DFT Study of Alkali Metal Atom Adsorption on Defect-Free MgO(001) Surface

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The adsorption of isolated alkali metal atoms (Li, Na, K, Rb, and Cs) on defect-free surface of MgO(001) has been systemically investigated with density functional theory using a pseudopotential plane-wave approach. The adsorption energy calculated is about $-0.72$ eV for the lithium on top of the surface O site and about one third of this value for the other alkali metals. The relatively strong interaction of Li with the surface O can be explained by a more covalent bonding involved, evidenced by results of both the projected density of states and the charge density difference. The bonding mechanism is discussed in detail for all alkali metals.

Key words: Alkali metal atom, Adsorption, Density functional theory

I. INTRODUCTION

The adsorption of alkali metals on oxide surfaces has attracted a growing interest due to its important role in many applications [1–7]. Among these, the most important application is heterogeneous catalysis. For example, Karolewskik et al. and Huang et al. have reported that the co-adsorption of the alkali metal (Li, Na, K, and Cs) with water on MgO(001) surface can promote the dissociation of water on the surface [8, 9]. Besides this application as catalyst, the addition of alkali metals to oxide surfaces can also improve the electrical, conducting, and chemical properties of materials. One typical example is that the adsorption of lithium on MgO(001) can create the electron deficient oxygen center and then facilitate the activation of methane [10, 11].

To understand the above experimental results, it is of great importance to gain insights on the adsorption behavior and stabilization mechanism of alkali metal atoms on oxide surface. It is worth noting that the shape and size of the alkali metal clusters that were adsorbed on oxide surfaces play the determinant role for the quality of catalyst and surface activation. Anyway, before studying this more complex situation, it is the first step to study the low coverage situation, which may allow the understanding of the fundamental features of the adsorption behavior of alkali metal atoms on oxide surfaces.

The interactions between isolated alkali metal atoms and MgO surface have been studied from both the experimental and theoretical aspects by several groups [12–20]. Recently, Finazzi et al. systematically investigated the properties of small amounts of alkali metal atoms (Li, Na, and K) deposited on different sites of MgO surfaces by means of electron paramagnetic resonance (EPR) spectroscopy and density functional theory (DFT) cluster method [7]. For the adsorption of alkali metals on terrace site, the conclusions are as follows. Li forms relatively strong bonds with surface O and can be stabilized at low temperature (less than 50 K). This interaction is attributed to the polarization contribution. Na and K interact much more weakly with MgO than Li. Similar results have been obtained by Brazzelli et al. using embedded-cluster DFT calculations [12]. However, these two groups mainly emphasized on the study of the magnetic properties of isolated alkali metal atoms on different adsorption sites. The details of adsorption behavior and bonding mechanism needed to be further investigated.

In this work, the adsorption of isolated alkali metals on defect-free MgO(100) is systematically studied by plane wave DFT approach. The heavier members of the group, i.e., Rb and Cs, are also included. The projected density of states and the charge density difference are presented to understand the adsorption behavior and bonding mechanism. The relatively strong interaction for the lithium on top of the oxygen site is attributed to a more covalent contribution in the stabilization mechanism.

II. COMPUTATIONAL DETAILS

The spin-polarized calculations based on DFT at the level of the generalized gradient approximation
(PW-91 exchange-correlation functional [21, 22]) were performed. The method is implemented in the Vienna *ab initio* simulation package (VASP) [23, 24] which uses a plane wave basis set, a projector augmented wave method for the treatment of core electrons and a kinetic energy cutoff of 400 eV.

A repeated slab model, in which one slab includes three MgO atomic layers and a vacuum region of 15 Å, was used. The bottom of the slab has a bulk-like structure. Adatoms are introduced only on one side of the slab. A $3\sqrt{2}\times3\sqrt{2}$ surface unit cell with one adatom was considered. The distance between two adsorbed alkali metal atoms is more than 12.6 Å which is large enough to prevent any horizontal interaction between two adjacent alkali metal atoms. Some tests were calculated for vacuum thickness, and 15 Å is thick enough to prevent any interaction in the z-direction. The alkali metal atom is placed perpendicular to the surface above the surface oxygen of defect-free MgO(001).

The adatom and the atoms in the top two layers were allowed to relax while the atoms in the bottom layer were fixed. The geometry optimization is achieved until the forces on all the unconstrained atoms are smaller than 0.02 eV/Å. The optimized atomic geometry is shown in Fig.1 for the lithium on top of the surface oxygen. For geometry optimization, the Brillouin zone was sampled in a $3\times3\times1$ Monkhorst-Pack set while the density of states (DOS) and the charge density difference were evaluated with a $6\times6\times1$ grid.

The adsorption energy $E_{ads}$ of alkali metal atom on MgO(001) surface has been calculated by the followed formula:

$$E_{ads} = E_{M/MgO} - E_{M} - E_{MgO}$$ (1)

where $E_{M/MgO}$ is the total energy of the whole system; $E_{M}$ is the total energy of the isolated alkali metal atom, calculated in a large cubic cell, and $E_{MgO}$ is the total energy of the clean MgO slab, and the spin polarization is considered in the calculations of all the systems. M stands for metal. The negative adsorption energies indicate the exothermic processes. Monopole, dipole and quadrupole corrections along the direction perpendicular to the slab and Vosko-Wilk-Nusair interpolation were applied.

