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Adsorption and diffusion studies of an O adatom on TiO_2 anatase surfaces with first principles calculations

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ABSTRACT

The oxygen adatom adsorption and diffusion on the TiO_2 anatase (101) and (001) surfaces are studied with the density functional theory (DFT) calculations coupled with the nudged elastic band method (NEB). The dissociation of a O_2 molecule on a (001) surface is exothermic and is endothermic on a (101) surface. However, the oxygen adatom diffusion barriers on a (101) surface are lower than that on a (001) surface.

1. Introduction

Due to its unique physical and chemical properties, titanium dioxide attracts many scientific interests. For example, it can be used in photocatalytic water splitting and hydrogen production [1,2], dye sensitization and solar energy conversion [3,4], and photochemical air and water treatments [5–7]. Henderson and Fujishima reviewed this topic recently [8,9].

Oxygen molecule and adatom adsorption on TiO_2 surfaces may play an important role in photo-oxidation of organic pollutants. They serve as not only the main oxidizing reagents but also electron scavengers in photo-oxidation processes [10]. So, it is interesting to investigate the oxygen molecule adsorption and dissociation on TiO_2 surfaces. After the oxygen molecule dissociation, the oxygen adatom diffusion on the surface is the kinetic step for the photo-oxidation reactions, oxygen adatom diffusion on the TiO_2 surfaces may influence the chemical reaction rates.

Rutile and anatase are the two major phases of titanium dioxide which are widely used in the industry. For example, P-25 is mixed anatase and rutile commercial TiO_2. Since rutile (110) surface is thermodynamically most stable termination of rutile [9], rutile (110) surface has been extensively studied. Oxygen molecule adsorption, dissociation, and the diffusion of O_2 or O adatom on rutile (110) have been studied with scanning tunneling microscopy (STM), temperature-programmed desorption (TPD) [11–15] and density functional theory calculations [16] in the last decade. But the oxygen atom adsorption and diffusion on anatase surfaces are not well understood. The (101) and (001) surfaces are two prominent surface terminations of anatase TiO_2 [9]. We mainly concentrate on these two surfaces in this study. Recently, we studied oxygen molecule adsorption on anatase surfaces and edges [17].

In this work we study the oxygen adatom adsorption and diffusion on the anatase (001) and (101) surfaces with first principles calculations coupled with nudged elastic band method (NEB). Because the configurations of adatom adsorption are the initial and final images of the NEB calculations, the oxygen adatom adsorption is studied before the NEB calculations.

2. Computational methods

The density functional theory (DFT) [18,19] calculations are carried out to calculate the ground state energy of the systems. All the DFT calculation are perfomed with Vienna Ab initio Simulation Packages (VASP) [20–22]. The projected augmented wave (PAW) method [23,24] is used to deal with the strong oscillation of wave function near the core region. Both of the local density approximation (LDA) [25] and the generalized gradient approximation (GGA) [26] are used in the energy calculations. The energy cutoff is 400 eV

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Table 1
TiO_2 anatase lattice constants. Compared with the experimental data. a and c are the lattice constants and d is the Ti–O bond length.

	a (Å)	c/a	c (Å)	d (Å)
LDA	3.77	2.51	9.46	1.97
GGA	3.83	2.51	9.61	2.00
Expt [28]	3.78	2.51	9.50	1.98

and the convergence criteria for the electronic and ionic relaxation are 10^{-4} eV and 0.05 eV/Å respectively. A $4 \times 4 \times 1$ Monkhorst–Pack [27] k-point mesh is used in all of the calculations. Since a single oxygen atom has un-paired electrons and the ground state of an O_2 molecule is triplet, the spin polarization is used in all the calculations.

The lattice constants for TiO_2 anatase structure are listed in Table 1. The data from both LDA and GGA agrees with the experimental data well. In order to eliminate the influence from the nearest neighbor cells for the periodic calculations, a $[200] \times [020]$ surface cell is used for the (001) surface calculations, and a $[020] \times [10\bar{1}]$ surface cell is used for the (101) surface calculations. In each super cell, there are 18 atomic layers, six Ti atom layers and twelve O atom layers. These unit cells are large enough for a single oxygen adatom diffusion on the anatase surfaces. A vacuum layer of a thickness of 7 Å is used to reduce the interaction between the periodic slabs. During the relaxation of the slabs and the adsorption systems, top 12 atomic layers of the 18 atomic layers thick slab are free to move and the bottom 6 atomic layers are fixed.

