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Ab initio Hartree–Fock study on surface desorption process in tritium release

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Abstract

Dissociative adsorption of hydrogen on Li_2O (1 1 0) surface has been investigated with ab initio Hartree–Fock quantum chemical calculation technique. Heat of adsorption and surface potential energy for H_2 dissociative adsorption were evaluated by calculating the total energy of the system. The calculated results on adsorption heat indicated that H_2 adsorption is endothermic. However, when an oxygen vacancy exists adjacent to the adsorption site, the heat of adsorption became less endothermic and the activation energy required to dissociate the H–H bonding was smaller than that for the terrace site. This is considered to be caused by the excess charge localized near the defect. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Lithium oxide is one of the candidate materials for the fusion reactor blanket because of its high tritium breeding performance. Tritium produced by neutron irradiation is released into the sweep gas through diffusion into the grain, diffusion along grain boundaries and desorption from the surface. Recent experimental results have strongly suggested the importance of surface processes. In numerous in-pile tritium release experiments, enhancement of tritium release by adding H_2 into the sweep gas has been reported [1–3]. Therefore it is of great interest to understand the interaction of H_2 with Li_2O surface.

The adsorption and desorption behavior of H_2 has been investigated using infrared absorption spectroscopy [4,5]. Results from these studies indicate that hydrogen is dissociatively adsorbed on the Li_2O crystal surface to produce surface –OH and that the nature of –OH is affected by the oxygen potential near the surface. In the present study, we performed quantum chemical calculations in order to simulate the dissociative adsorption of H_2 on the surface of Li_2O. On the surface of oxide materials such as MgO and Ti_2O, H_2 is known to dissociate only on the defective sites [6,7]. Therefore, we focused on the effects of surface defects on dissociation of H_2, especially oxygen vacancy.

2. Calculation method

For calculation, we used the CRYSTAL 92 program [8] which can be used for ab-initio quantum chemical calculations in the periodic systems. This computational program enables us to conduct the ab-initio Hartree–Fock calculations for 2 or 3-dimensional periodic systems such as the bulk or surface of the crystal. In this calculation code, the crystalline orbital is expressed by the linear combination of the atomic orbital. The basis set used in this work was the optimized one by Dovesi and co-workers for bulk Li_2O [9]. This basis set is of triple zeta quality for the oxygen and includes the polarization function for the lithium atom. It is reported that the lattice constant, elastic constant and some other properties for Li_2O crystal could be calculated accurately by using this basis set. Furthermore, Sutjianto and co-workers studied the dissociative adsorption of hydrogen on Li_2O using the same basis set and showed that low coordinated oxygen in surface step structure may play an important role in the chemisorption process [10]. For the hydrogen atom of the adsorbed H_2,

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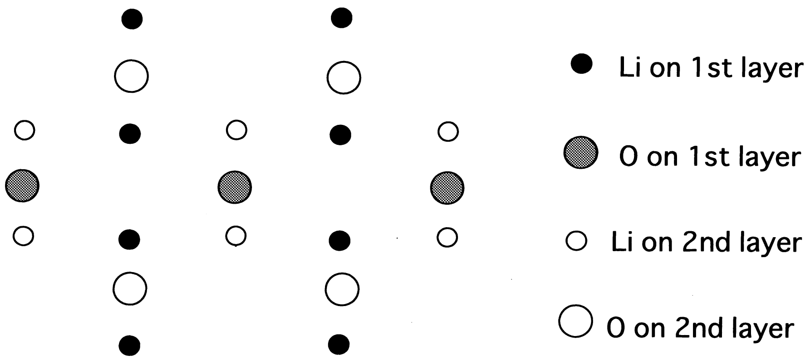

Fig. 1. The $Li_{14}O_7$ cluster used in this work: Closed and open circles represent the first and second layer respectively. In this surface model, ions below the third layer are neglected.

the STO-3G (Slater-type orbital expressed by three Gaussian-type orbitals) basis set was adopted.

