EFFECT OF SCANDIUM ON HIDROGEN DISSOCIATION ENERGY AT MAGNESIUM SURFACE: *AB INITIO* DFT STUDY

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ABSTRACT

The dissociative chemisorption of hydrogen on both pure and Sc-incorporated Mg(0001) surfaces have been studied by ab initio density functional theory (DFT) calculation. The calculated dissociation energy of hydrogen molecule on a pure Mg(0001) surface (1.200 eV) is in good agreement with comparable theoretical studies. For the Sc-incorporated Mg(0001) surface, the activated barrier decreases to 0.780 eV due to the strong interaction between the molecular orbital of hydrogen and the d metal state of Sc. This could explain the experimentally observed improvement in absorption kinetics of hydrogen when transition metals have been introduced into the magnesium materials.

Keywords: *Dissociation, Adsorption, Chemisorptions, DFT, Magnesium*

INTRODUCTION

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 [1]. 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 [2-3]. 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 [4]. The kinetics is considered to be limited by several factors, such as the poor dissociative chemisorptions of the H_2 molecule and a highly stable surface hydride film blocking the diffusion of atomic hydrogen into the magnesium [5].

Experimentally, many studies have been devoted to the catalytic effect on hydrogen adsorption of mixing transition metals into Mg hydride powder during ball milling [6-9]. The transition metals have been considered to act as catalysts for accelerating hydrogen sorption that is enhancing the breaking up of molecular hydrogen into adsorbed atoms [10]. However, the catalytic mechanism involved when these additives are used is still not clearly established. Theoretically, *ab initio* density functional theory (DFT) calculations have shown considerable predictive power for catalysis [11]. Much insight can be gained from first-principle modeling for the process of designing alloy catalysts [12-13]. There have been some theoretical calculations to study the role of transition metals in magnesium hydrides, focusing mainly on substituting one Mg atom with a Ti, Ni, or Fe atom in the bulk [14-16].

The theoretical groups have shown recently that transition metal atoms such as Sc and Ti coated on carbon fullerenes and nanotubes can bind molecular hydrogen with gravimetric density of up to 8 wt % [17-18]. This can be understood by the facts that (i) Ti or Sc is first ionized due to charge transfer between carbon and Ti (Sc) and (ii) the transition metal cations then polarizes molecular H_2. The situation that ensues upon incorporation of Sc into the Mg surface is very interesting as it could help to further clarify the role of transition metal catalysts for hydrogen sorption in relation to recent experimental findings.

In this paper, the interactions of a series of hydrogen with Sc-incorporated Mg(0001) surfaces were studied by *ab initio* DFT calculations. The energetic for the dissociation of hydrogen on Mg(0001) and Sc-incorporated Mg(0001) surface was systematically investigated. The last section draws relevant conclusions.

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 and $LANL_2DZ$ for Sc. In order to determine the equilibrium bulk parameters of Mg, we have uniformly scaled the lattice vectors and calculated the energy as function of

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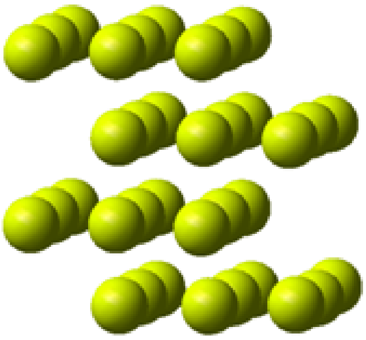

Fig 1. Model Mg(0001) with 22 Mg atoms

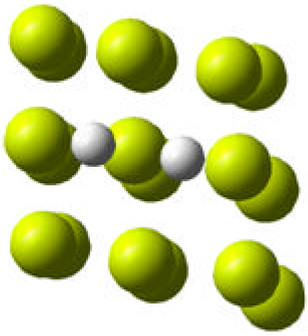

Fig 2. H_2 on Mg(0001) surface

Table 1 The H−H distance, dissociation height (h_d), and relative energy (E_r) of dissociation process of H_2 on Mg(0001) surface

Reaction coordinate	H−H distance (Å)	$l_{Mg(0001)-H2}$ (Å)	E_r (eV)
0	0.748	6.306	0.000
1	0.747	4.986	0.169
2	0.748	4.967	0.128
3	0.750	4.150	0.121
4	0.751	3.386	0.012
5	0.770	2.666	0.181
6	0.779	1.882	0.737
7	1.179	1.266	1.200
8	2.274	0.770	-2.512
9	3.209	0.651	-5.616

the unit cell volume. The lattice constants used are a = 0.319 nm and c/a = 1.62 nm. The Sc-incorporated Mg (0001) surface was modeled by using a surface unit cell with 2 layers of Mg atoms. To determine dissociation barriers energy, the variation coordinate reaction is used.

