Research paper

Adsorption mechanism of H_2O molecule on the Li_4SiO_4 (0 1 0) surface from first principles

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ABSTRACT

The adsorption and dissociation behaviors of molecular H_2O on the Li_4SiO_4 (0 1 0) surface have been systematically studied by first-principles calculations. It is found that the adsorbed H_2O molecule mainly interacts with the O and Li atoms of the surface, that is, H atom bonds with O atoms of the surface while O atom bonds with the surface Li atoms due to the hydrogen bond effect. According to the different adsorption energies and vibrational frequencies of H_2O, different adsorption types can be classified. These results may explain the origin of multiple desorption peaks in TDS experiments.

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1. Introduction

Silicates are widely used materials in various technology fields, ranging from nuclear energy through applied chemistry to biological systems [1–5]. Lithium silicates as solid electrolytes in high-energy lithium secondary battery have attracted researchers' interests because of their better energies density and lithium ion conductivity [6]. In recent decades, another possible application for lithium silicates has been found: as CO_2 sorbents to fight global warming [5,7]. In the nuclear technology, due to their low chemical reactivity and excellent compatibility with other materials, lithium silicate as solid breeder materials was proposed by China and the European Union [2,8]. As we all known, the released tritium is generated by the ^6Li (n, α) ^3H reactions [9]. It has been established that tritium is extracted from irradiated lithium ceramics mainly in (90–95%) the chemical form of tritiated water [4,10]. But Li_4SiO_4 has a strong tendency for water adsorption, which results in a change in the surface chemistry of Li_4SiO_4 [10–12]. Before extracting tritiated water from Li_4SiO_4 surface, it is crucial to study its existent formations and adsorption mechanism clearly. The water desorption spectrum of non-irradiated Li_4SiO_4 pebbles clearly shows four peaks, which are denoted as Peak-1 (86 °C), Peak-2 (126 °C), Peak-3 (225 °C), and Peak-4 (400 °C), respectively [11]. However, extensive researches about reaction mechanism within theoretical methods are limited in literature probable due to the complexity of crystal structure. Moreover, there have been no reports about surface structure of Li_4SiO_4 found else and the underlying adsorption mechanism is not clear. Therefore, it is necessary to find out the stable surface and explore adsorption mechanism of H_2O molecule on the Li_4SiO_4. In the present work, periodic density functional theory calculations are carried out to investigate the interaction of H_2O with the Li_4SiO_4 (0 1 0) surface.

The paper is organized as follows. Description of the theoretical procedure that accounts for the DFT calculation details is made first. The results and discussion section begins with an instruction about the surface geometric structure, followed by the adsorption of H_2O molecule on the Li_4SiO_4 (0 1 0) surface, partial dissociation energy barrier of H_2O. Finally, the main conclusions are summarized in Section 4.

2. Computational method

First-principles calculations are carried out with the Vienna *ab initio* simulation package (VASP) code [13,14]. The PW91 generalized gradient approximation and projector–augmented wave potential are employed to describe the exchange-correlation energy and treat valence electrons-ion interaction [15,16], respectively. After careful test, both $5 \times 5 \times 5$ and $2 \times 2 \times 1$ grid of Monkhorst-Pack special k points are used to sample the Brillouin zone [17] for the bulk and slab model, and the cut-off energy of 400 eV is chose for the plane-wave expansion. The convergence criterion for the electronic self-consistent cycle has been fixed to 10^{-6} eV in the total energy per cell. Geometry optimizations are
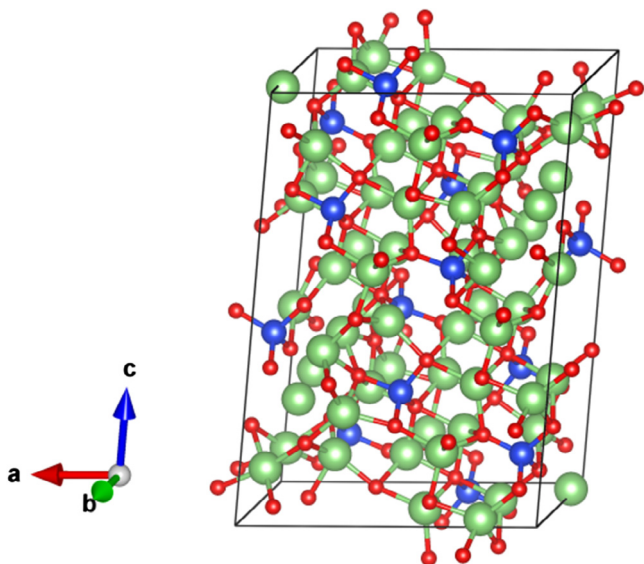
Fig. 1. The lattice structure of Li_4SiO_4 unit cell.

Table 1
The calculated equilibrium lattice parameter of Li_4SiO_4.

Parameters	Present	△ (%)	Expt [20]	Cal [7]
a (Å)	11.643	0.96%	11.532	11.644
b (Å)	6.138	1.04%	6.075	6.142
c (Å)	16.866	1.13%	16.678	16.875
β (°)	99.060	0.02%	99.04	99.10

Table 2
The formation energies of low Miller index surface of Li_4SiO_4. And their structure models refer to Supplementary Materials.

