

# Study on the behavior of hydrogen isotopes on solid breeder surfaces by ab-initio calculations

Masaki Taniguchi and Satoru Tanaka

(Department of Quantum Engineering and Systems Science)

## Abstract

Dissociative adsorption of hydrogen on  $\text{Li}_2\text{O}$  (110) surface has been investigated with ab-initio Hartree-Fock quantum chemical calculation technique. Potential energy surface for  $\text{H}_2$  dissociative adsorption was evaluated by calculating the total energy of the system. Calculation results on adsorption heat indicated that  $\text{H}_2$  adsorption is endothermic. However, when an oxygen vacancy exists adjacent to the adsorption sites, 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.

## 1. INTRODUCTION

Lithium oxide is one of the candidate materials for the fusion reactor blanket because of its high tritium breeding performance. Recent experimental results have strongly suggested the importance of surface processes. In numerous in-pile tritium release experiments, enhancement of tritium release by adding  $\text{H}_2$  into the sweep gas has been reported. Therefore it is of great interest to understand the interaction of  $\text{H}_2$  with  $\text{Li}_2\text{O}$  surface. In the present study, we performed quantum chemical calculations in order to simulate the dissociative adsorption of  $\text{H}_2$  on the surface of  $\text{Li}_2\text{O}$ . We focused on the effects of surface defects on dissociation of  $\text{H}_2$ , especially oxygen vacancy.

## 2. CALCULATION METHOD

For calculation, we used the CRYSTAL 92 program 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  $\text{Li}_2\text{O}$ .

## 3. RESULTS AND DISCUSSIONS

Fig.1 shows the cluster for  $\text{Li}_2\text{O}$  (110) surface used in this work. This cluster contains 14 lithium ions and 7 oxygen ions and ions below third layer of the crystal was neglected. Using this cluster, we studied the activation energy for  $\text{H}_2$  dissociative adsorption on  $\text{Li}_2\text{O}$  surface. Adsorption site for  $\text{H}_2$  considered in this work is also shown in fig.1. In order to evaluate the activation energy for  $\text{H}_2$  dissociative adsorption on  $\text{Li}_2\text{O}$ , we calculated the potential energy surface for this reaction using ab-initio methodology. Potential energy surface 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.

1) The angle of  $\text{H}_2$  molecular axis against the surface is maintained the same angle as the H–H axis of the final state ( $\text{H}_2$  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  $\text{H}_2$  and the surface) as shown in fig.2. Total energy of the system was calculated as a function of parameters h and d. Parameter h was changed from 0.94 Å to 2.20 Å and parameters d was from 0.65 Å to 1.75 Å. Calculated potential energy surfaces are shown in fig.3(a)-(b). In this figure, the darker point represents the lower energy and the more stable structure. The point A corresponds to the initial state ( $\text{Li}_2\text{O}$  surface + free  $\text{H}_2$  molecule) and point F corresponds to the final state ( $\text{H}_2$  adsorbed surface) of the reaction. Therefore,  $\text{H}_2$  dissociative adsorption is considered to proceed from point A to F along the reaction path shown with the dashed line in fig.3. 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 longer distance point from the surface compared with the terrace site as shown in figs.3(a) and 3(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.

#### 4. CONCLUSIONS

Dissociative adsorption of  $H_2$  on the surface of  $Li_2O$  was studied by ab-initio quantum chemical calculation technique using the CRYSTAL92 code. 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 oxygen vacancy exists adjacent to the adsorption sites. This might be caused by the excess charge which is localized near the defect structure.

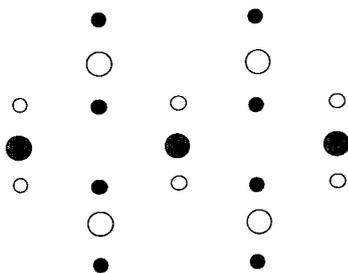


Fig.1: Cluster of  $Li_2O$  (100) surface.

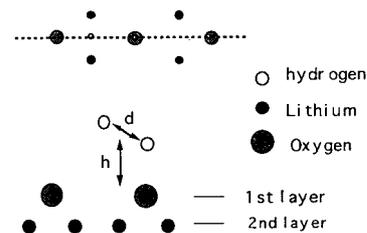


Fig.2: Adsorption site for  $H_2$  dissociative adsorption.

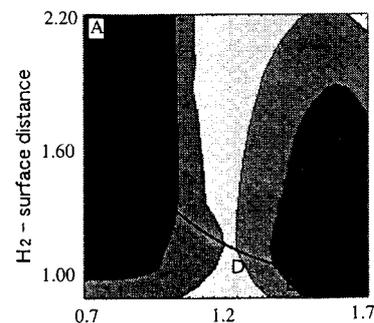
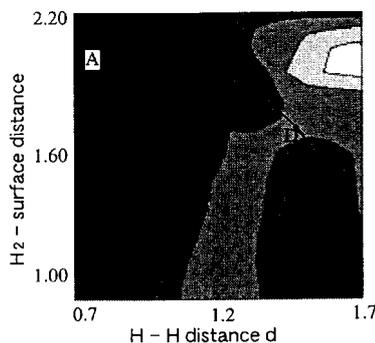


Fig.3: Potential energy surface for  $H_2$  dissociative adsorption: (a) oxygen vacancy was introduced adjacent to the adsorption site (left); (b) adsorption on terrace site. The point A corresponds to the initial state ( $H_2$  + surface) and the point F to the final site ( $H_2$  adsorbed surface) of the reaction (right).