3. Results and discussions

3.1. *Dissociative adsorption of H_2 on Li_2O*

In order to study the surface phenomena by this kind of calculations, we need to approximate the surface because it is impossible to treat all the atoms included in the cluster. In the previous work to investigate the H_2 and H_2O adsorption on the terrace site of Li_2O surface, we used a slab model, which corresponds to the finite atomic layers parallel to the selected plane of the crystal [11]. However, this approach may not be adequate for the system which contains the defective structure such as oxygen vacancy because of the low symmetry configurations. Therefore in this work, we mainly used the cluster model to approximate the surface. In the CRYSTAL 92 code, cluster could be easily created from the crystalline structure and we can conduct ab-initio calculations for this cluster. Fig. 1 shows the cluster for Li_2O (1 1 0) surface used in this work. This cluster contains 14 lithium ions and 7 oxygen ions and ions below the third layer of the crystal were neglected. In the case of surface adsorption and desorption phenomena, bonding orbital which causes the chemisorption is localized near the adsorbate. Therefore it is sufficient to treat the electronic state near the adsorbate. The structure of the cluster was optimized including the effect of surface rumpling and relaxation which plays an important role in adsorption and desorption behavior [11]. The calculation results showed that at the stable surface structure, lithium ion moves 0.04 Å outward and oxygen ion moves 0.04 Å inward compared to the atomic position of the bulk.

The heat of water adsorption on the ideal surface evaluated by this cluster showed good agreement with that obtained by the slab model. This indicates that this cluster is sufficient to treat the adsorption phenomena and we can neglect the cluster size effect.

Using the cluster described above, we evaluated the possible sites for H_2 dissociative adsorption. Three types of configurations shown in Fig. 2(a)–(c) were examined as adsorption sites. In site A, hydrogen atom of H_2 is adsorbed on surface oxygen ion to produce hydroxyl group and extra hydrogen is attracted to the neighboring lithium ion. In site B, extra hydrogen is adsorbed between the two nearest lithium ions on the top layer. In site C, two hydroxyl groups are created by H_2 dissociation. In each case, we assumed that surface hydroxyl group (O–H bonding) or Li–H bonding is created by the dissociative adsorption of H_2 molecule. In previous experiments using infrared absorption spectroscopy, surface hydroxyl groups were observed on the surface of Li_2O under H_2 atmosphere [4,5]. J.P. Kopasz and coworkers also observed the Li_2O surface by the same method and they reported the formation of Li–H bonding under H_2 atmosphere especially at high temperatures [12].

To find the position suitable for the adsorbed hydrogen atom on the surface at the givp@p^Ä“½en configuration, we have optimized the distance between hydrogen atom and the surface by minimizing the total energy of the system. For simplification, we assumed that O–H or Li–H bonding is always perpendicular to the surface. Using the total energy of the optimized system, we can estimate the heat of H_2 dissociative adsorption by the following equation:

$$E_{ad} = E_{(Li_2O+H_2)} - [E_{(Li_2O)} + E_{(H_2)}].$$

In this equation, $E_{(Li_2O+H_2)}$ represents the energy of the H_2 adsorbed surface, $E_{(Li_2O)}$ denotes the energy of the cluster used in this calculation, and $E_{(H_2)}$ the energy of free H_2 in the gas phase. The energy of free H_2 was evaluated by optimizing the H–H distance of H_2. The basis set for the hydrogen atom used to calculate the H_2