### III. RESULTS AND DISCUSSION

For the alkali metal adsorption on defect-free MgO(001) surface, the most favorable adsorption site is on top of a surface O atom, which has already been concluded by previous works and confirmed by our results as well [12]. For example, the adsorption energy for the lithium on top of a surface Mg site is about $-0.13$ eV, smaller than that on top of O site. The same conclusion holds true for all alkali metals on top of a surface Mg site and hollow site. Therefore, only the adatoms on top of a surface O site are investigated in detail below.

Table I summarizes the calculated structural parameters and adsorption energies. The adsorption energies of isolated alkali metal atoms on both frozen and relaxed MgO(001) surface were calculated, and a similar trend can be observed. The Li binds relatively strongly with the MgO(001) surface while the other alkali metals interact very weakly with the surface O. This trend is generally in line with the previous work reported by Finazzi *et al.* that the adsorption energies of Li, Na, and K are $-1.05$, $-0.44$, and $-0.18$ eV, respectively [7]. The different value obtained is presumably due to no correction of the basis set superposition error in the shell-mode embedded cluster method that they used. The adsorption energy for each alkali metal seems to inversely correlate with the M–O distance. However, an almost constant value is obtained if this quantity is divided by the atomic van der Waals radius of each alkali atom. Thus, the decrease of adsorption energy is not due to the longer M–O distance. Rather, the electropositivity of alkali metal atoms is presumably responsible for this trend, as discussed below in more detail.

For all the alkali metal atoms, the small adsorption energy means that the adatom could be stabilized at this site only at very low temperature. Even for the lithium, annealing experiments monitored by EPR signal intensity reveal that the Li adatom start to diffuse on the clean MgO(001) surface above 50 K [7, 12]. Thus, under the general experimental condition (the temperature often used is above the liquid nitrogen temper-

![FIG. 1](image-url) (a) Top view and (b) side view of relaxed structures for Li atom adsorption on top of surface oxygen site of defect-free MgO(001) surface. O atoms are in red, Mg atoms in green, and the Li atom in purple. For interpretation of the color in this figure legend, the reader can refer to the web version of this article.
TABLE I Adsorption energies and geometrical parameters of alkali metal atom on frozen and optimized surfaces. \(d(M-O)\): shortest \(M-O\) distance; \(d(M-Mg)\): shortest \(M-Mg\) distance. In parentheses, the standard \(M-Mg\) distances are defined as the average of \(M-M\) and \(Mg-Mg\) distances in metal and Mg bulks.

<table>
<thead>
<tr>
<th>Atom</th>
<th>(E_{\text{ads}}/\text{eV})</th>
<th>(d(M-O)/\text{Å})</th>
<th>(d(M-Mg)/\text{Å})</th>
<th>(E_{\text{ads}}/\text{eV})</th>
<th>(d(M-O)/\text{Å})</th>
<th>(d(M-Mg)/\text{Å})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>-0.55</td>
<td>2.01</td>
<td>2.91</td>
<td>-0.72</td>
<td>1.89</td>
<td>3.03 (3.12)</td>
</tr>
<tr>
<td>Na</td>
<td>-0.24</td>
<td>2.70</td>
<td>3.42</td>
<td>-0.28</td>
<td>2.47</td>
<td>3.40 (3.46)</td>
</tr>
<tr>
<td>K</td>
<td>-0.22</td>
<td>3.21</td>
<td>3.84</td>
<td>-0.26</td>
<td>2.93</td>
<td>3.75 (3.87)</td>
</tr>
<tr>
<td>Rb</td>
<td>-0.22</td>
<td>3.46</td>
<td>4.05</td>
<td>-0.25</td>
<td>3.14</td>
<td>3.91 (4.08)</td>
</tr>
<tr>
<td>Cs</td>
<td>-0.23</td>
<td>3.61</td>
<td>4.18</td>
<td>-0.28</td>
<td>3.27</td>
<td>4.03 (4.25)</td>
</tr>
</tbody>
</table>

The alkali metal adatoms will easily diffuse to low-coordinated sites, such as steps and oxygen vacancies [12], and then these adatoms form clusters or even larger nano-particles, which act as catalyst to promote the dissociation of water or activate the methane just as mentioned in the introduction section [8−10].

As shown in Table I, the distance between each alkali metal and the four surface Mg atoms adjacent to O is a little shorter than the standard \(M-Mg\) distance which are defined as the average of \(Mg-Mg\) and \(M-M\) distance in Mg and metal bulks [25]. This indicates that although it is obvious that the interaction with O is dominant since alkali metal is right on top of surface O atom, the interaction of alkali metals with the nearest Mg atoms may not be negligible. In particular, a very small increase of the adsorption energy for the cesium compared with that of the rubidium likely arise from the large size of cesium leading to a relative stronger interaction of M atom with the neighboring four Mg atoms.

