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ARTICLE

Study on H_2 Adsorption and Dissociation Properties on Mg(0001) Surface

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Abstract: By the first-principles calculations method based on the density functional theory, H_2 adsorption and dissociation properties on clean, vacancy defective and Pd atom coadsorption Mg(0001) surfaces are investigated systematically. The calculation results show that the model of H_2 adsorption on clean surface is weak physisorption, and there is a high energy barrier, i.e., 1.3774 eV, when H_2 dissociates into two separate H atoms. Vacancy defect not only benefits enhancing of the physisorption interaction between H_2 and Mg surface, but also decreasing of the energy barrier, i.e., 1.2221 eV, of H_2 dissociation to some extent. For Pd atom coadsorption Mg(0001) surface, there is a strong chemisorption interaction between Pd atom and H_2, and the energy barrier, i.e., 0.2860 eV, of H_2 dissociation is reduced significantly. Further analysis of electronic structures shows that the catalytic activity for H_2 adsorption and dissociation on three different surfaces is closely related to the bonding electrons number of *s* orbital of the topmost layer metal atoms which interact directly with H_2 around Fermi level.

Key words: Mg(0001) surface; adsorption; dissociation; energy barrier

Mg-based alloys are considered to be one of the most promising candidates as hydrogen storage media because of their high storage capacity, light weight, low cost and great abundance. However, the sluggish sorption kinetics becomes one of the key bottlenecks which limit their practical applications [1]. As far as the worse kinetics of Mg-based hydrogen storage alloys is concerned, there are several influencing factors. Commonly, the dissociative chemisorption of H_2 is the rate-limiting step during the initial hydrogenation stage of pure magnesium [2]. With proceeding of hydrogen atoms diffusion on magnesium, the multiple passivation layers of hydride and oxide are found to form on magnesium surface, which hinder significantly the further diffusion of hydrogen atoms into magnesium bulk [3].H ere, the diffusion of hydrogen atoms becomes the rate-limiting step during the process of pure magnesium hydrogenation. Therefore, the slow sorption kinetics of magnesium originates from the poor dissociation of H_2 on magnesium surface and the stable hydride or oxide surface film blocking the penetration of hydrogen atoms into magnesium bulk, but no consensus has been reached, and it is essential to study H_2 adsorption and dissociation properties on Mg (0001) surface.

In recent years, several investigations have been carried out related to H_2 adsorption and dissociation on magnesium thin film. For example, Plummer *et al*.[4] employed electron-energy loss spectroscopy(EELS) and thermal dissociationspectrum (TDS) to study the interactions among hydrogen atom, molecular and Mg, and found that H_2 adsorption and dissociation on Mg(0001) surface need to be activated. In addition, a strongly chemisorbed surface hydride layer was also observed. Nørskov *et al*.[5] used *ab initio* calculations to investigate H_2 adsorption and dissociation on Mg(0001) surface. They found that there was a chemisorption state between molecular hydrogen and Mg surface, and for H_2 dissociation, an activation energy is essential, i.e., 0.5 eV. Bird *et al*.[6] thought the bridge site to be favored for H_2 dissociation and an energy barrier was 0.4 eV based on first-principles calculations. Vegge [7] studied the dissociation of molecular hydrogen on Mg(0001) surface and the subsequent diffusion of atomic hydrogen into magnesium substrate. They found H_2 dissociation to be also in the bridge site, but yielding a substantially

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high activation energy of 1.15 eV. In addition, no chemisorbed molecular state was observed. From the above investigations, some debatable results concluded from the informed researches on H_2 adsorption and dissociation properties, especially the barrier of H_2 dissociation, can be evidently seen. Although many efforts have been performed experimentally and theoretically to improve the sorption kinetics of magnesium, few theoretical studies on H_2 adsorption and dissociation on modified Mg surface have been reported. Grounded on this, the first-principles calculations method based on density functional theory is employed to investigate H_2 adsorption and dissociation properties on clean, vacancy defective and Pd atom coadsorption Mg(0001) surfaces systemically, and the microscopic mechanisms of surface defects and doped transition metals improving the sorption kinetics of magnesium are also analyzed and discussed. Some results are expected to provide theoretical guidance for designing advanced Mg-based hydrogen storage alloys.

1 Calculation Model and Method

Considering the boundary effect and computational cost, the clean Mg(0001) (2×3) surface model with five layer slabs is constructed, and the vacuum space is set as 2 nm, as shown in Fig.1a. By removing an Mg atom in the topmost layer of the clean surface, the vacancy defective Mg(0001) surface model is obtained, as shown in Fig.1b. By stable adsorbing a Pd atom on clean surface, the Pd atom coadsorption Mg(0001) surface is achieved, as shown in Fig.1c. For the structural optimization of all above constructed models , the two top layers Mg atoms and the adsorbed H atom, H_2 molecule or Pd atom are allowed to be relaxed freely, and the three bottom layers Mg atoms are fixed at the bulk positions.

