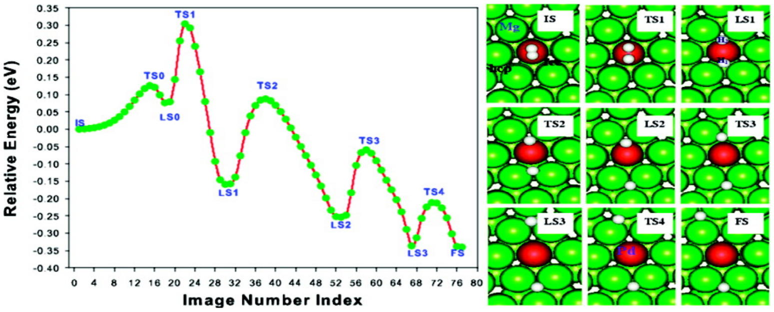
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

Hydrogen Spillover Mechanism on a Pd-Doped Mg Surface as Revealed by ab initio Density Functional Calculation

A. J. Du, Sean C. Smith, X. D. Yao, and G. Q. Lu

J. Am. Chem. Soc., **2007**, 129 (33), 10201-10204• DOI: 10.1021/ja0722776 • Publication Date (Web): 31 July 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S

A R T I C L E S

Hydrogen Spillover Mechanism on a Pd-Doped Mg Surface as Revealed by ab initio Density Functional Calculation

A. J. Du,[†,‡] Sean C. Smith,*[,†,‡] X. D. Yao,[‡] and G. Q. Lu[‡]

Contribution from the Centre for Computational Molecular Science and ARC Centre for Functional Nanomaterials, Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, QLD 4072, Brisbane, Australia

Received April 1, 2007; Revised Manuscript Received June 11, 2007; E-mail: s.smith@uq.edu.au; a.du@uq.edu.au

Abstract: The hydrogenation kinetics of Mg is slow, impeding its application for mobile hydrogen storage. We demonstrate by ab initio density functional theory (DFT) calculations that the reaction path can be greatly modified by adding transition metal catalysts. Contrasting with Ti doping, a Pd dopant will result in a very small activation barrier for *both* dissociation of molecular hydrogen *and* diffusion of atomic H on the Mg surface. This new computational finding supports—for the first time by ab initio simulation—the proposed hydrogen spillover mechanism for rationalizing experimentally observed fast hydrogenation kinetics for Pd-capped Mg materials.

Introduction

To develop efficient and safe storage materials for hydrogen is becoming increasingly important for promoting the “hydrogen economy”. Magnesium and its alloys have been considered among the most promising candidates for automotive applications due to its high capacity in the stoichiometric limit (7.6 wt %) and low cost.[1,2] Unfortunately, the application is primarily limited by the hydrogenation reaction temperature and slow kinetics. One of the possible reasons is that the hydrogen molecules do not readily dissociate on a Mg surface.[3,4] Experimentally, many studies have been devoted to the catalytic effect on hydrogen adsorption of mixing transition metals into Mg hydride powder during ball milling.[5−8] The transition metals, such as Ti, Nb, and V, etc., are believed to act as catalysts for enhancing the breaking up of the molecular hydrogen into adsorbed atoms, albeit at the cost of a partial reduction of weight-percent capacity.[9] Recently, a palladium-capped Mg thin film was found to hydrogenate very quickly even at room temperature.[10−12] However, the catalytic mechanism involved when using Pd additives was not clear.

The activation barrier for the dissociative chemisorption of H_2 onto a clean magnesium surface is known to be very high (more than 1.0 eV).[13−15] We have recently studied computationally the catalytic effects of Ti on dissociation of hydrogen on Mg surface.[15] However, the subsequent diffusion of the dissociated H atoms away from the metal site was not elaborated. To provide a full rationalization, herein we have performed state-of-art ab initio DFT calculations to investigate both the dissociation of H_2 and the subsequent diffusion of atomic H away from the metal sites on Ti- and Pd-doped Mg (0001) surfaces. Remarkably, the Pd dopant is found to modify the minimum energy pathway (MEP) greatly for both the dissociation of H_2 and the diffusion of atomic H on the Mg (0001) surface. This supports the proposal of a hydrogen spillover mechanism on the Pd-doped Mg (0001) surface close to room temperature, potentially explaining the underlying mechanism for Pd catalysis as observed in recent experiments.[10,12] In the next section, we outline our computational method. The Results and Discussion section presents our calculated results for the dissociation of the hydrogen molecule and diffusion of atomic H on Ti- or Pd-doped Mg (00001) surface. The last section is devoted to the conclusions.

