

The Role of Ti as a Catalyst for the Dissociation of Hydrogen on a Mg(0001) Surface

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In this paper, the dissociative chemisorption of hydrogen on both pure and Ti-incorporated Mg(0001) surfaces are studied by ab initio density functional theory (DFT) calculations. The calculated dissociation barrier of hydrogen molecule on a pure Mg(0001) surface (1.05 eV) is in good agreement with comparable theoretical studies. For the Ti-incorporated Mg(0001) surface, the activated barrier decreases to 0.103 eV due to the strong interaction between the molecular orbital of hydrogen and the d metal state of Ti. This could explain the experimentally observed improvement in absorption kinetics of hydrogen when transition metals have been introduced into the magnesium materials.

I. Introduction

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 its low cost.^{1–3} 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 Mg surface.^{4–5} Experimentally, many studies have been devoted to the catalytic effect on hydrogen adsorption of mixing transitional metals into Mg powder during ball milling.^{6–9} The transitional metals have been considered to act as catalysts for accelerating hydrogen sorption, i.e., enhancing the breaking up of the molecular hydrogen into adsorbed atoms.¹⁰ However, the catalytic mechanism involved when using these additives is still not clearly established. Theoretically, ab initio DFT calculations have shown considerable predictive power for catalysis.¹¹ Much insight could be gained for the process of designing alloy catalysts just from first principle simulations.^{12–13} There have been some theoretical calculations to study the role of transition metals in magnesium hydride, but they are mainly limited to bulk calculation by substituting one Mg atom with a Ti, Ni, or Fe atom.^{14–16} Only very few calculations on the dissociative chemisorption of H₂ onto a pure magnesium surface have been performed to establish the energetically favored pathway and the activation barrier in this process.^{17–19} To further clarify the role of transition metal in relation to recent experimental findings, investigations on the dissociation of H₂ on transition metal incorporated Mg surfaces are highly desirable.

In this paper, H₂ interactions with both pure and Ti-incorporated Mg(0001) surfaces were studied by ab initio DFT calculations and the nudged elastic band (NEB) method. The

dissociation barrier of H₂ on a clean Mg(0001) surface was first calculated and compared with other existing theoretical studies. The energetics for dissociation of H₂ on the Ti-incorporated Mg(0001) surface was then computed and the catalytic role of the transition metal was elaborated. In section II we outline our computational method. Section III presents our calculated results on hydrogen interaction with pure and Ti-incorporated Mg(0001) surface. The last section draws relevant conclusions.

II. Computational Methods

The calculations were performed mainly using the plane-wave basis VASP code^{20,21} implementing the generalized gradient approximation (GGA) of PBE exchange correlation functional.²² An all-electron description, the projector augmented wave method (PAW),^{23–24} is used to describe the electron–ion interaction. Using the PAW method, the lattice constant of bulk Mg was calculated to be 3.191 Å, which was only 0.5% in error compared with the experimental value. The cutoff energy for plane waves is chosen up to 312.5 eV for a very accurate energy calculation. The pure and Ti-incorporated Mg(0001) surfaces were modeled by using a (2 × 2) and a (3 × 3) surface unit cell with five layers of Mg atoms, respectively. A (4 × 4 × 1) Monkhost-Pack grid and three k-points were used in the Brillouin-zone sampling²⁵ for each surface. The vacuum space was at least 15 Å, which was large enough to guarantee a sufficient separation between periodic images. Additionally, using the ESPRESSO/PWSCF code,²⁶ we have carried out DFT calculations based on the plane wave pseudopotential approach with the local density approximation (LDA) only for the purpose of comparison with other existing theoretical results. To determine dissociation barriers and minimum energy paths (MEP), the NEB method was used.^{27–28} 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 forces in each image are less than 0.02 eV/Å.

