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First principle investigation of atomic hydrogen adsorption on Pd-doped MgB_2

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Utilizing density functional theory calculations, the atomic adsorption of hydrogen on a Pd-doped Mg-terminated MgB_2 (0001) surface was investigated in terms of total energies and structural properties. Pd doping of about 11% Mg surface sites in MgB_2 caused the lattice parameters *a* and *c* to be reduced by 1.3% and 1.7%, respectively. The hollow site far from the Pd impurity was found to be the most preferred site for atomic hydrogen adsorption, which can be explained by the availability of additional electrons. The present results provide an initial understanding of the mechanisms for atomic H adsorption on Pd-doped MgB_2 (0001).

KEYWORDS

magnesium diboride, palladium, hydrogen storage, density functional theory, adsorption

INTRODUCTION

Research on materials for hydrogen fuel storage has been widely explored in order to address the main concerns of the hydrogen-based economy (Kolasinski 2012). In particular, the development of practical and efficient storage materials is a vital component in the widespread use of H_2 fuel (Spiegel 2007). Recent studies have focused on solid-state metal hydride systems for hydrogen storage applications because of their safe and compact storage capacity as compared to high pressure cylinders and liquid hydrogen (Schlapbach and Zuttel 2001). However, problems in the hydrogenation of these storage materials, such as slow kinetics and limited reversibility, must be addressed (Vajo and Olson 2007).

The coupled $LiBH_4/MgH_2$ system is considered one of the most promising storage materials because of its fully reversible hydrogen storage property given by this chemical reaction:

$$2LiBH_4(s) + MgH_2(s) \longrightarrow 2LiH(s) + MgB_2(s) + 4H_2(g) \quad (1)$$

which corresponds to a relatively high theoretical hydrogen storage capacity of 11.5 wt% (Vajo et al. 2005).

As seen in Equation (1), the hydrogenation of MgB_2 is an important step in reversible hydrogen storage in the coupled $LiBH_4/MgH_2$ system. Diffusion of dissociated atomic H on a Mg-terminated MgB_2 (0001) surface has been calculated to be almost barrierless (Du et al. 2009). Additionally, hydrogen adsorption on MgB_2 can play a critical role in the synthesis of $Mg(BH_4)_2$, which is another promising storage material with high hydrogen content and low decomposition enthalpy (Pistidda et al. 2010, Matsunaga et al. 2008). Therefore, improving the kinetics of hydrogen adsorption on MgB_2 is necessary for more favorable operating conditions of storage systems.

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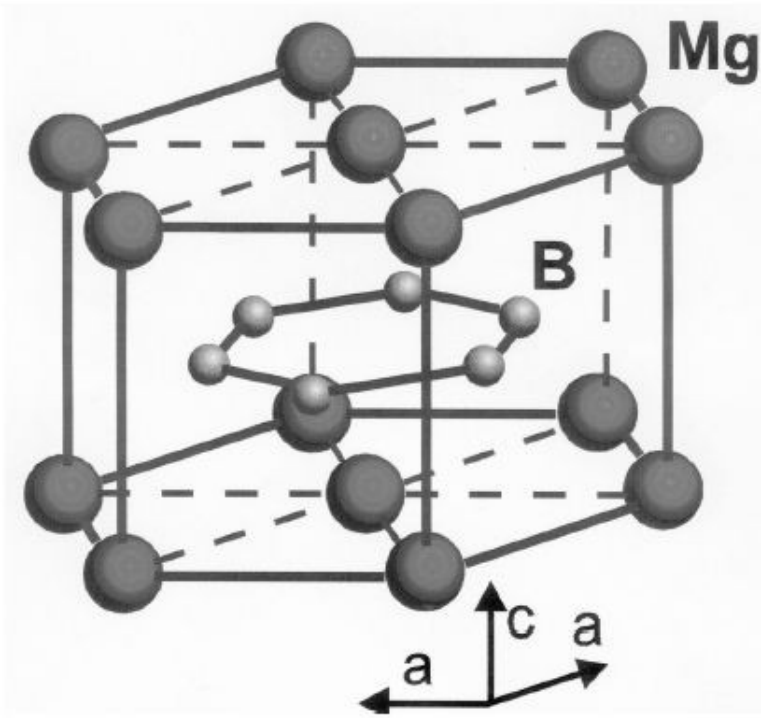

Figure 1. Crystal structure of MgB_2.