Computational Methods

All of the calculations were performed using the plane-wave basis VASP code[16,17] implementing the generalized gradient approximation (GGA) of PBE exchange correlation functional[18] and the projector augmented wave method.[19,20] The lattice constant of bulk Mg was calculated to be 3.191 Å, which was only 0.5% in error compared with

---

[†] Centre for Computational Molecular Science.

[‡] ARC Centre for Functional Nanomaterials.

(1) Schlapbach, L.; Zuttel, A. *Nature* **2001**, *414*, 23.
(2) Liang, G.; Huot, J.; Van Neste, A.; Schulz, R. *J. Alloys Compd.* **1999**, *292*, 247.
(3) Zaluska, A.; Zaluski, L.; Strom-Olsen, J. O. *Appl. Phys. A: Mater. Sci. Process.* **2001**, *72*, 157.
(4) Von Zeppelin, F.; Reule, H.; Hirscher, M. *J. Alloys Compd.* **2002**, *330−332*, 723.
(5) Shang, C. X.; Guo, Z. X. *J. Power Source* **2004**, *129*, 73.
(6) Hanada, N.; Ichikawa, T.; Fujii, H. *J. Phys. Chem. B* **2005**, *109*, 7188.
(7) Rivoirard, S.; de Rango, P.; Fruchart, D.; Charbonnier, J.; Vempaire, D. *J. Alloys Compd.* **2003**, *356−357*, 622.
(8) Liang, G. *J. Alloys Compd.* **2004**, *370*, 123.
(9) Schimmel, H. G.; Huot, J.; Chapon, L. C.; Tichelaar, F. D.; Mulder, F. M. *J. Am. Chem. Soc.* **2005**, *127*, 14348.
(10) Yoshimura, K.; Yamada, Y.; Okada, M. *Surf. Sci.* **2004**, *566−568*, 751.
(11) Shalaan, E.; Schmitt, H. *Surf. Sci.* **2006**, *600*, 3650.
(12) Berlouis, L. E. A.; Honnor, P.; Hall, P. J.; Morris, S.; Dodd, S. B. *J. Mater. Sci.* **2006**, *41*, 6403.
(13) Vegge, T. *Phys. Rev. B* **2004**, *70*, 035412.
(14) Norskov, J. K.; Houmoller, A. M. *Phys. Rev. Lett.* **1981**, *46*, 257.
(15) Du, A. J.; Smith, S. C.; Yao, X. D.; Lu, G. Q. *J. Phys. Chem. B* **2005**, *109*, 18037.
(16) Kresse, G.; Furthmuller, J. *Comput. Mater. Sci* **1996**, *6*, 15.
(17) Kresse, G.; Furthmuller, J. *Phys. Rev. B* **1996**, *54*, 11169.
(18) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
(19) Blochl, P. E. *Phys. Rev. B* **1994**, *50*, 17953.
(20) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.

10.1021/ja0722776 CCC: $37.00 © 2007 American Chemical Society

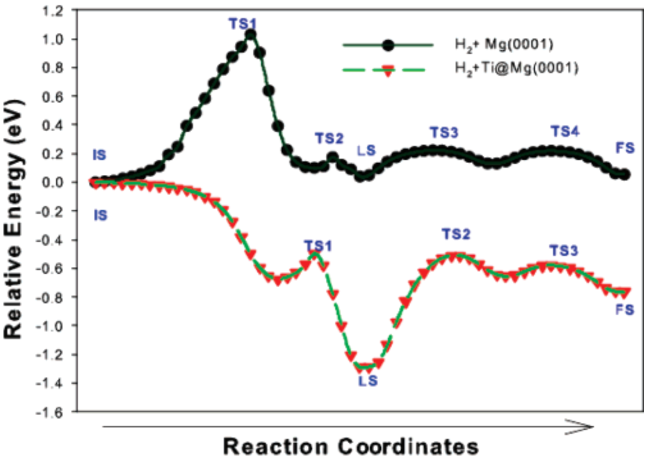


Figure 1. The energy profiles for the dissociation of H_2 and diffusion of atomic H on pure the Mg (0001) surface and the Ti-doped Mg (0001) surface. Here IS, TS, LS, and FS represent the initial state, transitional state, local minimum state, and final state, respectively.