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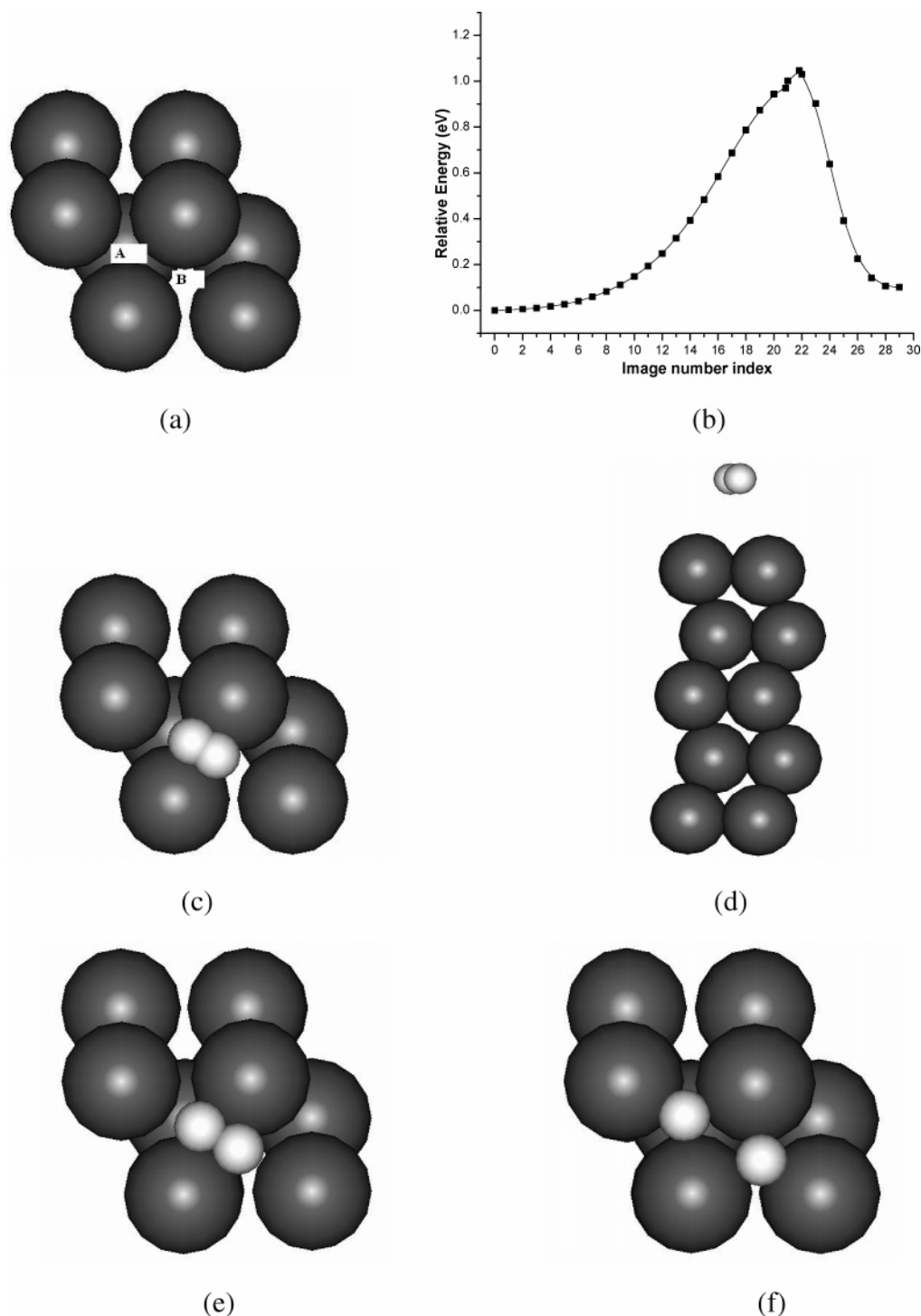


Figure 1. Energetically preferred pathway and corresponding energy profile for the dissociation of a hydrogen molecule on a Mg(0001) surface. (a) Mg(0001) surface. A and B represent a hcp and fcc site, respectively. (b) MEP. (c) Top view of the initial state (IS). (d) Same as (c) but a side view. (e) Top view of the transition state (TS). (f) Top view of the final state (FS). The black and white balls represent Mg and H atoms, respectively.

III. Results and Discussions

According to previous studies of H_2 dissociation on a pure Mg(0001) surface,^{17–19} the energetically favored pathway involves H_2 dissociating at a bridge site and the nascent atoms moving into A (a hcp site) and B (a fcc site) (see Figure 1a). The dissociated H atom on the hcp site will then quickly diffuse onto another neighboring fcc site. Despite the fact that two fcc sites are energetically preferred, the final state (FS) in our calculation is chosen to be a “meta” configuration, in which the hydrogen atoms are positioned on the A and B sites, respectively. This should not affect the activated barrier of H_2

dissociation on Mg surface and simplifies our NEB calculation. We set one hydrogen molecule onto the relaxed Mg (0001) surface at a distance of 5 Å as the initial state (IS). The MEP and the transition state (TS) were obtained by building a chain of images laying between IS and FS and minimizing an appropriate effective force acting on each image. The energy profile, as revealed by our NEB calculation is reported in Figure 1b. H_2 is dissociated at 1.02 Å from the top of the Mg surface and the effective barrier for the dissociation of a hydrogen molecule on the Mg(0001) surface is 1.05 eV. Three specific configurations corresponding to the IS, TS, and FS along the