The surface energy is defined as

$$E_{surf} = \Delta E^{rel}_{slab} + E^{unrel}_{surf} \quad (1)$$

where the ΔE^{rel}_{slab} is the energy difference between the relaxed and unrelaxed slab and the E^{unrel}_{surf} is the surface energy of the unrelaxed surface.

The adsorption energy of an oxygen adatom is defined as

$$E_{Oad} = E_{surf+O} - E_{surf} - \frac{1}{2}E_{O_2}. \quad (2)$$

Since the reference energy of the oxygen adatom is half the energy of the O_2 molecule. The negative adsorption energy means that the bond break of O_2 on the surface is thermodynamically favored. And the bond break process is endothermic for a surface with positive adsorption energy.

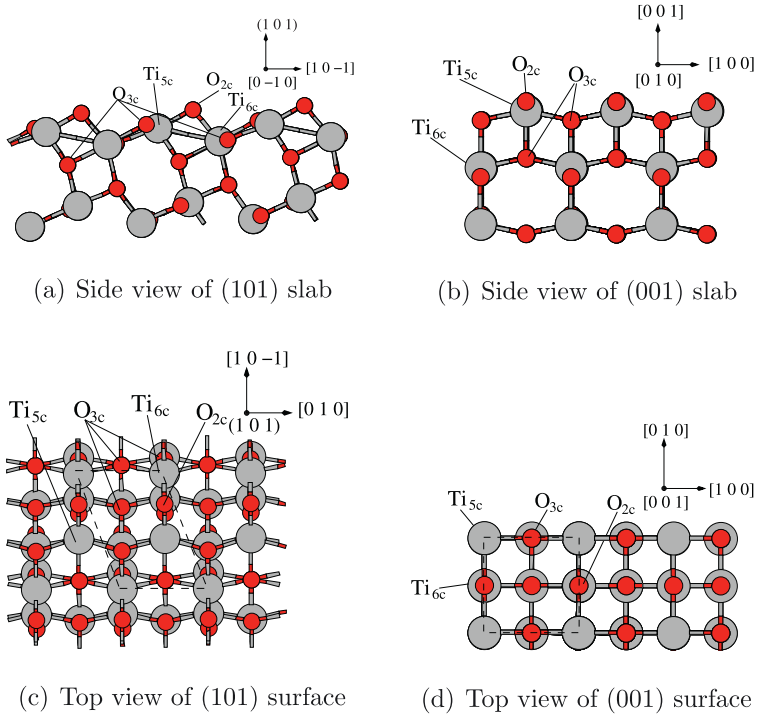
The climb image nudged elastic band (CI-NEB) method [29–31] is used to search the minimal energy diffusion paths and the saddle points of an O adatom diffusion on anatase surfaces. There are four images between the initial and the final images which are fixed during the NEB calculations.

3. Results and discussions

3.1. Anatase (101) and (001) surfaces

Before the O atom adsorption and diffusion calculations, the anatase (001) and (101) surface structures are relaxed and the surface energies are calculated. The lattice constants of anatase calculated in previous work [32] are used in this work. The side view and top view of the slabs used for (001) and (101) surface calculations are shown in Fig. 1. The saw-tooth like anatase (101) surface exposes both fully coordinated and undercoordinated Ti atoms and O atoms, Ti_{6c}, O_{3c}, and Ti_{5c}, O_{2c}, respectively. The surface unit cell contains two (TiO_2) units and each primitive surface cell has one Ti_{5c} atom and one Ti_{6c} atom on the surface. On anatase (001) surface, there are rows of two fold coordinated oxygen atoms O_{2c} and five fold coordinated titanium atoms Ti_{5c}. Each O_{2c} connects to two Ti_{5c} and they form $-Ti_{5c}-O_{2c}-$ chains which are perpendicular to the O_{2c} rows. These surface chains are connected by O_{3c} atoms. There is no Ti_{6c} atom on the outermost (001) surface. The Ti_{6c} atoms are under the outermost (001) atomic layer.

The surface energies for both of the surfaces have been calculated and listed in Table 2. The surface energy for a (001) surface is very close to that of our previous works, while the surface energy



(a) Side view of (101) slab (b) Side view of (001) slab

(c) Top view of (101) surface (d) Top view of (001) surface

Fig. 1. The side view and top view of the slabs used for the (001) and (101) surface calculations. The dash line shows the primitive surface cell.