the experimental value. The Ti- or Pd-incorporated Mg (0001) surface was modeled by using a (4 × 4) surface unit cell with five layers of Mg atoms. Only γ point was used for the Brillouin-zone sampling due to the large cell used, and the cutoff energy for plane waves was 312.5 eV. The vacuum space was up to 16 Å, which is large enough to guarantee a sufficient separation between periodic images. To determine dissociation barriers and MEP, the nudged elastic band (NEB) method was used.[21,22] This method involves optimizing a chain of images that connect the reactant and product state. Each image is only allowed to move into the direction perpendicular to the hyper-tangent. Hence the energy is minimized in all directions except for the direction of the reaction path. A damped molecular dynamics was used to relax ions until the force in each image is less than 0.02 eV/Å.

Results and Discussion

Figure 1 presents the energy profiles for the dissociation of H_2 onto two fcc sites and diffusion of atomic H between two fcc sites on the pure Mg (0001) surface and the Ti-doped Mg (0001) surface. Clearly, the effective barrier for the dissociation of a hydrogen molecule on the Mg (0001) surface (IS→TS1→TS2→LS) is considerable (E_a = 1.05 eV). The diffusion of atomic H from one fcc to another fcc site (LS→TS3→TS4→FS) is predicted to be around 0.182 eV, which indicates a fast migration at room temperature. However, on the Ti-incorporated surface, the hydrogen molecule can dissociate on top of the Ti atom spontaneously with an activation barrier of 0.103 eV only. However, one should note that the LS (TiH_2-like species) is very stable compared to the IS (see Figure 1). This may suggest a significant diffusion barrier of atom H away from the surface-incorporated Ti site. A good catalyst should not bind hydrogen strongly. As shown in Figure 1, diffusion away from the Ti site is found to be strongly unfavorable (endothermic, 0.53 eV) and the activation barrier is as high as 0.77 eV. This implies that the rate-determining step has shifted in the presence of the Ti dopant from the molecular dissociation step to the diffusion step, but still there remains a significant activation barrier for the overall process.

To explore the apparent catalytic role of Pd on the hydrogenation of Mg, a reasonable model should be a Pd-incorporated Mg (0001) surface (Pd@Mg(0001)), in which one surface Mg atom was substituted with a Pd atom. The energy for formation of single Mg vacancy on a Mg (0001) surface is calculated to be 0.86 eV. Mg vacancies may not be difficult to create and then be easily filled by a Pd atom during a high-energy ball milling and DC magnetron sputtering process. Starting from an initial guess, wherein one surface Mg is replaced by Pd, full structural relaxation shows the position of the Pd atom changing slightly (0.45 Å, downward) along the z-axis. The formation energy (E_f) of the Pd@Mg(0001) surface (coverage $\theta = 1/16$) was calculated by the following equation[23]

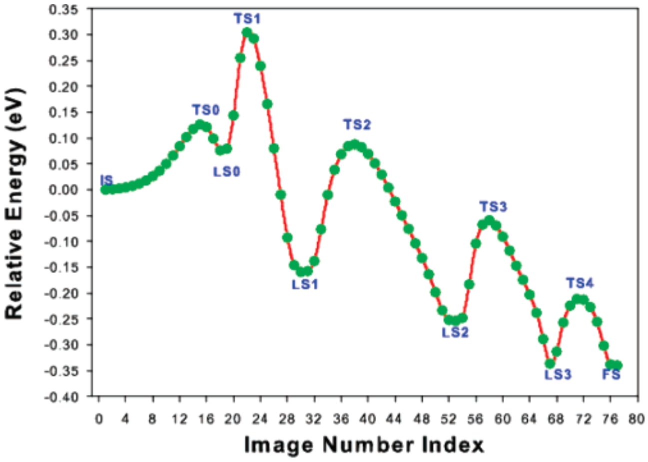


Figure 2. Similar to Figure 1 but for the energy profile of the dissociation of H_2 and diffusion of first and second atomic H on the Pd-doped Mg (0001) surface.

$$E_f = E_{Pd/Mg(0001)} + E_{Mg} - E_{Pd-atom} - E_{Mg(0001)}$$

where $E_{Pd/Mg(0001)}$, E_{Mg}, $E_{Pd-atom}$, and $E_{Mg(0001)}$ represent the total energy of the relaxed Pd-incorporated Mg (0001) surface, the bulk Mg atom, the isolated Pd atom, and the clean Mg (0001) slab, respectively. The formation energy is up to −4.62 eV, which indicates high thermodynamic stability.