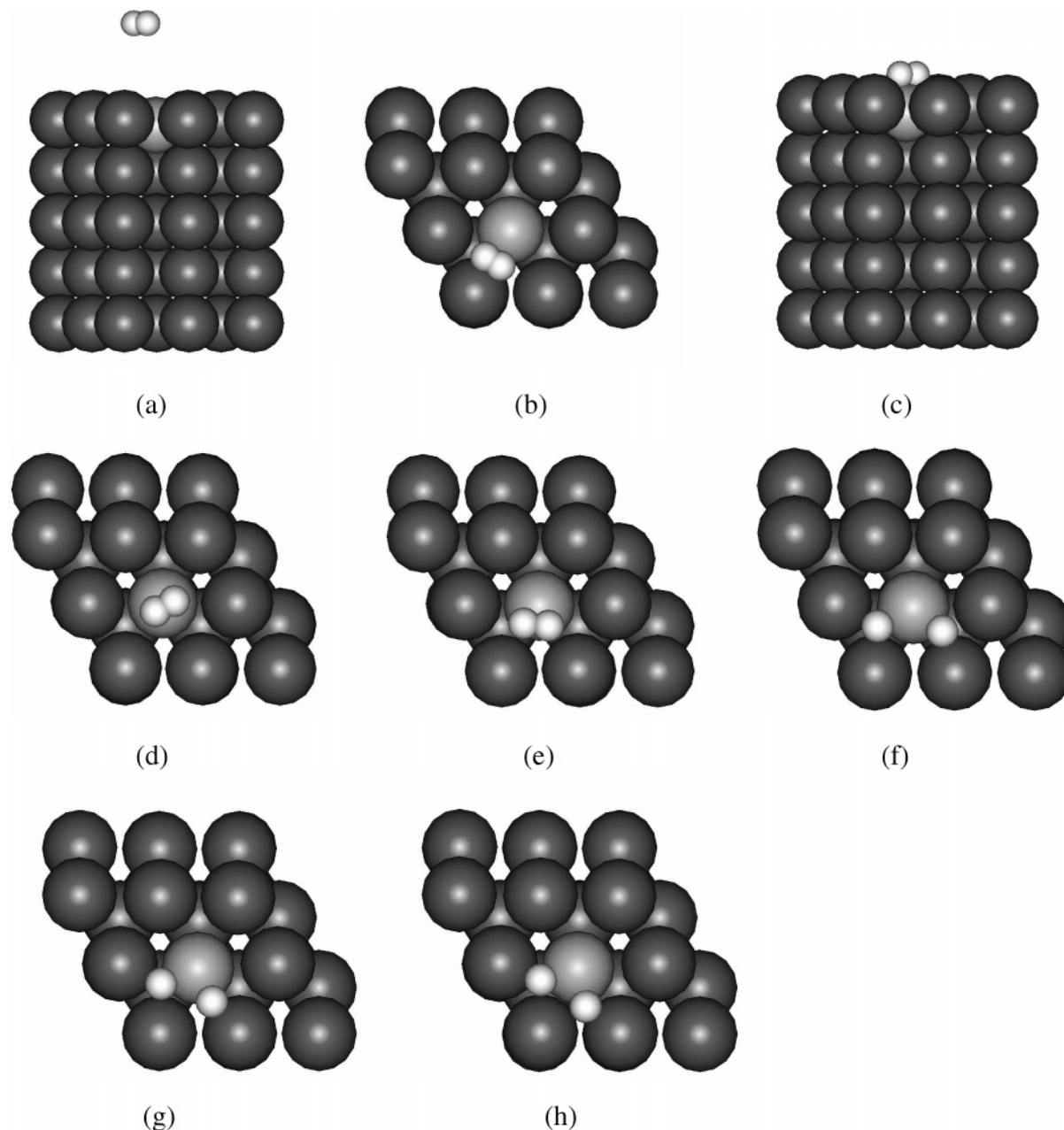


Figure 2. The dissociation pathway for a hydrogen molecule on a Ti-incorporated Mg(0001) surface: (a) a side and (b) a top view of the initial state (IS). (c) Side view of the first local minimum state (LS1). (d) Same as (c) but a top view. (e) First transition state (TS1). (f) Second local minimum state (LS2). (g) Second transition state (TS2). (h) Final state (FS). The black, gray, and small white balls represent Mg, Ti, and H atoms, respectively.