In the present work, all calculations are performed using the Dmol package based on the density functional theory (DFT) and the PW91[8] exchange-correlation functional is adopted for GGA correction. All-electron Kohn-Sham wave functions are expanded in a Double Numerical basis (DND) [9,10]. Sampling of the irreducible wedge of Brillouin zone is performed with a regular Monkhorst-Pack grid of special *k*-points and it is set as (4×2×1). The positions of selected atoms in the structures are relaxed to get the final structure with minimum total energy. The convergence criteria of optimization are $\leq 2.0\times10^{-5}$ Ha(1Ha=27.2114 eV), 0.04 Ha/nm and 0.0005 nm for energy, gradient and atomic displacement, respectively. To determine the dissociation energy barriers of H_2 on three different surfaces, the transition states of H_2 dissociation are calculated by adopting TS Search module based on Complete LST/QST[11] method, and the minimum energy paths (MEP) of H_2 dissociation are further examined by Nudged-Elastic Band (NEB) method [12]. Meanwhile, the smearing energy is set as 0.005 Ha to realize the rapid energy convergence. Under these calculation conditions, both Mg bulk and H_2 molecule are well tested.

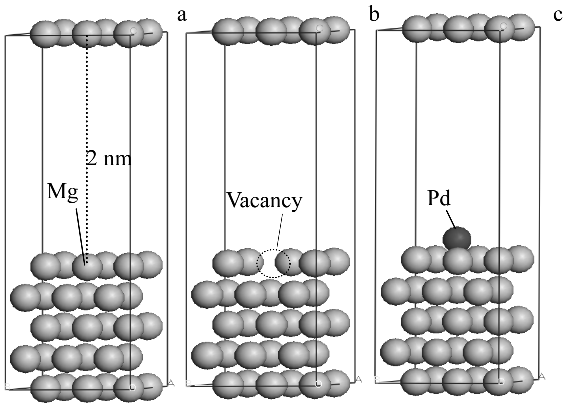

Fig.1 Calculation models: (a) clean Mg (0001) surface, (b) Mg (0001) surface with vacancy defect, and (c) Mg (0001) surface with Pd atom coadsorption

To examine the rationality of vacancy defective and Pd atom coadsorption Mg(0001) surface models, the vacancy formation energy $E_{\mathrm{van}}(\mathrm{Mg})$ of Mg atom and adsorption energy $E_{\mathrm{ads}}(\mathrm{Pd})$ of Pd atom on clean Mg(0001) surface are calculated by the following expressions (1) [13] and (2) [14] respectively:

$$E_{\mathrm{van}}(\mathrm{Mg})=E_{\mathrm{tot}}[\mathrm{Mg(0001)_{van}}]+E_{\mathrm{tot}}(\mathrm{Mg_{atom}})-E_{\mathrm{tot}}[\mathrm{Mg(0001)_{per}}] \quad (1)$$

$$E_{\mathrm{ads}}(\mathrm{Pd})=E_{\mathrm{tot}}[\mathrm{Mg(0001)_{per}}]+E_{\mathrm{tot}}(\mathrm{Pd_{atom}})-E_{\mathrm{tot}}[\mathrm{Mg(0001)_{per+Pd_{atom}}}] \quad (2)$$

Where $E_{\mathrm{tot}}[\mathrm{Mg(0001)_{per}}]$, $E_{\mathrm{tot}}[\mathrm{Mg(0001)_{van}}$ and $E_{\mathrm{tot}}[\mathrm{Mg(0001)}$-$_{\mathrm{per+Pd_{atom}}}$ are the total energies of clean, vacancy defective and Pd atom coadsorption Mg (0001) surfaces, respectively; $E_{\mathrm{tot}}(\mathrm{Mg_{atom}})$ and $E_{\mathrm{tot}}(\mathrm{Pd_{atom}})$ are the total energies of single Mg or Pd atom in freedom states, respectively. The calculation results are listed in Table 1.