RESULT 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 (Fig. 1). These values are in good agreement with the corresponding experimental values of a = 0.321 nm and c/a = 1.624 [19]. 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} [20].

Dissociation Energy H_2 on Mg(0001) Surface

We now discuss the dissociation pathways for H_2 dissociation on the Mg(0001) surface. Initial states (IS) and final states (FS) are optimized firstly from candidate geometries. The results of the calculated relative energy (E_r) of dissociation process of H_2 on Mg(0001) surface are presented in Table 1. The initial physisorbed state is observed in which the H−H bond length is calculated to be 0.0748 nm (Fig. 2), which is the same as the DFT optimized gas-phase bond length [21]. It should be noticed that no chemisorbed molecular state was observed in our calculation, which is in agreement with the results of Vegge [22]. In order to further validate this conclusion, we calculate the adsorption of H_2 molecule on Mg(0001) surface with different heights. No charge transfer is obtained, which proves our conclusion arrived above. The calculated H_2 dissociation on Mg(0001) surface pathway is plotted in Fig. 3

Following the reaction coordinate, the transition state for dissociation is found to be in the bridge site, which is in agreement with the theoretical and experimental results [23-25] with a longer bond length of 1.179 Å. A dissociation activation barrier of 1.200 eV was found to be consistent with the results of Vegge

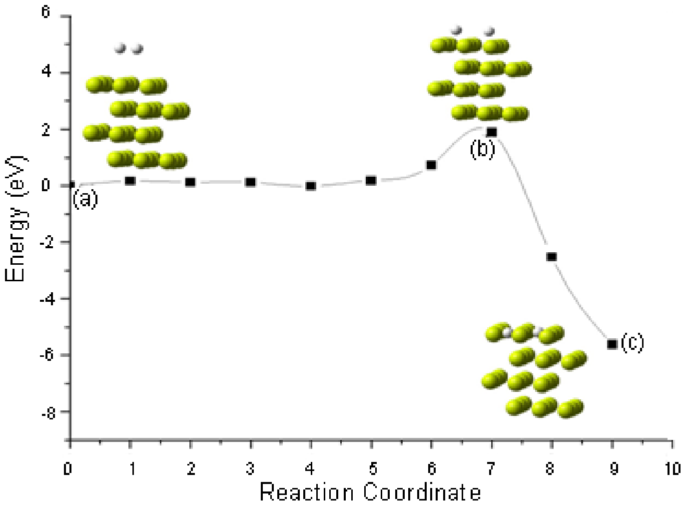

Fig 3. The minimum-energy path (MEP) for H_2 dissociation on Mg(0001) surface (a) Initial state, (b) transition state, (c) final state

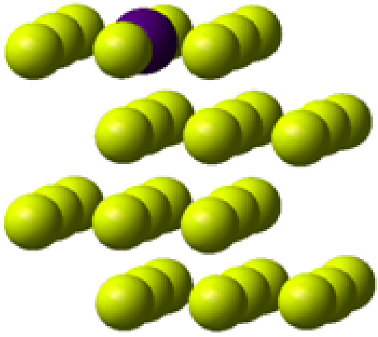

Fig 4. Sc-incorporated Mg(0001)

[22] (1.15 eV) and Du [24] (1.05 eV), but much higher than the result calculated by Nørskov [53] (0.5 eV) and the experiment result of Johansson et al. [26] (0.6−0.9 eV). The difference can perhaps be explained by the presence of step sites that have a lower barrier for dissociation than terrace sites. Such effects have been observed for several diatomic dissociation reactions [27-28].

Meanwhile, when H_2 is dissociated into two fcc-site adsorption positions, the relevant barrier for recombination in connection with desorption is 1.09 eV, which is in good agreement with the experimental TDS result obtained by Sprunger and Plummer [25,29], who found that E_{des} = 1.0 eV and this is indicating that there are strong interactions between Mg and H. Our results show that dissociation and desorption are the rate-limiting steps in the process of storing hydrogen on the surface of pure magnesium.