MEP were also shown in Figures 1c, 1d, 1e, and 1f. For comparison, some other theoretical calculations for the activated barrier of H_2 on Mg and Ti surfaces are also listed in Table 1. It can be seen clearly that our results are in good agreement with them for both LDA and GGA calculations. All the LDA calculations give a substantially lower dissociation barrier compared to the GGA calculations. This can be understood by the well-known fact that LDA leads to strong over-binding,²⁹ in particular for calculations involving bond breaking and reforming of light H atoms. Results obtained with both RPBE and PBE exchange correlation functional (GGA) are able to reproduce the recombination barrier for desorption of H_2 in relation to the experimentally observed TDS value of 1.0 eV.³²

The transition metal–Mg interface plays an important role in the dissociation of H_2 on a Mg surface. A reasonable model for studying the effect of Ti on Mg surface could be a Ti-incorporated Mg(0001) surface, in which one Mg atom is

TABLE 1: Comparison of Present Calculations for the Activation Barrier of Hydrogen Dissociation on a Mg(0001) Surface with Previous Theoretical Studies^a

| computational method | dissociation barrier | reference |
|----------------------------------|----------------------|-----------|
| Jellium model (LDA) | 0.50 eV | 17 |
| DFT (LDA) PES | 0.37 eV | 18 |
| DFT (RPBE[30]) and NEB | 1.15 eV | 19 |
| DFT (LDA) and NEB | 0.35 eV | this work |
| PAW (PBE) and NEB | 1.05 eV | this work |
| DFT (GGA) PES [Ti(0001) surface] | negligible | 31 |

^a Also included is an extant calculation for hydrogen dissociation on Ti(0001) surface.

substituted by one Ti atom. First, the Ti-incorporated Mg(0001) surface was fully relaxed using a conjugated gradient method. The position of Ti atom after relaxation changed a little (0.3 Å) along the z -axis. To verify the thermodynamical stability of

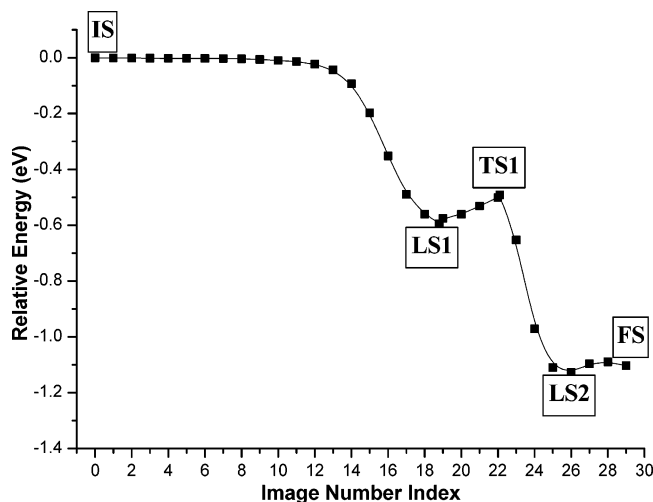


Figure 3. The minimum-energy-pathway profile for the dissociation of a hydrogen molecule on a Ti-incorporated Mg(0001) surface. IS, LS1, TS1, LS2, and FS represent the initial state, first local minimum state, first transition state, second local minimum state, and final state, respectively.

the Ti-incorporated Mg(0001) surface, the formation energy of a hydrogen molecule on a Ti-incorporated Mg(0001) surface must be calculated first. This process involves the creation of a Mg vacancy on Mg(0001) surface in the first step, and the vacancy is then occupied by a Ti atom. Taking them together gives the adsorption energy ($\theta = 1/9$) at the surface-substitutional site:³³

$$E_{\text{ad}}^{\text{subs}} = E_{\text{Ti/Mg(0001)-subs}} + E_{\text{Mg}} - E_{\text{Ti-atom}} - E_{\text{Mg(0001)}}$$

where $E_{\text{Ti/Mg(0001)-subs}}$, E_{Mg} , $E_{\text{Ti-atom}}$, and $E_{\text{Mg(0001)}}$ represent the total energy of the relaxed Ti-incorporated Mg(0001) surface, the bulk Mg atom, the isolated Ti atom, and the clean Mg(0001) slab, respectively. The adsorption energy is calculated to be -4.09 eV, which indicates that Ti-incorporated Mg(0001) surface is thermodynamically stable.