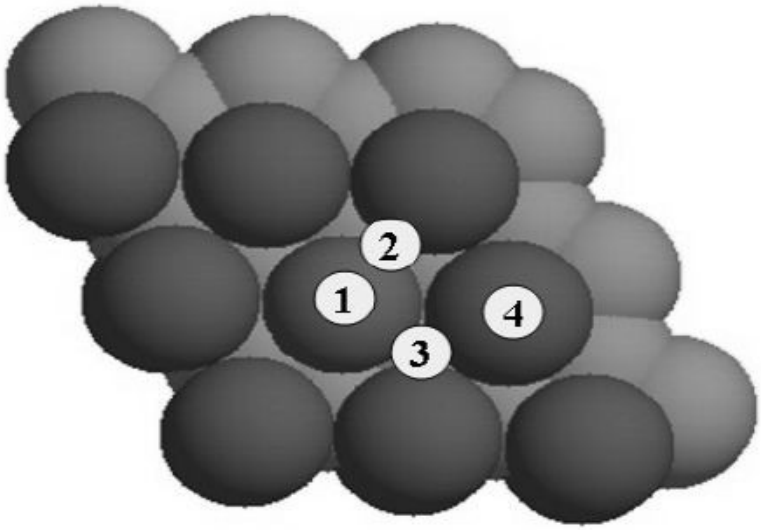

Figure 2. Pd-doped MgB_2 (0001) surface model used in the calculations and specific H atom binding sites 1-4. The dark grey, medium, and light grey balls represent Pd, B, and B atoms, respectively.

Recent studies have shown that catalysts including carbon materials and transition metal chlorides can enhance the hydrogen storage performance of the $LiBH_4/MgH_2$ coupled system (Sridechprasat et al. 2010, Matsunaga et al. 2008). Weng et al. (2010) later demonstrated that doping with Pd nanoparticles promotes better dehydrogenation performance of the coupled system, as evidenced by lower hydrogen desorption temperatures. However, the effect of Pd doping on the kinetics of rehydrogenation in the system has not been fully investigated. This study aims to examine the possible catalytic effect of Pd doping on the atomic hydrogen adsorption of MgB_2 using first principle simulation. An initial understanding of the reaction mechanism can potentially aid in the rational design of improved storage materials.

COMPUTATIONAL METHOD

First principle calculations were done using the Atomic Simulation Environment (ASE) – Jacapo calculator (Bahn and Jacobsen 2002), which implemented the generalized gradient approximation of the exchange correlation function proposed by Perdew et al. (1996).

MgB_2 has a hexagonal AlB_2-type crystal structure (space group *P6/mmm*) which is composed of graphene-like sheets of boron and Mg atoms between the centers of hexagons on neighboring B layers. The crystal structure is shown in Figure 1.

The initial configuration of a Mg-terminated MgB_2 (0001) surface was obtained from bulk MgB_2. The clean MgB_2 slab was modeled using a 3 x 3 surface unit cell composed of four layers of alternating Mg and B with a total thickness of 7.04 Å. Periodic boundary conditions were employed and the cutoff energy used was 900eV. Brillouin-zone integrations were used on a 3 x 3 x 1 grid using Monkhorst-Pack special *k*-points (Monkhorst and Pack 1976). The vacuum space between the slab and its periodic image was set to about 10 Å.

The two bottom layers were fixed for the calculations of atomic H adsorption on the Pd-doped surface. Meanwhile, the top two layers for the slab were relaxed. The structural

optimization of the Pd-doped surface and adsorbate was performed until the residual force was less than 0.05 eV/Å. Figure 2 presents the top view of the Pd-doped surface and the selected binding sites for H atom adsorption, namely Pd top (1), bridge (2), hollow (3), and Mg top (4). The Pd doping was then modeled by replacing the center Mg on the surface with a Pd impurity atom. This results in the coverage of about 11% of the Mg surface sites that were doped with Pd. The plots of charge density distributions were obtained using a Mayavi visualization tool (Ramachandran and Varoquaux 2011).

The adsorption energies for atomic H adsorption were calculated based on the following definitions:

$$E_{ads-H} = E_{H/surface} - (E_{surface} + E_H) \quad (2)$$

where E_{ads-H} is the adsorption energy of the system with adsorbed H atom, E_H is the total energy of the H atom, $E_{surface}$ is the total energy of the Pd-doped MgB_2 slab without the absorbed species, and $E_{H/surface}$ is the total energy of the system with adsorbed H atom.

