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Ab-initio pseudopotential study of electronic structure and chemisorption of oxygen on aluminium surface

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ABSTRACT

Chemisorption of oxygen atom on aluminium (1 1 1), (1 1 0) and (1 0 0) surfaces is studied using *ab-initio* plane wave pseudopotential method based on density functional theory (DFT). Oxygen atom chemisorbed on three different high symmetry sites; top, short-bridge and hollow sites on the aluminium surfaces are examined. It has been found that the O-adatom adsorbed at the hollow site on aluminium (1 1 1), (1 1 0) and (1 0 0) plane yield energetically most stable structure. Calculation of chemisorption energies of O-adatom on aluminium surfaces shows that oxygen is most strongly bound to aluminium atoms on Al(1 1 1) plane and the calculated value of the chemisorption energy of O-adatom at the hollow site on Al(1 1 1) surface is 4.8 eV. In this work, the chemisorption energies calculated for O-adatom on Al(1 1 0) and Al(1 0 0) surfaces are reported for the first time. The electronic structures and the electronic charge density distributions of the oxygen chemisorbed aluminium surfaces are also investigated. Calculations show that for aluminium, *p* orbitals also contribute significantly along with the *s* orbitals during the bond formation with oxygen atom. Therefore, the possibilities of hybridizations lead to the strong bonding configurations.

1. Introduction

Oxidation of aluminium is an unavoidable natural phenomenon. Metallic aluminium is prone to oxidation at room temperature as well as at elevated temperature wherever it is used. Oxidation of aluminium has been studied for a long time. The adsorption of oxygen atoms on the aluminium surface through a chemical reaction initiates oxidation of aluminium. In 1978, Flodström et al. [1] presented the experimental evidences that oxidation of aluminium starts with the development of an oxygen chemisorption phase on the surface and finally at high oxygen exposure or at elevated temperature, this chemisorption phase forms a bulk aluminium oxide layer. However, the study of oxidation of aluminium or oxygen chemisorption on aluminium metal surface has significant importance from the viewpoint of technological applications as metallic aluminium has plenty of use in daily life. Furthermore, chemisorption of oxygen atom on aluminium metal surface is considered to be the fundamental model system to investigate similar kind of phenomena of chemisorption of different gaseous atoms on different metallic surfaces [1–4]. Therefore, a number of theoretical and experimental research works have been carried out to investigate the mechanism of chemisorption and dissociation of oxygen on aluminium surface [5–10], where the maximum importance is given on aluminium (1 1 1) surface. Still a theoretical modeling of the mechanism of oxygen chemisorption on different crystallographic planes of aluminium, their detail structural information, the chemosorption energies and the electronic structure of the O-chemisorbed Al surfaces are yet to be reported comprehensively.

In this context, here we present an *ab-initio* plane wave pseudopotential density functional theory (DFT) [11,12]-based calculations of oxygen chemisorption on aluminium metal surfaces focusing on their chemisorption energies, structural and electronic properties. Chemisorption of O-adatom on (1 1 1), (1 1 0) and (1 0 0) crystallographic planes of aluminium is studied in details. First principles total energy quantum mechanical simulations were carried out to investigate the energetically most favorable position of chemisorbed O-adatom on the Al surface among the three high symmetry sites, namely top, short-bridge and hollow sites. Chemisorption energies of oxygen adatom adsorbed on Al(1 1 1), (1 1 0) and (1 0 0) surfaces were calculated to study the most preferable chemisorption site on the surface. Here, for the first time, we have calculated the chemisorption energies of oxygen adatom adsorbed on Al(1 1 0) and (1 0 0) surfaces. Calculations show that generally oxygen atom has a tendency to adsorb on Al(1 1 1) crystallographic plane and the simulated results agree with the previous experimental evidences

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[1,6,9]. We also have studied the electronic structure of O-chemisorbed Al surfaces. Partial density of states (PDOS) is investigated for O-chemisorbed Al surfaces and unperturbed Al surfaces for a comparative study to understand the relative change in their electronic structure. The PDOS of the unperturbed and O-chemisorbed aluminium (1 1 0) and (1 0 0) surfaces have been reported for the first time. Furthermore, the distribution of electronic charge density on O-chemisorbed Al surfaces was also computed and displayed.

2. Computational methodologies

First principles total energy calculations based on DFT is performed using Purdue Burke Ernzerhof (PBE) generalized gradient approximation (GGA) electron exchange correlation functional form [13,14]. Plane wave ultra-soft pseudopotential calculations are carried out employing the CAmbridge Sequential Total Energy Package (CASTEP) code [15,16].

The equilibrium lattice parameter of bulk aluminium unit cell is calculated first. Using this equilibrium structure, Al(1 1 1), Al(1 1 0) and Al(1 0 0) surface slabs are constructed. Each surface slab contains six atomic layers of Al atom, in which two consecutive slabs are separated by a vacuum of 10 Å to avoid the interaction between the slabs. The slabs of six atomic layers thickness are tested to be enough to avoid the interactions among the atoms of the outermost atomic layers. Oxygen chemisorption is modeled on the outermost atomic layer of the surface slab by choosing three high symmetry sites on it. Oxygen atom is added on the (i) top, (ii) short-bridge and (iii) hollow sites on the surface slabs. In this study, the average Al–O bond length is considered as 1.8 Å. O-chemisorbed surface slabs are geometry optimized allowing relaxation of the top three atomic layers of Al along with the oxygen adatom so that the energy of the structure is minimized. For all the first principles calculations of O-chemisorbed Al surface slabs, we have tested that good convergence can be achieved by expanding the Kohn–Sham orbital in a plane wave basis set up to the cutoff energy value of 300 eV and by choosing a $4\times4\times1$ grid of Monkhorst–Pack k-points [17].