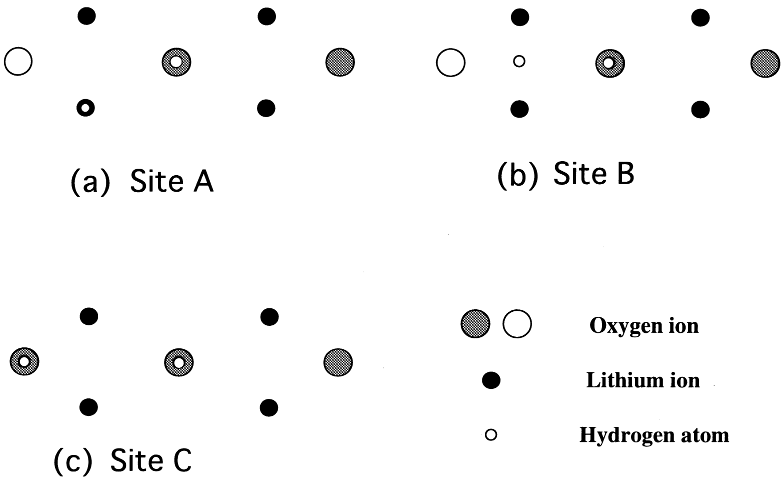

Fig. 2. The model for the H_2 adsorbed Li_2O (1 1 0) cluster. Hydroxyl group or lithium hydride was supposed to be produced by the adsorption of H_2. Large and small circles denote the oxygen ion and lithium ion respectively. Oxygen ion represented by open circle is removed when an oxygen vacancy is created on the surface.

energy was the same as that used for calculation of the hydroxyl group in this work. In the case of sites A and B, a calculation was also conducted for the oxygen removed cluster (removed oxygen is shown in Fig. 2) in order to investigate the effect of oxygen vacancy on H_2 adsorption. The purpose of the calculation using this simple defect model is to study the effect of surface electronic structure on H_2 adsorption behavior. Such a structure might not be the realistic model, but is useful to clarify this problem. The estimated heat of adsorption for each site is summarized in Table 1. A′ and B′ denotes the adsorption energy for sites A and B with oxygen vacancy respectively.

The adsorption was endothermic for all the sites considered in this work. However, in the case of site B′, the difference in energy between the initial state (before H_2 adsorption) and the final state (H_2 adsorbed surface) is small enough to exist as a stable adsorption site on the surface. It was found that the heat of adsorption was larger for a vacancy introduced cluster than that for the perfect cluster. This suggests that the surface containing an oxygen vacancy is more reactive than the ideal surface. When an oxygen vacancy is created on the surface, the rearrangement of the electron occurs and the surface electronic structure is considered to be changed. To clarify this, we conducted the Mulliken population analysis for the cluster used in this work. Table 2 summarizes the net charge of the oxygen ion, which forms the O–H bond when H_2 is adsorbed on the surface. It is shown that an oxygen ion with neighboring oxygen vacancy has negatively larger electron charge than that without vacancy site. This may cause the strong O–H bonding, leading to the large adsorption energy.

3.2. Activation energy for hydrogen dissociation

In order to evaluate the activation energy for H_2 dissociative adsorption on Li_2O, we calculated the surface potential energy for this reaction using ab-initio methodology. As the first step of our investigations, we studied the adsorption sites B and B′ of the previous section, which had the largest adsorption energy considered in this work. Surface potential energy could be obtained by plotting the total energy of the system as a function of the position of the atom which concerns the reaction. However, such a calculation is inconsistent with reality because of the large computational time. Therefore, to reduce the parameter which can be varied independently, we made the following assumptions.

Table 1
Energy for the H_2 dissociative adsorption

	Adsorption energy (eV)
A	+0.502
A′	+0.330
B	+0.220
B′	+0.05
C	+1.80

Table 2
Net charge for oxygen ion of the cluster estimated by the Mulliken population analysis

	Net Charge	
	Oxygen ion	Lithium ion
Defective site	−9.985	+2.054
Terrace site	−9.690	+2.027

1. The angle of H_2 molecular axis against the surface is maintained the same as the angle of H–H axis of the final state (H_2 adsorbed surface) during the reaction.
2. The axis of O–H bonding for hydroxyl group is always perpendicular to the surface.

