

ANALYSIS OF HYDROGEN ADSORPTION AND DIFFUSION ON Mg(0001) SURFACE: AN *AB INITIO* DFT STUDY

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ABSTRACT

Ab initio density functional theory (DFT) calculations are performed to study the adsorption of H₂ molecules on a Mg(0001) surface. First, the adsorption energy was investigated. In the calculation of the adsorption process of molecular hydrogen, observation showed a physical adsorption of molecular hydrogen rather than chemisorptions. The diffusion process of atomic hydrogen on Mg (0001) was also presented. Finally, we are comparing all of our calculation with results from previous experiments.

Keyword: *DFT, Adsorption, Diffusion, Mg(0001), H₂*

Background

Hydrogen is an ideal clean carrier for storage, transport, and conversion of energy. However, a key problem is its storage, especially for its use as fuel for zero-emission mobile applications (Wagemans, *et al.* 2005). Among the metal hydrides under study as possible hydrogen storage media, magnesium hydride is one of the most promising candidates for automotive applications due to its very high capacity in the stoichiometric limit (7.6 wt %) and low cost (Schwarz, *et al.* 1999, Schlapbach, *et al.* 2001, and Liang, *et al.* 1999) The main disadvantages of Mg-based alloys as hydrogen storage materials are the high temperature of hydrogen discharge, slow desorption

kinetics, and easy making of a close oxide layer (Barkhordarian, *et al.* 2004). The kinetics is considered to be limited by several factors, such as a highly stable surface hydride film blocking the diffusion of atomic hydrogen into the magnesium, but no consensus has been reached. For pure Mg, diffusion is not the limiting step initially because no material has been reacted and there are sufficient active sites available, but chemisorption is the slowest step (Sakintuna, *et al.* 2007). As the reaction progresses, hydrogen diffusion takes place and the hydride layer grows, producing a nearly impermeable layer. Diffusion through this hydride layer becomes the rate-limiting step in the

hydride formation process (Barkhordarian, *et al.* 2004).

Hydrogen adsorption and desorption on Mg thin films have been extensively studied over the last decade (Zhou, 2006). Experimentally, Plummer and Sprunger (Sprunger, *et al.* 1991, and Sprunger, 1994) have used electron energy loss spectroscopy (EELS) and thermal desorption spectrometry (TDS) to study the interaction between both of atomic and molecular hydrogen and Mg, finding a strongly chemisorbed surface hydride. The diffusional properties of hydrogen in magnesium have been investigated by Renner and Grabke (1978), who determined a diffusion constant (D) of $4.0 \times 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$ at 300 K. Using neutron scattering, Töpler *et al.* (1982) found H-diffusion in MgH_2 to be three orders of magnitude lower than that in Mg (at 350 K). Jacobson *et al.* (2002) have used spin-polarized electron-density calculations to determine the diffusion of H on Mg (0001) from surface to bulk with a barrier of 0.5 eV.

From the above review, we can conclude that both of theories and experiments show discrepancies for the process of hydrogen molecule and atom adsorption on a magnesium surface. Meanwhile, there is also considerable theoretical researches which focus on the

effect of desorption property of hydrogen storage materials with different adulterated transition-state elements (Vajeeston *et al.* 2002, 2006, and Song, 2004). Only a few investigations of the diffusion of H atom on magnesium have been carried out. In this study, we report results of calculations on the energetics of Mg (0001) surface and H atom diffusion on the Mg(0001) surface and further to provide the microscopic mechanism and theoretical data.

Computational Methods

All the calculations were performed with *ab initio* DFT implementing generalized gradient approximation (GGA) using the basis set 6-31G for Mg and H. In order to determine the equilibrium bulk parameters of Mg, we have uniformly scaled the lattice vectors and calculated the energy as function of the unit cell volume. The lattice constants used are $a = 0.319 \text{ nm}$ and $c/a = 1.62 \text{ nm}$. The Mg (0001) surface was modeled by using a surface unit cell with 2 layers of Mg atoms. To determine the adsorption and diffusion energy, the variation coordinate reaction is used.

RESULTS AND DISCUSSION

Bulk property

In order to determine the equilibrium bulk parameters of Mg, we

have uniformly scaled the lattice vectors and calculated the energy as function of the unit cell volume. The data were then fitted to experimental data, which predicted lattice constants of $a = 0.319$ nm and $c/a = 1.62$ nm. These values are in good agreement with the corresponding experimental values of $a = 0.321$ nm and $c/a = 1.624$ (Amonenko, *et al.* 1962). The cohesive energy (E_{coh}) was calculated as a difference between the total energy per atom in a bulk crystal and the total energy of a free atom. The calculated E_{coh} was -1.05 eV·atom $^{-1}$, which is in good agreement with the corresponding experimental value of -1.48 eV·atom $^{-1}$ (Ashcroft, *et al.* 1976).