Based on the data of Table 1, it is found that the value of the vacancy formation energy $E_{\mathrm{van}}(\mathrm{Mg})$ of Mg atom on clean Mg(0001) surface presents positive, equal to 0.176 Ha; the values of the adsorption energy $E_{\mathrm{ads}}(\mathrm{Pd})$ of Pd atom at different sites (i.e. top, bridge, fcc and hcp sites) on clean Mg(0001) surface are all positive, too. This is suggested that Mg(0001) surfaces with Mg atom vacancy or Pd atom coadsorption can both exist stably. Due to the maximum value of $E_{\mathrm{ads}}(\mathrm{Pd})$ for the case of Pd atom coadsorption at hcp site on clean Mg (0001) surface, it can be concluded that hcp site is the preferable adsorption site of Pd atom on Mg(0001) surface. Therefore, the stable configuration of Mg(0001) surface with Pd atom adsorption at hcp site is employed to be the calculation model of Pd atom coadsorption Mg(0001) surface in this paper.

2 Results Analysis and Discussion

2.1 Adsorption configurations of H_2 on clean, vacancy defective and Pd atom coadsorption Mg(0001) surfaces

Table 1 The vacancy formation energy E_{van}(Mg) of Mg atom and adsorption energy E_{ads}(Pd) of Pd atom on clean Mg(0001) surface

Mg atom vacancy and Pd atom coadsorption	$E_{tot}[Mg(0001)_{per}]$/ Ha	$E_{tot}(Mg_{atom})$/ Ha	$E_{tot}(Pd_{atom})$/ Ha	$E_{tot}[Mg(0001)_{van}]$/ Ha	$E_{tot}[Mg(0001)_{per}+Pd_{atom}]$/ Ha	E_{van}(Mg)/ Ha	E_{ads}(Pd)/ Ha
Mg vacancy	-6003.026	-199.952	-	-5802.898	-	0.176	-
Pd coadsorption (top)	-6003.026	-	-4940.574	-	-10943.728	-	0.129
Pd coadsorption (bridge)	-6003.026	-	-4940.574	-	-10943.730	-	0.130
Pd coadsorption (fcc)	-6003.026	-	-4940.574	-	-10943.728	-	0.129
Pd coadsorption (hcp)	-6003.026	-	-4940.574	-	-10943.730	-	0.131

To investigate the effects of vacancy and Pd atom on the adsorption property of H_2 on Mg(0001) surface, the adsorption energies $E_{ads}(H_2)$ of H_2 on clean, vacancy defective and Pd atom coadsorption Mg (0001) surfaces are calculated, respectively. Subsequently, the average adsorption energies $\overline{E}_{ads}(H_2)$ are further calculated and compared based on the calculation results of $E_{ads}(H_2)$. The calculation equations of adsorption energy $E_{ads}(H_2)$ and average adsorption energy $\overline{E}_{ads}(H_2)$ are expressed as following[14]:

$$E_{ads}(H_2)=E_{tot}(\mathrm{surf})+E_{tot}(H_2)-E_{tot}(\mathrm{surf}+H_2) \tag{3}$$

$$\overline{E}_{ads}(H_2)=\frac{1}{N}[E_{tot}(\mathrm{surf})+E_{tot}(H_2)-E_{tot}(\mathrm{surf}+H_2)] \tag{4}$$

Where $E_{tot}(\mathrm{surf}+H_2)$ and $E_{tot}(\mathrm{surf})$ are the total energies of Mg(0001) surfaces with and without H_2 adsorption, respectively, $E_{tot}(H_2)$ is the total energy of free H_2 molecule, and N is the atomic number of metals which interact directly with H_2 adsorbed. The corresponding calculation results are listed in Table 2.

From Table 2, it is found that the values of adsorption energy of H_2 on three different surfaces all exhibit positive, which means that these adsorptions are exothermic and can perform easily. Because of the influences of both atomic kinds and numbers on the topmost layer of surface models, the value of adsorption energy $E_{ads}(H_2)$ (0.025 Ha) for the case of H_2 adsorption on clean Mg(0001) surface is evidently bigger than that of on vacancy defective (0.023 Ha) and Pd atom coadsorption (0.007 Ha) Mg(0001) surfaces. However, it is clear from the calculation results of average adsorption energies $\overline{E}_{ads}(H_2)$ that these values increase in the order of clean (0.004 Ha/atom), vacancy defective (0.005 Ha/atom) and Pd atom coadsorption (0.007 Ha/atom) Mg(0001) surfaces, which reveals that both vacancy defect and Pd atom benefit enhancing of the adsorption abilities of H_2 on Mg(0001) surface.