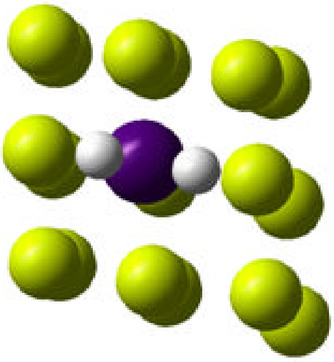

Fig 5. H_2 on Mg (0001)+Sc surface

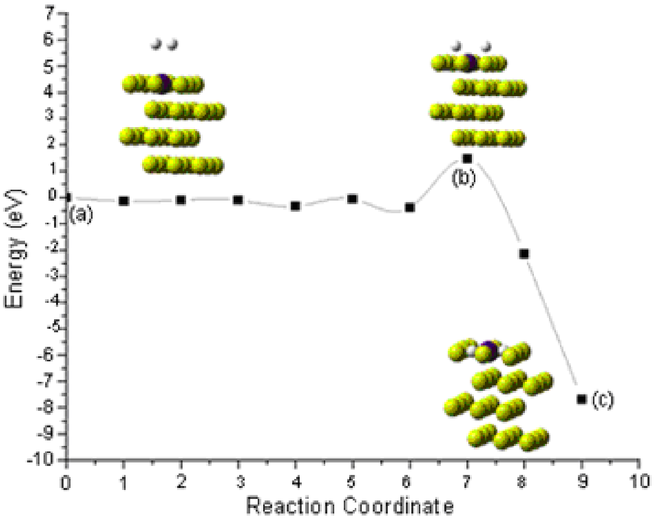

Fig 6. The minimum-energy path (MEP) for H_2 dissociation on Mg(0001) surface (a) Initial state, (b) transition state, (c) final state

Dissociation Energy H_2 on Mg(0001)+Sc Surface

The Sc-incorporated Mg (0001) we design surface by substituting one surface Mg atom with a Sc atom ($Mg_{22}Sc$) [30]. This process involves the creation of a Mg vacancy on Mg(0001) surface in the first step and subsequent occupation of the vacancy by a Sc atom (Fig. 4). The formation energy is calculated to be -4.01 eV, which indicates that the Sc-incorporated Mg(0001) surface is thermodynamically stable.

There are reasons we choose a model based on substituting one Mg atom with a Sc atom is 2-layer. First, the substituted Sc at Mg(0001) surface should occur commonly since the Mg vacancy will not be difficult to create during the high-energy ball milling experiment and may then easily be filled by a Sc atom. Second, the results can be used to directly compare to the existing results for H_2 dissociation on the pure Mg(0001) surface and it will also be convenient for subsequent study of the diffusion of atomic H into bulk.

Subsequently, we study the interaction of a hydrogen molecule with the Sc-doped Mg(0001) surface, wherein two dissociated H atoms are already bound to the Ti atom (i.e., $Mg_{21}ScH_2$, shown in Fig. 5). The initial state (IS) composed of one hydrogen molecule at a distance of 6,306 Å from $Mg_{21}TiH_2$ surface. The length of Ti-H bonds increased by about 0.024 Å compared with $Mg_{22}TiH_2$. Result of the hydrogen dissociative calculation at Mg(0001)+Sc shown on the minimum-energy path (MEP) for H_2 dissociation on Mg(0001)+Sc surface (Fig. 6).

Fig. 6 presents the energy profile for this complex reaction and displays a series of configurations along the reaction coordinate. On the Sc-doped Mg(0001) surface, dissociation of the H_2 has an activation barrier (0.780 eV) lower then pure Mg(0001), but higher than the result calculated by Du on Mg(0001)+Ti (0,145 eV) [31]. The different influenced by condition 3d orbital bonding Ti which have more electron than bonding orbital Sc.

Based on this result it can be explained that scandium will decrease the activation energy barrier of H_2 on Mg(0001) surface. The decrease in activation energy barrier can make chemisorptions state on adsorption process more easily occur because H_2 will be rapidly dissociated after overcome an activation energy barrier. Ability of the scandium to decrease activation barrier energy dissociation can be explained by back donation process. When the Mg(0001)–H_2 bond is activated by Sc, the electrons of the bonding orbital of the H-H are donated to the unoccupied orbital of the Sc (*donation*), and subsequently, the electrons of the occupied orbital of the Sc are back donated to the antibonding orbital of the H-H (*back donation*). This largely contributes to the donation of the electrons from the bonding orbital of H-H, resulting in the easier H-H dissociation [32].

CONCLUSION

Ab initio DFT calculation were performed to study adsorption hydrogen gas on a Sc–doped on Mg(0001) surface. We found that adsorption energy H on surface Mg(0001) increase when it is doped by Sc. Furthermore, we found that H_2 will be dissociated on top of Sc-doped Mg(0001) with lower activation barrier (0.780 eV) than on clean Mg(0001) surface. This phenomenom is attribute to the polarisation of H_2 by the Sc atom that results from the prior chemisorption events.

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