The IS and FS were chosen to be the same situations as those for the calculation of hydrogen dissociation on a pure Mg surface. In the relaxed FS, the positions of the H atoms on the fcc and hcp sites were located around 0.8 Å from the surface. The distance between H and the Ti atom was about 1.90 Å. In Figure 2, we presented a series of configurations (IS, LS1, TS1, LS2, TS2, and FS) along the MEP after the NEB calculation. Studying this energetically favored pathway, we find that the hydrogen molecule first moves toward the Ti atom and dissociates nearly on the top of it, around 1.32 Å from the Mg surface. This could be understood in terms of the strong interaction between the molecular orbital of H_2 and the metal d orbitals, since there was charge donation from the s orbital of H_2 to the d orbital of Ti.³¹ Figure 3 shows the energy profile for the dissociation of H_2 on a Ti-incorporated Mg(0001) surface. The result is in marked contrast to a pure Mg surface. Preliminary clustering of molecular hydrogen onto the Ti atom occurred with an exothermicity of ca. 0.6 eV, followed by dissociation of the H_2 with an activation barrier of only 0.103 eV. As indicated in Figure 2g and Figure 3, the effective barrier (0.015 eV) for a second transition state is due to the translation or bond rotation of H atoms on Mg(0001) surface. Compared to the clean Mg(0001) surface, the decreased barrier on the Ti-incorporated surface implies that the absorption kinetics of H_2 will be significantly improved. This was in good agreement with recent experimental findings.^{6–9} In fact, depending on the speed of thermalisation of the excess energy (ca. 0.6 eV) associated

with the initial clustering of molecular hydrogen onto the Ti atom, it might be argued that the effective barrier should be negligible. However, this excess energy is likely to be concentrated initially along the H_2 –Ti separation coordinate rather than the actual dissociation coordinate. This likelihood would tend to allow time for partial relaxation (or perhaps complete thermalization) to occur prior to the subsequent dissociation of the H_2 molecule. If this is the case, then there would be an observable (albeit small) barrier for the dissociation.

It should be pointed out here that the contribution from zero-point energy was excluded from all the above calculations because such effect was found to only change the hydrogen binding energy by less than 0.05 eV.¹² As reported in ref 19, the zero-point energy between IS and TS can be as high as 0.08 eV. However, the principal result of this study, namely the difference between H_2 dissociation on pure and Ti-incorporated Mg surfaces, should not be affected greatly by inclusion of zero point energy corrections.

Additionally, the hydrogenation of Mg involves not only hydrogen dissociation on Mg(0001) surface in the first step, but also the dissociated surface H atoms will diffuse into the Mg matrix later. The FS (a TiH_2 -like species embedded in the Mg surface) is very stable compared to the IS. This implies a considerable diffusion barrier for the H atom from surface to bulk. Experimentally, it has been shown that the activation energy for H_2 desorption from magnesium hydride is about 156 kJ/mol during ball milling,³⁴ while the activation energies for dehydrogenation of TiH_2 to TiH and TiH to Ti are measured to be 74.79 kJ/mol and 131.921 kJ/mol,³⁵ respectively. A good catalyst should not bind hydrogen too strongly. However, the surface Ti atom can be easily attacked by nonmetal atoms such as carbon, which could induce charge transfer between them. This could significantly improve the diffusion of hydrogen atom into the subsurface. This has been proved by experiment and our ongoing theoretical studies and will be the topic of a subsequent publication.

IV. Conclusions

In summary, dissociative chemisorption of molecular hydrogen on both pure and Ti-incorporated Mg(0001) surfaces has been studied utilizing ab initio DFT calculations and the NEB method. Our results for the dissociation of H_2 on a Mg(0001) surface were in good agreement with existing published work. For the Ti-incorporated Mg(0001) surface, the activated barrier was much smaller (0.103 eV) due to the strong interaction between the molecular orbital of H_2 with the metal d orbitals. This could explain the experimentally observed improvement in absorption kinetics of H_2 when transition metals have been introduced into the Mg materials.