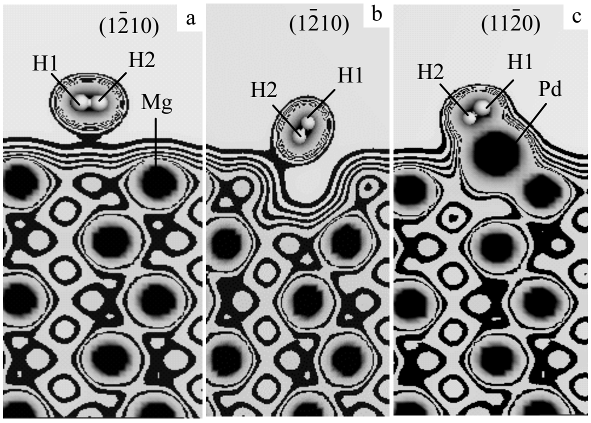

Fig.2 The electron density plots of the stable configurations of H_2 adsorption on clean, vacancy defective and Pd atom coadsorption Mg(0001) surfaces: (a)clean surface, (b) vacancy defective surface, and (c) Pd atom adsorption surface

Fig.2 presents the electron density plots of the stable configurations of H_2 adsorption on clean, vacancy defective and Pd atom coadsorption Mg(0001) surfaces. From Fig. 2ai t is found that no evident overlapping of electron cloud between H_2 and surface can be observed for the case of H_2 adsorption on clean Mg(0001) surface. The bond length between H and the nearest Mg atom is about 0.393 78 nm and bigger than the sum, i.e., 0.220 nm, of ionic radius of H^{1-}(0.154 nm) and Mg^{2+}(0.066 nm), which reveals that H_2 presents weak physisorption on clean surface. The bond length of H_2 adsorbed is 0.074 89 nm and nearly unchanged compared with that (0.074 76 nm) of free H_2 molecule. This is suggested that there is hardly any catalytic activity for H_2 dissociation on clean Mg(0001) surface. For the stable configuration of H_2 adsorption on vacancy defective Mg(0001) surface, as shown in Fig.2b, it is found that H_2 happens to twist and a little overlapping of electron cloud between H_2 and surface appears. Meanwhile, the bond length of H and the nearest Mg atom is about 0.360 15 nm, which is still bigger than the sum, i.e., 0.220 nm, of ionic radius of H^{1-}(0.154 nm) and Mg^{2+}(0.066 nm), but it decreases by about 0.034 63 nm compared with that of H_2 adsorption on clean Mg(0001) surface. Besides, the bond length of H_2 is also elongated as 0.075 56 nm, which means that the bond strength of H_2 is reduced to some extent. Based on this, it can be concluded that the vacancy defect not only enhances the physisorption ability of H_2 on Mg(0001) surface, but also exhibits some catalytic activity for H_2 dissociation[15]. For the stable configuration of Pd atom coadsorption Mg(0001) surface, it is found from Fig.2c that H_2 similarly happens to twists and a large overlapping of electron cloud between H_2 and Pd exists. The bond length between H and Pd atom is about 0.203 68 nm and evidently smaller than the sum, i.e., 0.234 nm

(0.219 nm), of ionic radius of H^{1-}(0.154 nm) and Pd^{2+}(0.080 nm)(Pd^{4+} 0.065 nm), which is suggested that there is a strong chemisorption interaction between Pd and H_2. Besides, it can also be seen that the bond length of H_2 adsorbed is elongated as 0.077 62 nm, meaning the bond strength of H_2 is reduced significantly compared with that of free H_2 molecule. Therefore, Pd atom coadsorbed on Mg(0001) provides a strong chemisorption for H_2; on the other hand, it also presents remarkable catalytic activity for H_2 dissociation [16].

The Mulliken population analysis of three stable configurations of H_2 adsorption on clean, vacancy defective and Pd atom coadsorption Mg(0001) surfaces is also performed and the corresponding results are listed in Table 3. It is found that H_2 adsorbed on clean Mg(0001) surface charges a little negatively (-0.015) and Mg atoms on the topmost layer charge a little positively (0.035), which is suggested that quite a few charges are transferred from Mg(0001) surface to H_2 adsorbed. For the case of H_2 adsorption on vacancy defective Mg(0001) surface, the charges of H_2 obtained from Mg (0001) surface increase compared with that of H_2 adsorption on clean Mg(0001) surface. For the case of Pd atom coadsorption Mg(0001) surface, the direction of charge transfer is just reverse to that of the former two cases, i.e., the charges happen to be transferred from Mg(0001) surface and H_2 to Pd atom. Here, both H_2 and Mg atoms on the topmost layer charge greatly positively (0.048, 0.109), whereas Pd atom charges greatly negatively (-0.524).