Total energy calculations are carried out on different O-chemisorbed Al surface slabs for different chemisorption sites of oxygen adatom to obtain the most energetically favorable position for oxygen adatom on the Al(1 1 1), Al(1 1 0) and Al(1 0 0) plane. Chemisorption energies (E_{chem}) of O-adatom chemisorbed on the most favorable sites on Al(1 1 1), Al(1 1 0) and Al(1 0 0) plane are calculated by using the formula

$$E_{\mathrm{chem}} = E_{\mathrm{O-Al}} - E_{\mathrm{Al}} - \tfrac{1}{2}E_{\mathrm{O_2}} \quad (1)$$

Here, the first term on the right-hand side presents the total energy of the Al surface slab containing chemisorbed O-adatom in it. Second term is the total energy of Al surface slab without the chemisorbed oxygen atom. The third term is the half of the total energy of oxygen molecule. Total energy of oxygen molecule is computed by putting oxygen molecule in a cubic box of length 8 Å and the total energy calculation is carried out using Γ-point energy calculation employing PBE (GGA) exchange correlation functional form. In this present calculation, oxygen–oxygen equilibrium bond length is taken as 1.48 Å.

3. Results and discussion

The calculated lattice constant of the equilibrium structure of bulk aluminium unit cell is 4.04 Å. Al(1 1 1), Al(1 1 0) and Al(1 0 0) surface slabs are constructed using this value of lattice constant. Energies of the bare (unperturbed) Al(1 1 1), Al(1 1 0) and Al(1 0 0) surface slabs are calculated first allowing relaxation of the atoms of the top three layers. Chemisorption of oxygen adatom on Al(1 1 1), Al(1 1 0) and Al(1 0 0) surface slabs are modeled at the top, short-bridge and hollow sites. The energies of the O-chemisorbed Al surface slabs as simulated using total energy method for the above three high symmetry sites on Al(1 1 1), (1 1 0) and (1 0 0) plane show that the surface slabs having chemisorbed O-adatom at the hollow site are energetically most stable compared with that on the top or short-bridge sites. The above-mentioned theoretically simulated result agrees with the previous experimental and theoretical works reported [6,8,18]. As computed, hollow site being the energetically most favorable position of chemisorbed O-adatom on the Al surfaces, in this study, we have investigated other properties, like chemisorption energies and electronic structure of the O-chemisorbed Al surfaces for the hollow site only.

3.1. Chemisorption energies

In the next part of the work, we have studied chemisorption energies of O-adatom chemisorbed on the hollow site of Al(1 1 1), Al(1 1 0) and Al(1 0 0) crystallographic planes. Chemisorption energies of O-adatom on aluminium surfaces are calculated using Eq. (1) and the results are summarized in Table 1.

It is clear from the above results that the chemisorption energy of O-adatom chemisorbed at the hollow site on Al(1 1 1) surface is much higher compared with that on Al(1 1 0) and Al(1 0 0) surface. Table 1 shows that the chemisorption energy of O-adatom chemisorbed at the hollow site on Al(1 0 0) is minimum among the three surfaces. Here, it is important to discuss that the chemisorption energy can be correlated with the activation energy. The high value of chemisorption energy indicates that the activation energy for desorption of the chemisorbed atom should also be large. Therefore, the chemisorbed O-adatom forms most strong bonding with the first layer aluminium atom on the Al(1 1 1) surface because of the high value of chemisorption energy. On the other hand, the chemisorption energy of the O-adatom chemisorbed on Al(1 0 0) surface being the lowest among the three, O-adatom will form the weakest bonding with the aluminium surface atom and can be uprooted easily compared with that of the others. However, it can be inferred that the initiation of the chemisorption phase due to the interaction of oxygen atom with Al surface atom is quite significant and strong on the most closed pack Al(1 1 1) crystallographic plane and the chemisorption of oxygen on aluminium (1 0 0) is the weakest. Based on the calculations, it should be noted that O-chemisorption on hollow site of Al(1 1 1) plane should predominates over that of other planes. The above prediction is also supported by the experimental evidences available [1,9,19]. Our calculated value of chemisorption energy of O-adatom chemisorbed on the hollow site on Al(1 1 1) surface agrees well with that of a previous theoretical work, where the reported value is close to 5 eV [20], whereas the reported experimental value for the same is nearly 5.8 eV [21]. However, in this work, the values of chemisorption energies for the O-adatom on aluminium (1 1 0) and (1 0 0) plane

Table 1
Chemisorption energies of O-adatom chemisorbed at the hollow site on the aluminium surfaces.

Aluminium surface	O-adatom chemisorption energies (eV)
Al(1 1 1)	4.8
Al(1 1 0)	4.3
Al(1 0 0)	3.3