RESULTS AND DISCUSSION

Using structural optimization for varying volumes of the lattice unit cell, MgB_2 bulk lattice parameters *a* and *c* were calculated to be 3.08 Å and 3.52 Å, respectively, based on the most stable configuration. These results are in good agreement with experimental values of *a* = 3.084 Å and *c* = 3.522 Å (Villars 1997). These initial calculations indicate that the applied set of parameters, such as pseudo-potentials, k-points sampling, and cutoff energy, can provide a good representation of total energies and structural properties of bulk MgB_2.

The optimized surface of the Pd-doped MgB_2 (0001) was then compared to that of pure MgB_2 (0001). The introduction of Pd impurity resulted in the reduction of lattice parameters *a* and *c* by about 1.3% and 1.7%, respectively. The addition of the Pd impurity was also found to affect the charge density distribution of the surface slab. Figures 3(a) and (b) show the color map of the charge density distributions along cross-sectional planes perpendicular to the pure and doped surfaces, respectively. Figure 3(c) gives the top view of the corresponding cross-sectional plane for the doped surface.

From Figures 3(a) and (b), it can be seen that the charge densities at the bottom two layers are not significantly affected by the doping of Pd impurity. However, the interaction of the Pd atom with neighboring Mg atoms and B atoms at the top two layers resulted in the change of the distribution of charge densities. Figure 4 shows the difference in charge densities between the pure and doped slabs along the second layer composed of B atoms. This indicates that the second layer also plays a critical role in the redistribution of electrons on the surface slab.

Based on the bond charge densities, the B atoms of the second layer were found to interact more strongly with the neighboring Pd impurity than with the Mg atoms of the top layer. The charge density on the Pd-B bond in the doped slab was found to be 0.34 electrons/Å^3, which is higher than for the Mg-B binding of 0.17 electrons/Å^3. The interaction charge densities between neighboring atoms of the top two layers are

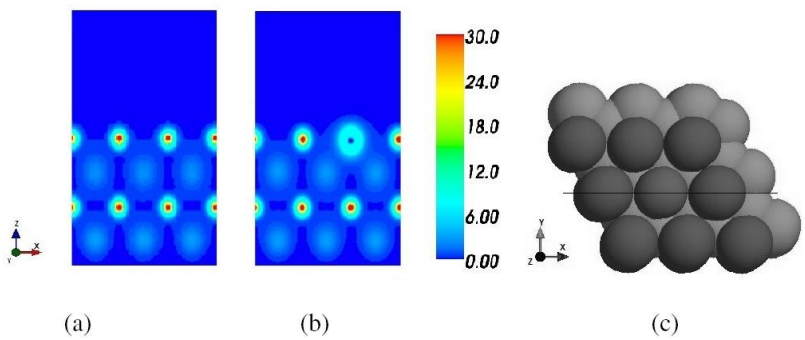

Figure 3. Charge density distributions (in electrons/Å^3) along the cross-sectional plane perpendicular to the pure (a) and Pd-doped (b) MgB_2 surfaces. The corresponding cross-sectional plane for the Pd-doped surface is indicated in (c).

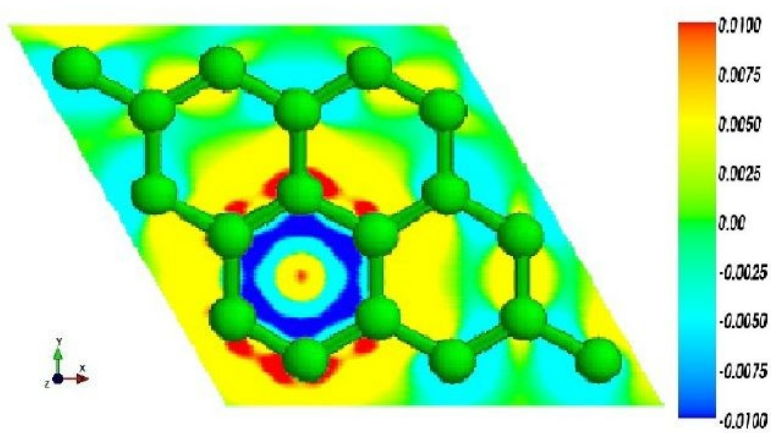

Figure 4. Difference in charge densities (in electrons/Å^3) due to Pd doping along the second layer with positions of the B atoms. Red and yellow regions indicate increase in charge density when Pd atom is doped, while light and dark blue regions indicate otherwise. Green areas correspond to no change in charge density.

summarized in Table 1. The interaction charge densities between other pairs of atoms such as Mg-Mg, Mg-B and B-B were not significantly affected by the Pd doping.