Surface	a (Å)	b (Å)	S (Å²)	E_{surf} (eV)
(0 0 1)	11.652	6.138	71.518	0.439
(0 1 0)	16.874	11.652	194.162	**0.197**
(0 1 1)	6.138	16.874	103.574	0.256
(1 0 0)	16.874	13.170	220.061	0.321
(1 0 1)	21.964	6.138	134.812	0.311
(1 1 0)	11.652	17.956	206.915	0.297
(1 1 1)	13.170	17.956	236.376	0.334

performed within a conjugate-gradient algorithm until the convergence criterion on forces (10^{-2} eV Å^{-1}) is reached. Our convergence tests show that single layer slab is thick enough for our surface model which contains 129 atoms. A vacuum layer of 15.0 Å is placed between the slabs in the z direction to avoid artfacts caused by the use of periodic boundary conditions in the direction perpendicular to the slab. In order to remove the net dipole effect induces by the asymmetry of slab, a dipolar correction along the normal direction of the slab has been introduced [18]. The partial dissociation barrier of H_2O is found by the climbing image nudged elastic band (CI-NEB) method [19].

3. Results and discussion

Li_4SiO_4 unit cell belongs to the space group (P2$_1$/m) [7], which will require a high computational effort due to the low symmetry, as shown in Fig. 1. After the full relaxation of the Li_4SiO_4 unit cell, the stable lattice constants at ground state are obtained, as shown in Table 1. The lattice constants a = 11.643, b = 6.138 and c = 16.866, respectively, are 0.96%, 1.04% and 1.13%, which are in good agreement with the previous theoretical results of Duan [7], slight higher than the experimental values [20].

In order to find out the most stable surface, we have checked all the low Miller index surface of Li_4SiO_4 by calculating the surface formation energy. The surface energy is calculated according to the equation:

$$E_{surf} = \frac{E_{slab} - nE_{unit}}{2A} \quad (1)$$

where E_{slab} and E_{unit} are the energies of relaxed slab system and unit cell, respectively. n stands for the number of Li_4SiO_4 formula units and A means the surface area of the slab.

Up to now, there has been no literature on the study of Li_4SiO_4 surface reported. The (0 1 0) plane is thermodynamically the most stable one among seven low-index surfaces depending on theoretical calculations (see Table 2). The investigation about the sensibility of the surface energy to the change in chemical potential of elements refers to Supplementary Materials. It can also be seen from Fig. 2 that the (0 1 0) plane is closer to the stratified configuration of the highly symmetric metal crystal.

In the subsequent calculations on H_2O interacting with the Li_4SiO_4 (0 1 0) slab, the atoms of topmost three layers are allowed to

relax while the two bottom layers are frozen to their bulk positions. The adsorption energy of a H_2O molecule on Li_4SiO_4 surfaces (E_{ads}) is defined as:

$$E_{ads} = E_{slab+H_2O} - E_{slab} - E_{H_2O} \quad (2)$$

where E_{slab+H_2O} and E_{slab} are the total energies of the Li_4SiO_4 surface with and without H_2O adsorption, respectively, E_{H_2O} is the total energy of a free H_2O molecule.

3.1. Adsorption structure and energy

From Fig. 2(a), we can see that the Li_4SiO_4 (0 1 0) surface is irregular and there almost no high symmetry point exists. Several sites have been chosen to test, and three types of adsorption energies have been found. Our tests show that H atoms in the H_2O molecule and the O atoms of the surface play a key role. So we only consider four top sites for the adsorption studies: O-top, Li-top, Si-top and O_{sub}-top. Regarding the spatial orientation of H_2O molecule, its molecular plane is set to be parallel and perpendicular to the surface and it is placed above the surface 3 Å. The adsorption energy of the H_2O molecules are obtained after reaching the steady state and listed in Table 3. The adsorption energy ranges from −0.670 to −1.366 eV, which agrees well with the experimental observations [7]. Fig. 3 shows that the H_2O molecules do not completely dissociate on the selected surfaces, but only distorted. Regarding the case of H_2O initially perpendicular to the Li_4SiO_4 (0 1 0) plane, the surface hydroxyl —O_mH_m (subscript m means the atom from the H_2O molecule) in the air is approximately 0.967 (or 0.968) Å, while the hydroxyl bond —O_mH_s (subscript s means the atom H bond the atom of surface) pointing to the surface slightly elongates, of which increases to 1.056, 1.038, 1.083, and 1.084 Å, respectively. And the H_s atom in the molecule bonds to the surface O_s atom, of which the H—O distance is about 1.492, 1.596, 1.405, and 1.440 Å, respectively. The distances between the O_m atom of the water molecule and the nearest neighbor Li_{NN} atom are 1.995 and 2.006 Å at position 1 and 2, while 1.889 and 1.893 Å at position 3 and 4. From the equilibrium geometries, the distances between O_m atoms of the H_2O molecule and the surface Li_{NN} atom at the former two positions are larger than the latter two positions. The weak O_m—Li_{NN} bond may be the reason for the low adsorption energy. Additionally, we get the different results when H_2O starts with parallel arrangements on the Li_4SiO_4 (0 1 0) surface, as shown in Fig. 4. Comparing with the first condition, we find that the final adsorption structures