The weak interaction for all the alkali metal atoms except Li also indicates that the origin of this interaction is mainly from polarization contribution. For Li, the relative strong interaction suggests that a more covalent nature is involved in the bonding mechanism. To further investigate this interaction, the projected DOS is adopted to reveal the underlying bonding mechanism.

The total DOS of a clean MgO(001) and the projected DOS of a surface oxygen atom are shown in Fig.2. The valence band mostly consists of the bonding 2p orbits of O\(^{2-}\) and the corresponding band width is about 4.4 eV, which are both in agreement with previous theoretical work [26]. The \(p_z\) orbit exhibiting a different shape, as compared with the almost identical \(p_x\) and \(p_y\) orbits due to the symmetry, is observed in the partial density of states (PDOS) of a surface O atom.

For the adsorption of alkali metal atoms on top of the surface O, the magnitude of the adsorption energy is determined by the energy gain mainly resulting from the stabilization of the \(p_z\) orbit of the oxygen atom right below the metal atoms. This stabilization is directly related to the energy difference between the outmost ns and np orbits of metal atoms and 2\(p_z\) orbit of O atom, which decreases when the metal electronegativity increases, leading to the adsorption energy decrease from Li to Rb.

For the Li, the interaction can be explained by the PDOS of the M atom and the surface O right below the Li atom. As shown in Fig.3(a), the 2\(p_z\) orbit of the O in the energy range from \(-7.3\) eV to \(-3.2\) eV that exhibits a different shape compared with that of the clean surface O is pushed down with respect to the \(p_x\) and \(p_y\) orbits that are nearly unaffected. These results, showing a bonding character, serve as the evidence of the covalent interaction involved, leading to somewhat larger adsorption energy of the Li on top of O\(^{2-}\). The two Li orbits, 2s and 2\(p_z\), hybridize as shown in Fig.3(b), and interact with the surface O2\(p_z\) orbits, forming the bonding and anti-bonding levels. The lower one corresponds to the bonding level while the upper one close to

![FIG. 2 (a) Total DOS of MgO, O, and Mg. (b) Local DOS of O atom of clean MgO(001) surface. The vertical lines correspond to the Fermi level.](image-url)
FIG. 3 Local DOS for (a) the O under Li atom and (b) the Li atom above surface O for the systems of Li/MgO, (c) the O under Na atom and (d) the Na atom above surface O for the systems of Na/MgO, (e) the O under K atom and (f) the K atom above surface O for the system of K/MgO. The vertical lines correspond to the Fermi level.

FIG. 4 The maps of charge density difference for systems of (a) Li/MgO(001), (b) Na/MgO(001), and (c) K/MgO(001). View from the (010) plane. The solid and dashed lines correspond to the positive and negative values, respectively. The unit of charge density difference is e/Å³.

the Fermi energy corresponds to the anti-bonding level. The populations of anti-bonding level imply that the global interaction should not be very strong. In addition, the appearance of states around the Fermi level in gap indicates the enhancement of chemical activity for alkali metal atoms on MgO(001) surface.

For the other alkali metal atoms, the interaction is very weak as indicated from Fig.3 (c) to (f). The results for the rubidium and the cesium are not shown here due to the very similar figures obtained as that for the potassium. The p₂ orbits of O2⁻ show a similar shape to that of the clean surface O and the lowering of the energy of p₂ orbit decreases. Simultaneously, the hybridization of ns and np orbits of these alkali metals is not obvious as shown in Fig.3 (d) and (f). Therefore, the bonding and anti-bonding state can be negligible and the interaction mainly origins from the polarization contribution, leading to very small adsorption energy for these alkali metals.

The bonding nature for the adsorption can be further confirmed by plotting the electron density difference, i.e. (see Fig.4),

$$\Delta\rho(M/MgO) = \rho(M/MgO) - \rho(M) - \rho(MgO)$$

(2)
As for the lithium, a significant accumulation of electron in the region between Li and O\(^{2-}\) suggests a more covalent bonding contribution, while for the other alkali metals, the bonding mechanism mainly arises from intra-unit polarization. Besides the interaction between metal and O\(^{2-}\), a small accumulation of electron density in the region between metal and Mg\(^{2+}\) is also observed for all the alkali metals, indicating a small contribution from M–Mg interaction.

IV. CONCLUSION

The adsorption properties and stabilization mechanism of isolated alkali metal atom adsorption on defect-free MgO(001) surface was systemically investigated using VASP code, base on the density functional theory. It was found that lithium bind relatively strongly with the surface oxygen while the other alkali metal atoms interact very weakly with the MgO(001) surface. The hybridization of 2s and 2p\(_z\) orbit of the lithium enhance the interaction with the p\(_z\) orbit of the surface oxygen, leading to a more covalent bonding contribution. The interaction between the other alkali metal atoms and surface oxygen atom mainly results from the intra-unit polarization.