The activation barrier for the dissociation of a hydrogen molecule on the Pd@Mg(0001) surface was calculated first utilizing the NEB method. We set one H_2 molecule a large distance from the relaxed surface structure as the IS. In the relaxed FS, the positions of two H atoms were located around 0.75 Å from the surface with a Pd−H distance of 1.745 Å. Figure 2 presents the energy profile along MEP for the dissociation of H_2 on the Pd@Mg(0001) surface. Compared to the pure Mg surface, the effective barrier for the dissociation of molecule H_2 is decreased from 1.05 to 0.305 eV. It is about 10−12 times the thermal energy at room temperature. On the basis of the Arrhenius equation, the dissociation event on the Pd@Mg(0001) surface should be fast near room temperature. A series of configurations (IS, TS1, and LS1) along the MEP for the dissociation of hydrogen molecule are also shown in Figure 4. The hydrogen molecule first moves toward the Pd atom and dissociates nearly on the top of it, around 1.32 Å from the Mg surface. This can be understood in terms of the strong interaction between the molecular orbital of H_2 and the metal d orbitals of Pd.[24,25] Figure 3 presents a three-dimensional isosurface plot for charge density differences at the transition state

---

(21) Henkelman, G.; Jonsson, H. *J. Chem. Phys.* **2000**, *113*, 9978.
(22) Henkelman, G.; Uberuaga, B. P.; Jonsson, H. *J. Chem. Phys.* **2000**, *113*, 9901.
(23) Kiejna, A. *Phys. Rev. B* **2003**, *68*, 235405.
(24) Kubas, G. J. *Science* **2006**, *314*, 1096.
(25) Nobuhara, K.; Kasai, H.; Dino, W. A.; Nakanishi, H. *Surf. Sci.* **2004**, *566−568*, 703.

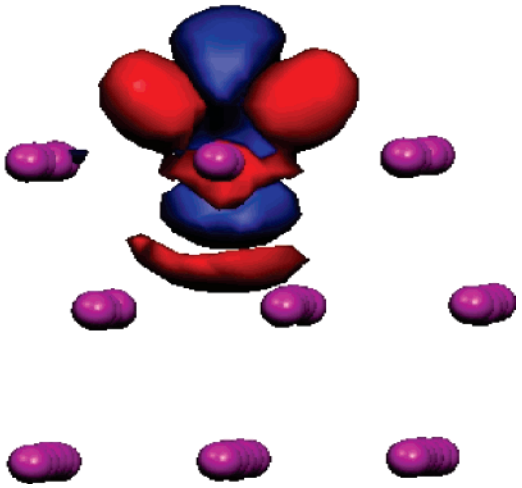


Figure 3. A 3D iso-surface plot for charge density difference of the transition state (TS1 shown in Figure 2) during the dissociation of H_2 on a Pd@Mg(0001) surface. The magenta balls represent Mg atoms. Red and blue surface represents charge accumulation and depletion in space, respectively.

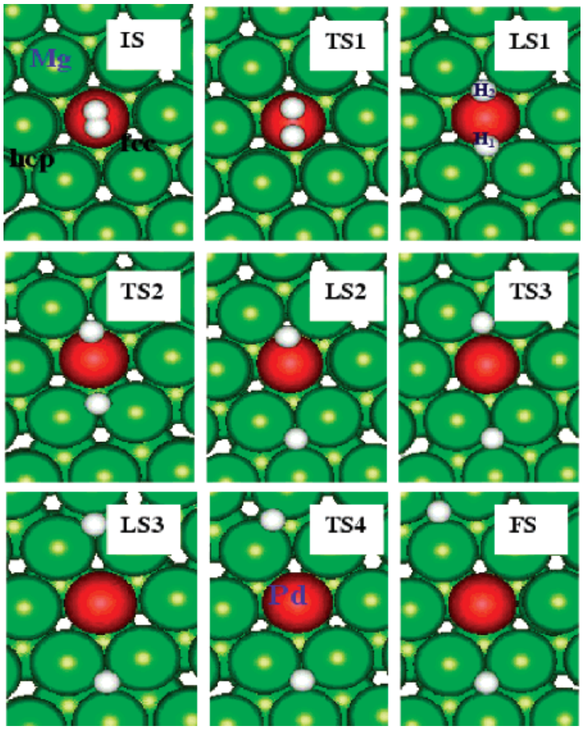


Figure 4. Corresponding configurations (IS, TS, LS, and FS) as shown in Figure 2. The green, red, and small white balls represent Mg, Pd, and H atoms, respectively.

