separation of sulfides. The floatability of minerals depends on the wettability at solid particle surfaces. However, many studies show that O_2 has large effect on the floatability of minerals [11,12]. It has been increasingly acknowledged that the oxidation of sulfide minerals themselves is fundamentally significant during flotation. Xanthates are often used in flotation operation as a collector for sulfide minerals, which attaches to the mineral surface and produces a hydrophobic surface. The xanthate oxidation process is accompanied by the concurrent reduction of oxygen [13], while the oxygen chemisorption energetically favors the oxidation of xanthate anions to produce an adsorbed hydrophobic species. This reaction can be expressed by the following equations:

$$O_2+e=(O_2^-)_{ads} \tag{1}$$

$$ROCS_2^-=(ROCS_2)_{ads}+e \tag{2}$$

Oxygen is a critical factor affecting the natural floatability of sulfide minerals. ROSSO et al [14] studied the interaction of gaseous O_2, H_2O and their mixtures with clean (100) surfaces of pyrite. Ab initio cluster calculations of adsorption energies and the interaction of O_2 and water species with the surface indicate that H_2O dissociatively sorbs when O_2 is present on the surface. The study of ROSSO et al [14] suggests that O_2 can be influential on H_2O adsorption on the sulfide surfaces. In addition, pyrite exhibits surface chemistry that can profoundly affect the very environment in which it is present. One of the most striking examples of how the reactivity of pyrite can affect an environment is associated with anthropogenic activities. The oxidative decomposition of pyrite at coal and metal mining sites leads to the devastating environmental problem known as acid mine drainage [15,16]. Therefore, the role of O_2 in the floatation of sulfides becomes one of the most important issues in the study of floatation of sulfides.

In this work, the interaction of O_2 with pyrite, marcasite and pyrrhotite surfaces was studied using density functional theory (DFT) method, including adsorption model, adsorption energy, surface charge distribution and charge transfer, and density of states (DOS). This study can provide important insight into the mechanism of O_2 adsorption and the subsequent flotation behavior of sulfides.

2 Computational methods and models

2.1 Computational methods

The calculations were performed using the Cambridge Serial Total Energy Package (CASTEP) developed by PAYNE et al [17]. DFT calculations within the generalized gradient approximation (GGA) using the Perdew, Burke and Ernzerhof (PBE) functional were carried out to study O_2 adsorption on the surfaces of pyrite, marcasite and pyrrhotite [18]. The interactions between valence electrons and ionic core were represented by ultrasoft pseudopotentials [19,20]. The valence electron configurations included Fe $3d^64s^2$, S $3s^23p^4$ states. Based on the test results, a plane wave cut-off energy of 270 eV was used for all calculations. The convergence tolerances for structure optimization and energy calculation were set to the maximum displacement of 0.002 Å, the maximum force of 0.08 eV/Å, the maximum energy change of 2.0×10^{-5} eV/atom and the maximum stress of 0.1 GPa, and the self-consistent field (SCF) convergence tolerance was set to 2.0×10^{-6} eV/atom.

2.2 Computational models

Common pyrite (FeS_2) possesses a cubic crystal structure, and has a space group of Pa3, which has good symmetry. The conventional unit cell is presented in Fig. 1(a). Each cell contains four FeS_2 units, with Fe atoms located at each of the corners and the centers of all the cube faces. Each Fe atom coordinates with adjacent six S atoms, each S atom is tetrahedrally coordinated by three Fe atoms and one S atom with the S_2 dimer formed. The mineral marcasite, sometimes called white iron pyrite, is iron sulfide (FeS_2) with orthorhombic crystal structure. It is a mineral with the same composition as pyrite, but differing in crystal structure. Both structures do have in common that they contain the disulfide S_2^{2-} ion having a short bonding distance between the sulfur atoms. The structures differ in how these dianions are arranged around the Fe^{2+} cations. The model of marcasite is shown in Fig. 1(b). Pyrrhotite is a nonstoichiometric compound, general formula of $Fe_{1-x}S$, based on Fe(II) and S^{2-} ions. The values for x vary from 0 (FeS) to 0.125 (Fe_7S_8). Each metal atom is in a
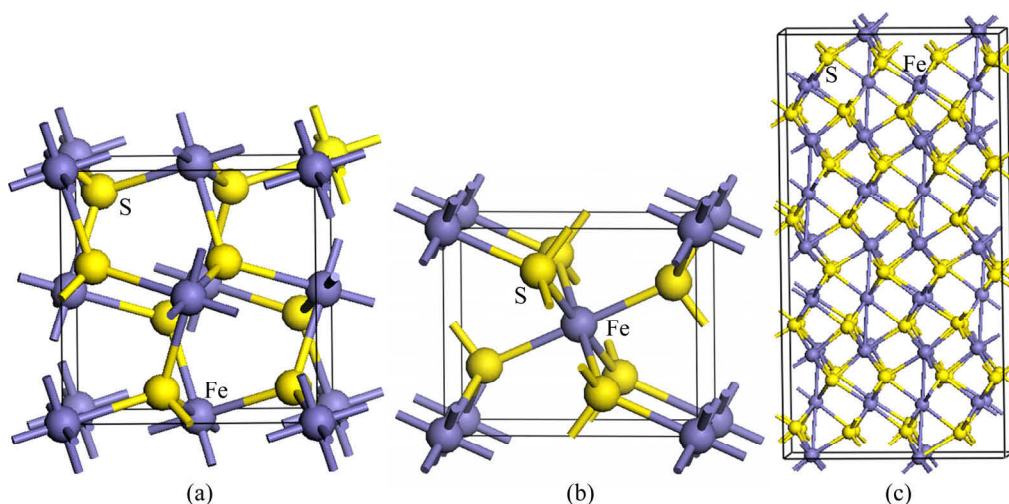

Fig. 1 Bulk FeS_2 unit cell of pyrite (a), marcasite (b) and pyrrhotite (c)