Adsorption energy of Mg(0001) surface

Next, we calculate the adsorption energies for the on-top, hcp, fcc, and bridge positions. The adsorption energies for atomic hydrogen are defined as:

$$E_{\text{ads-H/Mg(0001)}} = E_{\text{H/Mg(0001)}} - (E_{\text{Mg(0001)}} + E_{\text{H}})$$

where $E_{\text{ads-H/Mg(0001)}}$ is the adsorption energy, $E_{\text{H/Mg(0001)}}$ is the total energy of the system with adsorbed H, $E_{\text{Mg(0001)}}$ is the total energy of the Mg(0001) slab without adsorbed species, and E_{H} is the total energy of free H. With this definition, negative values of $E_{\text{ads-H/Mg(0001)}}$ denote

adsorption that is more stable than the corresponding clean surface and the free atom H. Zero-point energy correction is not included in these results. As a result, the calculated adsorption energies for H on Mg (0001) surface are presented in Table 1.

Table 1. Adsorption energy (E_{ads}), bond length (l) for different adsorption sites considered for H atom on Mg(0001) surface

Position	$l_{\text{Mg(0001)-H}}$ (nm)	E_{ads} (eV)
On top	0.176	-1.893
hcp	0.198	-2.120
fcc	0.195	-2.176
bridge	0.194	-2.414

Table 1 shows that H adsorption energy on top position more positive (-1.89 eV) than fcc, hcp and bridge position. Based on this result we can predict that H atom that adsorbed on top-site appeared to be unstable. It is agreement with the experiment fact which remarkable resemblance to the system of Na on Magnesium surface (Kiejna, *et al.* 2004). The H adsorption energy on fcc, hcp and bridge position was founded larger then on top position. This shows that H adsorption on these positions more stable than on top position. The reason for this adsorption stability is caused by the strong interaction between the H-s and Mg-p orbitals (Lia, *et al.* 2007).

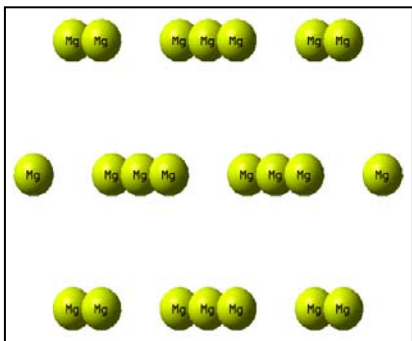


Figure 1(a) Model Mg (0001) with 22 Mg atoms

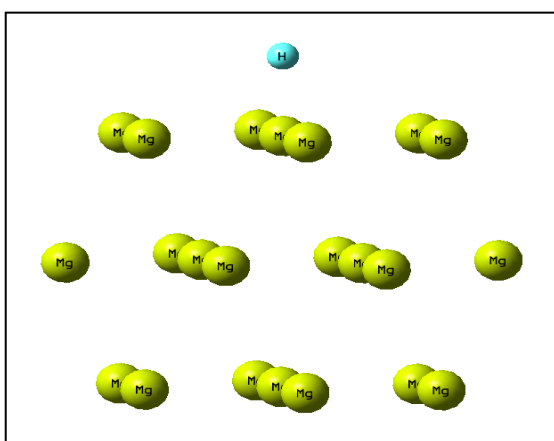


Figure 1(b) Model H adsorption on Mg (0001) surface

Diffusion of H on Mg (0001) surface

With the energetics of the H adsorption process on a Mg (0001) surface at hand, we proceeded to study H diffusion on the Mg(0001) surface and into the subsurface. In our calculation, only one hydrogen atom is left in the unit cell. It is initially placed in an on-top site and finally in a fcc-substrate site. The adsorption energies for atomic hydrogen are defined as:

$$E_{\text{diffusion}} = E_{\text{H/Mg(0001)-diffusion}} - (E_{\text{Mg(0001)-diffusion}} + E_{\text{H-diffusion}})$$

The calculated diffusion pathway from the on-top site to the fcc site on the surface is plotted in Fig.2 (a). The previous PES shows that the top sites have the lower energy. Meanwhile, diffusion results show that there are any energy barriers from the top site to the hcp site. The activation energy from the top site to the fcc site is 0,656 eV, which is in agreement with the previous theoretical values obtained by Jacobson *et al.* (2002) (0.15 eV) and Vegge (2004) (0.14 eV).