Under these conditions, we can identify the reaction path by two parameters d (the distance between the hydrogen atoms) and h (the distance between H_2 and the surface) as shown in Fig. 3. Total energy of the system was calculated as a function of the parameters h and d. Parameter h was changed from 0.94 to 2.20 Å and parameter d from 0.65 to 1.75 Å. Calculated surface potential energies are shown in Fig. 4(a) and (b). In this figure, the darker point represents the lower energy and the more stable structure. The point A corresponds to the initial state (Li_2O surface + free H_2 molecule) and point F corresponds to the final state (H_2 adsorbed surface) of the reaction. Therefore, H_2 dissociative adsorption is considered to proceed from point A to F along the reaction path shown with the dashed line in Fig. 4. This reaction is considered to have the transition structure at point D. The activation energy for H_2 adsorption reaction on Li_2O could be evaluated as the difference between E_D and E_A. Where, E_A represents the energy of the initial state and E_D represents the energy of the transition state of this reaction. In our calculation, it was 250 kJ/mol for the terrace (perfect surface) site and 192 kJ/mol for the defective site.

The activation energy for H_2 adsorption was larger on the terrace site than that for the oxygen vacancy site. In the case of the defect site, dissociation of the H–H bond seems to start at a point more distanced from the surface compared with the terrace site as shown in Fig. 4(a) and (b). This suggests that oxygen vacancy promotes the dissociation of the H_2 molecule on the surface of Li_2O. This is considered to be due to the rearrangement of the electronic structure of the surface by introducing the oxygen vacancy. It is well known that the H–H bond is stabilized when the bonding orbital is occupied with 1s electrons of hydrogen atoms. In order to overcome the strong H–H bonding, it is effective to introduce the electron to the anti-bonding orbital of the H_2 molecular orbital. The excess charge which exists on oxygen ion for the defective site might accelerate the dissociation of H–H bonding by this mechanism.

In this work, adsorption of H_2 on defective sites was investigated using the simple model of the oxygen vacancy. The structure of the actual surface must be more complicated especially at high temperature under H_2 or H_2O atmosphere. Moreover, we should note that the local relaxation of the surface due to the creation of an oxygen vacancy or adsorption of H_2 was neglected. In the actual case, surface ions (oxygen and lithium ion) are considered to move when an oxygen vacancy is created. There might exist a reaction path for H_2 dissociation with a smaller potential barrier by considering these surface defects or relaxation. Calculation of the activation energy including these effects will be the next step of our investigations.

4. Conclusions

Dissociative adsorption of H_2 on the surface of Li_2O was studied by ab-initio quantum chemical calculation technique using the CRYSTAL 92 code. Adsorption of H_2 on Li_2O was endothermic for the sites examined in this work. The presence of oxygen vacancy caused the

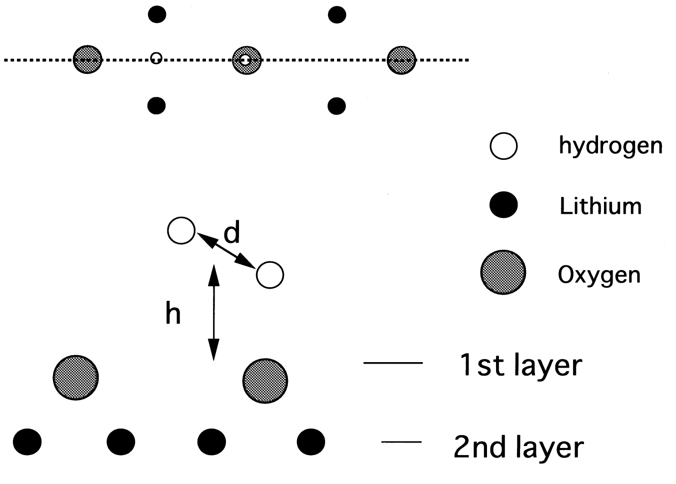

Fig. 3. Cross section of Li_2O cluster during the H_2 dissociation. The parameter d denotes the inter-atomic distance of H_2 molecule and h denotes the distance between H_2 and the surface. The angle of H–H axis against the surface during the dissociation process was supposed to be the same as that of the final state (hydrogen adsorbed surface) of the reaction.