The obtained charge density distributions show that Pd doping resulted in the redistribution of electrons on the MgB_2 surface slab. This change in charge density distribution can greatly affect the interaction of hydrogen with the surface. In particular, the Pd top and far hollow sites were found to have a higher electron density just above the surface, shown as yellow and red regions in Figure 5. The supply of additional elections can potentially lead to a more favorable binding for H atom adsorption. On the other hand, a decrease in the electron density was found at the Mg top sites near Pd, as indicated by light blue regions. The decrease in the charge density can instead lead to less favorability in H atom binding.

To analyze the adsorption of an H atom on the Pd-doped MgB_2 slab, an H atom was placed above or below the relaxed surface at varying positions along the z-direction. Potential energy curves (PEC), shown in Figure 6, were obtained for each binding site. Results show that the H atom can enter the surface slab via the bridge and hollow sites. In particular, the H atom can penetrate below the boron layer (Z = -1.76 Å) via the bridge site. Thus, diffusion of H atoms to the bulk layers via the bridge site might be possible. Table 2 summarizes the adsorption energies and adsorbate heights obtained from the PECs for each binding site.

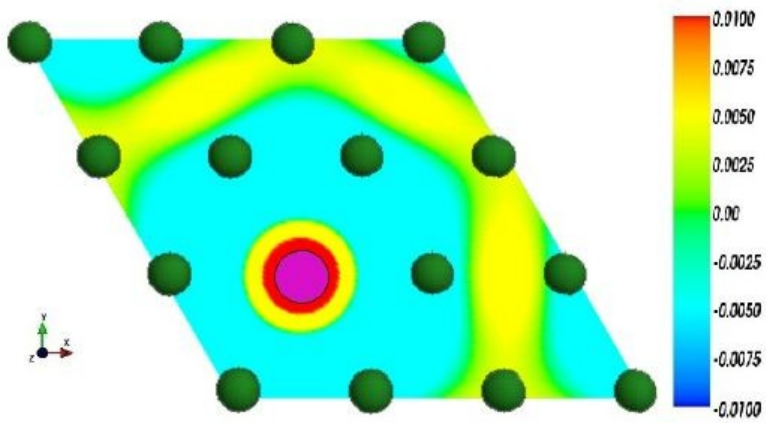

Figure 5. Difference in charge densities (in electrons/Å^3) due to Pd doping along the parallel plane about 1.5 Å above the surface.

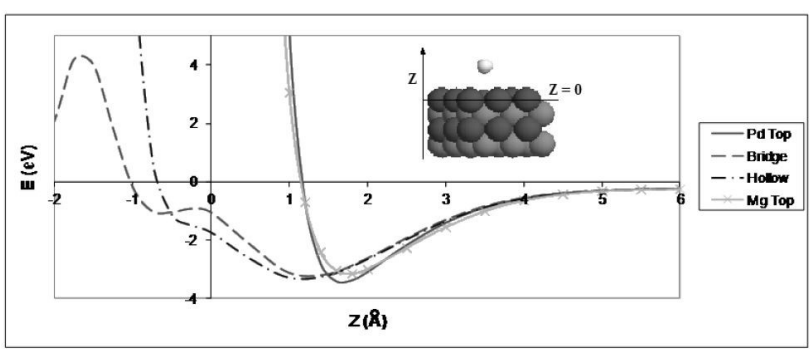

Figure 6. Potential energy curves of H atom adsorption for different sites. (Z =0) corresponds to the plane of the surface.

To obtain more accurate results, optimization was applied for each binding site wherein the H atom was relaxed in all directions. The relaxed H atom was initially placed at the corresponding adsorption height indicated in Table 2. The calculated binding energies and equilibrium geometries for each binding site are presented in Table 3.

Only the Pd top and hollow sites are found to be favorable. In the cases of bridge and Mg top sites, the adsorption energies are too low, so that the H atom moved to more stable sites during the optimization calculations. Notably, the H atom initially placed on the Mg top site moved to an adjacent hollow site away from the Pd impurity atom. The calculated binding energy for the fully optimized adsorption on this far hollow site is 4.12 eV, which is greater than the binding energy on Pd Top as indicated in Table 3. Therefore, the hollow site far from the Pd impurity is the most favorable site for H atom adsorption. This can be attributed to the availability of additional electrons as a result of the Pd doping in the MgB_2 system, which was indicated previously in Figure 5.