The calculated diffusion pathway from fcc to hcp is plotted in Fig. 2 (b). Following the reaction coordinate, the corresponding different energy from the fcc-surface to the fcc-inner is 0.60 eV, which is in agreement with the values obtained by Vegge [21] (0.53 eV) and Jacobson *et al.* (Jacobson, *et al.* 2002) (0.50 eV). Hence, we believe that surface effects affect the diffusion of H from surface to bulk. However, Vegge considered that surface effects were minimal. It is indicating that the range of surface effects is restricted within topmost two layers of Mg (0001) surface.

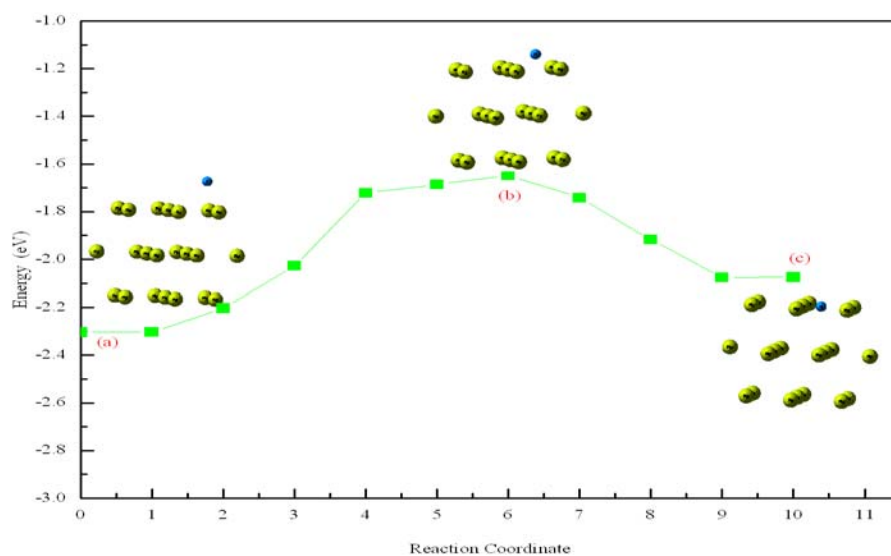


Figure 2(a) The minimum-energy path for H diffusion from top to fcc on surface (a) initial state (b) transition state (c) final state

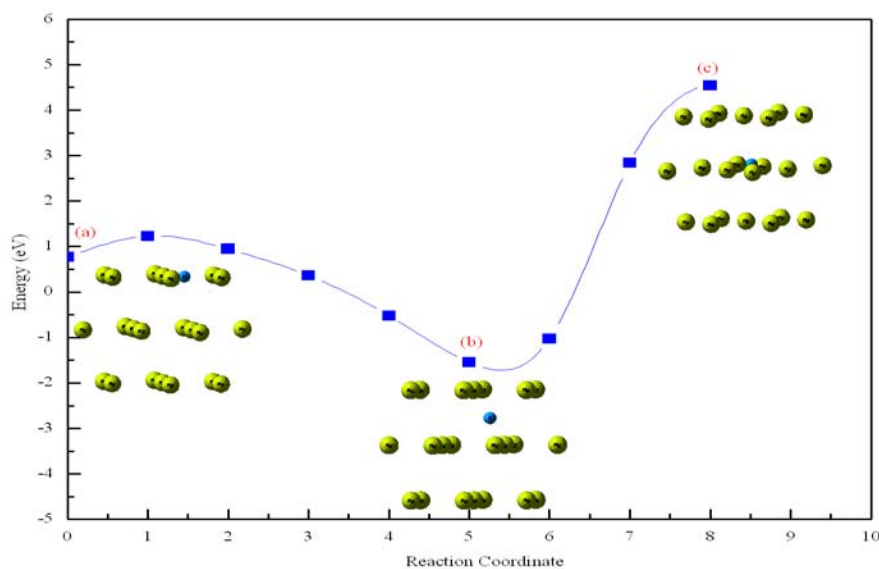


Figure 2 (b) the minimum-energy path for H diffusion from fcc-surface to fcc-inner (a) initial state (b) transition state (c) final state

Conclusions

We presented the results of first-principle total energy calculations for the adsorption properties and diffusion properties, respectively. The hydrogen adsorption process on Mg(0001), the higher adsorption energy found on bridge position.

This shows that H adsorption on these positions more stable than on top position. The reason for stabilisation adsorption is caused by the strong interaction between the H-s and Mg-p orbitals.

Based on the calculation of diffusion energy results, was known that there are any energy barriers from the top site to the hcp site. The activation energy from the top site to the fcc site is 0,656 eV, while the different energy from the fcc-surface to the fcc-inner is 0.60 eV.

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