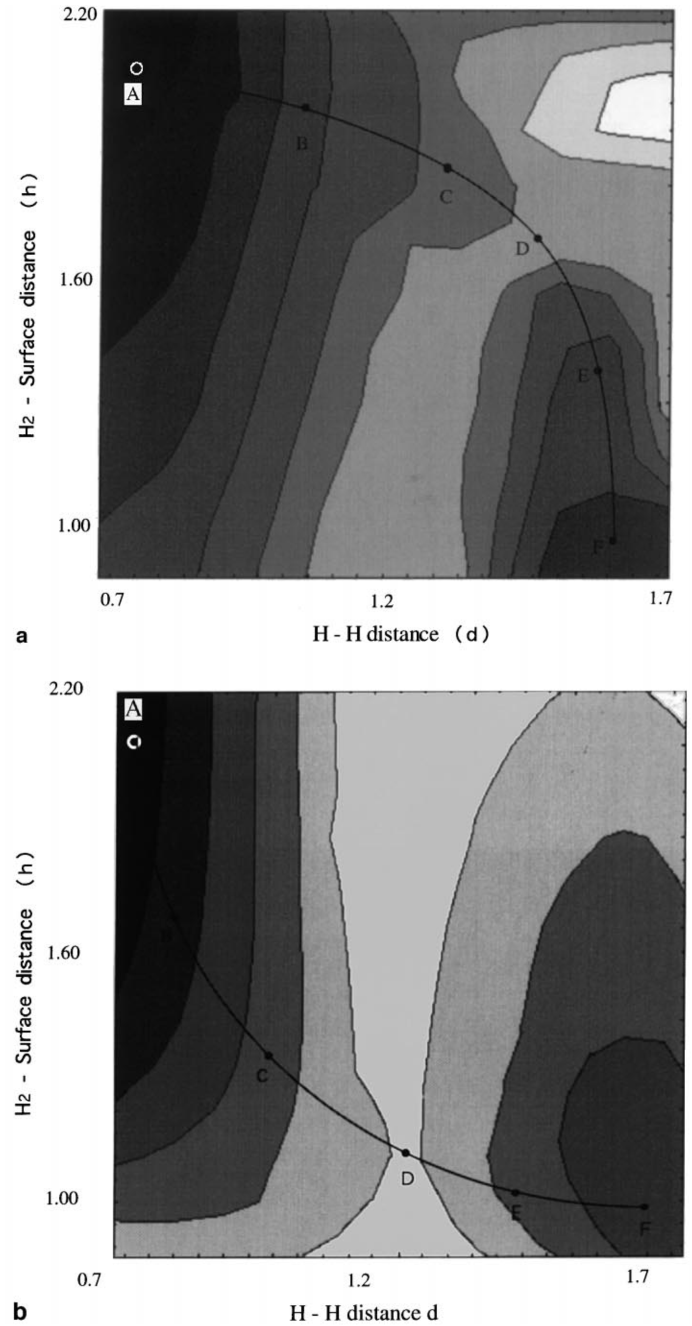

Fig. 4. Potential energy surface for H_2 dissociative adsorption: (a) oxygen vacancy was introduced adjacent to the adsorption site; (b) adsorption on terrace site. The point A corresponds to the initial state (free H_2 + surface) and the point F to the final state (H_2 adsorbed surface) of the reaction. H_2 adsorption reaction is considered to proceed along the solid line from A to F.

strong bonding between hydrogen and the surface oxygen ion to form surface –OH and the adsorption became less endothermic.

The potential energy surface for the dissociative adsorption of H_2 on Li_2O was obtained by calculating the total energy of the system. Activation energy for dissociation of H_2 became larger when an oxygen vacancy exists adjacent to the adsorption site. This might be caused by the excess charge which is localized near the defect structure.

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