(TS1 shown in Figure 2) during the dissociation of H_2 on a Pd@Mg(0001) surface. There is a charge donation from the σ orbital of H_2 to the d orbital of Pd first. Then the binding is stabilized by back-donation of electrons from the filled orbital of Pd to the antibonding orbital (σ^*) of the bound H_2, and finally two Pd−H bonds are formed.[24−2626]

As above, we now explore the diffusion of dissociated H atoms on the Pd-doped Mg (001) surface. The implementation details for obtaining the MEP are similar to those used in the former calculation. Path I (LS1→TS2→LS2) and Path II (LS2→TS3→LS3→TS4→FS), which indicate the diffusion of first and second atomic H to adjacent fcc sites, are also plotted in Figure 2. The corresponding configurations are shown in Figure 4. The two transition states (TS3 and TS4 shown in Figure 2) for the diffusion of the second atomic H are actually due to a two-step diffusion, namely, a move to an hcp site first and then to the neighboring fcc site. Clearly, the diffusion of the two dissociated H atoms on the Pd@Mg(0001) surface is energetically favorable, with exothermicities of −0.094 and −0.086 eV, respectively. The effective activation barriers for the diffusion of first and second atomic H atoms are calculated to be 0.247 and 0.195 eV, respectively. This indicates a fast migration of atomic H on Pd@Mg(0001) surface, even at room temperature.

Table 1. Comparison of the Dissociation of Hydrogen Molecule and the Diffusion of Atomic H on Mg (0001), Ti-Doped Mg (0001), and Pd-Doped Mg (0001) Surfaces[a]

systems		Mg (0001)	Ti@Mg(0001)	Pd@Mg(0001)
dissociation of	E_r	0.023	−1.289	−0.160
mol. H_2	E_a	1.051	0.103	0.305
diffusion of	E_r	0.015	0.525	−0.094
first H atom	E_a	0.182	0.780	0.247
diffusion of	E_r			−0.086
second H atom	E_a			0.195

[a] Units are all in electronvolts; E_r and E_a represent reaction enthalpy and activation energy (at 0 K), respectively.

In Table 1, we summarize the results for the dissociation of H_2 and diffusion of atomic H on pure, Ti-doped and Pd-doped Mg (0001) surfaces. We have found that the MEP involving the dissociation of H_2 and diffusion of atomic H atoms on a Mg surface can be greatly modified by the incorporation of a transition metal catalyst. Contrasting with the Ti-doped Mg (0001) surface, a Pd dopant will result in a small activation barrier *both* for dissociation of hydrogen molecule *and* migration of H atoms on the Mg surface. This finding supports the proposal of a hydrogen spillover mechanism on the Pd@Mg-(0001) surface, a phenomenon that has been proposed previously in order to explain experimental observations over supported metal catalyst on nanostructured carbon materials and metallo-organic frameworks.[27,2827−28] The present results not only help to clarify the experimentally observed fast hydrogenation kinetics for Pd-capped Mg materials but may also help to design new types of hydrogen storage materials for practical applications in the auto industry.

Conclusions

In summary, we have performed ab initio DFT calculations to study the effect of dopant (Ti and Pd) on the dissociation of H_2 on a Mg (0001) surface. We found that the reaction path can be greatly modified by adding transition metal dopant. In remarkable contrast with Ti doping, a Pd dopant will result in a very small activation barrier for *both* dissociation of molecular hydrogen *and* diffusion of atomic H on the Mg surface. This new computational finding supports—for the first time by ab initio simulation—the proposed hydrogen spillover mechanism for rationalizing experimentally observed fast hydrogenation kinetics for Pd-capped Mg materials.

Acknowledgment. We acknowledge generous grants of high-performance computer time from both the Computational

---

(26) Kubas, G. J. *J. Organomet. Chem.* **2001**, *635*, 37.

(27) Li, Y. W.; Yang, R. T. *J. Am. Chem. Soc.* **2006**, *128*, 8136.

(28) Lueking, A.; Yang, R. T. *J. Catal.* **2002**, *206*, 165.

Molecular Science cluster computing facility at The University of Queensland and the Australian Partnership for Advanced Computing (APAC) National Facility. The authors also greatly appreciate the financial support of the Australian Research Council and The University of Queensland through the ARC Centre for Functional Nanomaterials.

JA0722776