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Supporting Information Available: Structures for a (2×2) Mg(0001) and a (3×3) Ti incorporated Mg(0001) surface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Schwarz, R. B. *MRS Bull.* **1999**, *24*, 40.
- (2) Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 23.

- (3) Liang, G.; Huot, J.; Van Neste, A.; Schulz, R. *J. Alloys Compd.* **1999**, 292, 247.
- (4) Zaluska, A.; Zaluski, L.; Strom-Olsen, J. O. *Appl. Phys. A: Mater. Sci. Process.* **2001**, 72, 157.
- (5) Von Zeppelin, F.; Reule, H.; Hirscher, M. *J. Alloys Compd.* **2002**, 330–332, 723.
- (6) Bobet, J. L.; Chevalier, B.; Darriet, B. *J. Alloys Compd.* **2002**, 330, 738.
- (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) Hanada, N.; Ichikawa, T.; Fujii, H. *J. Phys. Chem. B* **2005**, 109, 7188.
- (10) Yavari, A. R.; de Castro, J.F.R.; Heunen, G.; Vaughan, G. *J. Alloys Compd.* **2003**, 353, 246.
- (11) Greeley, J.; Norskov, J. K.; Mavrikakis, M. *Annu. Rev. Phys. Chem.* **2002**, 53, 319.
- (12) Greeley, J.; Mavrikakis, M. *Nat. Mater.* **2004**, 3, 810.
- (13) Vang, R. T.; Honkala, K.; Dahl, S.; Vestergaard, E. K.; Schnadt, J.; Egsgaard, E.; Clausen, B. S.; Norskov, J. K.; Besenbacher, F. *Nat. Mater.* **2005**, 4, 160.
- (14) Shang, C. X.; Bououdina, M.; Song, Y.; Guo, Z. X. *Int. J. Hydrogen Energy* **2004**, 29, 73.
- (15) Song, Y.; Guo, Z. X.; Yang, R. *Phys. Rev. B* **2004**, 69, 094205.
- (16) Vegge, T.; Hedegaard-Jensen, L. S.; Bonde, J.; Munter, T. R.; Norskov, J. K. *J. Alloys Compd.* **2005**, 386, 1.
- (17) Norskov, J. K.; Houmoller, A. M. *Phys. Rev. Lett.* **1981**, 46, 257.
- (18) Bird, D. M.; Clarke, L. J.; Payne, M. C.; Stich, I. *Chem. Phys. Lett.* **1993**, 212, 518.
- (19) Vegge, T. *Phys. Rev. B* **2004**, 70, 035412.
- (20) Kresse, G.; Furthmuller, J. *Comput. Mater. Sci.* **1996**, 6, 15.
- (21) Kresse, G.; Furthmuller, J. *Phys. Rev. B* **1996**, 54, 11169.
- (22) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, 77, 3865.
- (23) Blochl, P. E. *Phys. Rev. B* **1994**, 50, 17953.
- (24) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, 59, 1758.
- (25) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, 13, 5188.
- (26) Baroni, S.; Dal Corso, A.; de Gironcoli, S.; Giannozzi, P. <http://www.pwscf.org>.
- (27) Henkelman, J.; Jónsson, H. *J. Chem. Phys.* **2000**, 113, 9978.
- (28) Henkelman, J.; Uberuaga, B. P.; Jónsson, H. *J. Chem. Phys.* **2000**, 113, 9901.
- (29) Kurth, S.; Perdew, J. P.; Blaha, P. *Int. J. Quantum Chem.* **1999**, 75, 889.
- (30) Hammer, B.; Hansen, L. B.; Norskov, J. K. *Phys. Rev. B* **1999**, 59, 7413.
- (31) Nobuhara, K.; Kasai, H.; Dino, W. A.; Nakanishi, H. *Surf. Sci.* **2004**, 566–568, 703.
- (32) Sprunger, P. T.; Plummer, E. W. *Chem. Phys. Lett.* **1991**, 187, 559.
- (33) Kiejna, A. *Phys. Rev. B* **2003**, 68, 235405.
- (34) Huot, J.; Liang, G.; Boily, S.; Van Neste, A.; Schulz, R. *J. Alloys Compd.* **1999**, 293–295, 495.
- (35) Bhosle, V.; Baburaj, E. G.; Miranova, M.; Salama, K. *Mater. Eng. A* **2003**, 356, 190.