The present results for H atom adsorption on a Pd-doped MgB_2 (0001) surface can be compared to a similar study on the hydrogenation of a pure MgB_2 (0001) surface. Du et al. (2009) had determined that the hollow site was the most favorable binding site for H atom adsorption on a pure Mg-terminated MgB_2 (0001) surface, which is consistent with the results of this study. However, the far hollow site was found to be the most favorable adsorption site for an H atom on the Pd-doped MgB_2 surface (0001). The corresponding binding energy for this site is stronger by 1.1 eV in a Pd-doped MgB_2 surface as compared to that in pure MgB_2. According to Greeley and Mavrikakis (2004), there is no direct correlation between the binding energy of an H atom to a surface and the kinetics of H_2 dissociation, especially for surface alloys. Thus, the calculation of activation barriers for H_2 dissociation on the surface must be performed in order to provide sufficient evidence for favorable dissociation kinetics.

Finally, the stronger binding of H atoms to

the doped surface may be generally thought to result in less favorable dehydrogenation, which may seem inconsistent with the results of Weng et al. (2010). However, the mechanism for hydrogen desorption does not necessarily involve MgB_2 as indicated in Equation (1). MgB_2 is only present during the rehydrogenation process of the $LiBH_4/MgH_2$ system.

CONCLUSIONS

First principle calculations and a nudged elastic method were employed to explore the hydrogen adsorption processes on a Pd-doped MgB_2 (0001) surface in terms of total energies and structural properties. Pd doping of about 11% on the Mg surface sites in MgB_2 caused the lattice parameters *a* and *c* to be reduced by 1.3% and 1.7%, respectively. The hollow site far from the Pd impurity was found to be the most favorable site for atomic hydrogen adsorption. Potential energy curves also show that diffusion of H atoms to bulk layers via the Mg-Mg bridge site may be possible.

The availability of additional electrons possibly caused the Pd top and far hollow sites to be favorable for H atom adsorption. Charge density distributions also show that the Pd impurity binds more strongly to nearby B atoms in the second layer than to the Mg atoms in the top layer. This interaction of the Pd atom with the system resulted in the redistribution of electrons on the surface.

The present results provide an initial mechanism for atomic H adsorption on Pd-doped MgB_2 (0001). In particular, this study can serve as the basis for the stable binding sites of H atom adsorption, which is useful for the study of different possible pathways for H_2 dissociation and corresponding activation barriers. Further studies must be undertaken in order to give a better understanding of the possible role of Pd as a catalyst for the hydrogenation of the $LiBH_4/MgH_2$ coupled system.

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Table 1. Interaction charge densities (in electrons/Å^3) between neighboring atoms on the top two layers of pure and Pd-doped slabs.

	Pure MgB_2	Pd-doped MgB_2
Mg-Mg	0.16	0.17
Mg-B	0.16	0.17
Mg-Pd	-	0.17
Pd-B	-	0.34
B-B	0.67	0.67

Table 2. Summary of parameters for H atom adsorption based on potential energy curves.

Binding Site	Adsorption Energy (eV)	Adsorbate Height (Å)
Pd Top (1)	3.43	1.66
Bridge (2)	3.22	1.25
Hollow (3)	3.31	1.17
Mg Top (4)	3.15	1.79

Table 3. Adsorption energies and equilibrium geometries for relaxed calculations of H atom adsorption

Binding Site	Adsorption Energy (eV)	Adsorbate Height (Å)	Pd-H Distance (Å)
Pd Top (1)	3.65	1.66	1.66
Bridge (2)	--[a]	--[a]	--[a]
Hollow (3)	3.63	1.20	1.83
Mg Top (4)	--[b]	--[b]	--[b]

[a] Moved to adjacent hollow site (3) near Pd atom
[b] Moved to adjacent hollow site away from Pd atom

cluster of the High Performance Computing Laboratory (HPCL), a shared computing facility between the College of Science (COS) and the Center for Natural Science and Environmental Research (CENSER) of De La Salle University.

CONFLICT OF INTEREST

The authors certify and declare there are no conflicts of interest associated with the presented study.

CONTRIBUTION OF INDIVIDUAL AUTHORS

PMA performed the calculations assisted by ARCV. MYD, PMA's adviser, and NBA were consultants in the analysis. PMA wrote the paper, with MYD, NBA, and ARCV acting as consultants in the writing of the manuscript.

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