2.2 H_2 dissociation on clean, vacancy defective and Pd atom coadsorption Mg(0001) surfaces

From the calculation results of H_2 adsorption configurations on clean, vacancy defective and Pd atom coadsorption Mg(0001) surfaces, no spontaneous H_2 dissociation can be observed and the activation energy is essential during the process. To further investigate the catalytic activity of H_2 on three different surfaces, the dissociation energy barriers of H_2 and the corresponding minimal energy path (MEP) are calculated using Nudged Elastic Band (NEB) method [12]. The stable adsorption configurations of H_2 on three surfaces are chosen as the reactants of H_2 dissociation, and the stable adsorption configurations of two separate H atoms at two fcc sites on three surfaces are predicted as the products of H_2 dissociation. The energy and structural evolution of the systems for H_2 dissociation on clean, vacancy defective and Pd atom coadsorption Mg(0001) surfaces are shown in Fig.3.

From Fig.3a, it can be found that there is a high energy barrier (E_{bar1}=1.3774 eV) for H_2 dissociation on clean Mg(0001) surface. The bond length of H-H in the transition state (TS1) has been elongated as 0.125 11 nm, which is suggested that H_2 has dissociated completely. The calculation value of E_{bar1} is slightly bigger than that (1.15 eV) of literature[7], and it is also found that there are some differences among the corresponding structures of transition state, which possibly originate from the differences of the supercell sizes and calculation parameters. Besides, two dissociated H atoms are found to be absorbed at two near fcc sites on clean Mg(0001) surface, which keeps consistent with the predicted dissociation product. Similarly, there is also a high energy barrier (E_{bar2}=1.2221 eV) for H_2 dissociation on vacancy defective Mg(0001) surface, as shown in Fig. 3b. However, the value of E_{bar2} is reduced to some extent compared with that of E_{bar1}, which means that vacancy defect benefits decreasing of the energy barrier of H_2 dissociation. The bond length of H-H in the transition state (TS2) has been elongated as 0.129 59 nm, revealing a complete dissociation of H_2. Dissimilarly, a local minimal value (Meta 2) on the energy curve, shown in Fig.3b, can be observed. Here, although two dissociated H atoms are adsorbed at two near fcc sites on vacancy defective Mg(0001) surface, the corresponding adsorption configuration is different from that of the predicted product, and their inter-transformations need overcome the energy barrier (E'_{bar2}) for H atom diffusion on vacancy defective Mg(0001) surface. For the case of H_2 dissociation on Pd atom coadsorption Mg(0001) surface, shown in Fig.3c, the dissociation energy barrier (E_{bar3}=0.2860 eV) is reduced significantly compared with that on clean and vacancy defective Mg(0001) surfaces, which means that the activation energy required for H_2 dissociation is decreased due to the catalytic role of Pd atom. The bond length of H-H in the transition state (TS3) is 0.078 09 nm, close to that of free H_2 molecule. H_2 happens to dissociate rapidly only after adjusting the relative position to Pd atom. Besides, a local minimal value (Meta 3) on the energy curve as shown in Fig.3c can also be seen. Here, two dissociated H atoms are adsorbed at both sides of Pd atom, which is different from that of the predicted product. Likewise, their inter-transformations also need overcome a high energy barrier (E'_{bar3}) for H atom diffusion on Pd atom coadsorption Mg(0001) surface.

Table 2 The adsorption energies $E_{ads}(H_2)$ and average adsorption energies $\overline{E}_{ads}$ (H_2) of H_2 adsorption on clean, vacancy defective and Pd atom coadsorption Mg(0001) surfaces

Surface type	E_{tot}(surf)/Ha	$E_{tot}(H_2)$/Ha	$E_{tot}(surf+H_2)$/Ha	$E_{ads}(H_2)$/Ha	N	$\overline{E}_{ads}$ (H_2)/Ha·atom^{-1}
Clean	-6003.026	-1.164	-6004.215	0.025	6	0.004
Vacancy defective	-5802.898	-1.164	-5804.085	0.023	5	0.005
Pd atom adsorption	-10943.730	-1.164	-10944.901	0.007	1	0.007

Table 3 The Mulliken population analysis of the stable configurations of H_2 adsorption on clean, vacancy defective and Pd atom coad sorption Mg(0001) surfaces

Surface	e_{H1}	e_{H2}	$e_{\mathrm{H1+H2}}$	$e_{\mathrm{Mg/atom}}$	e_{Pd}
Clean	-0.007	-0.008	-0.015	0.035	-
Vacancy defective	-0.003	-0.039	-0.042	0.049	-
Pd atom coadsorption	0.019	0.029	0.048	0.109	-0.524

Note: $e_{\mathrm{Mg/atom}}$ represents the charge numbers of average per Mg atom on the topmost layer of Mg(0001) surfaces

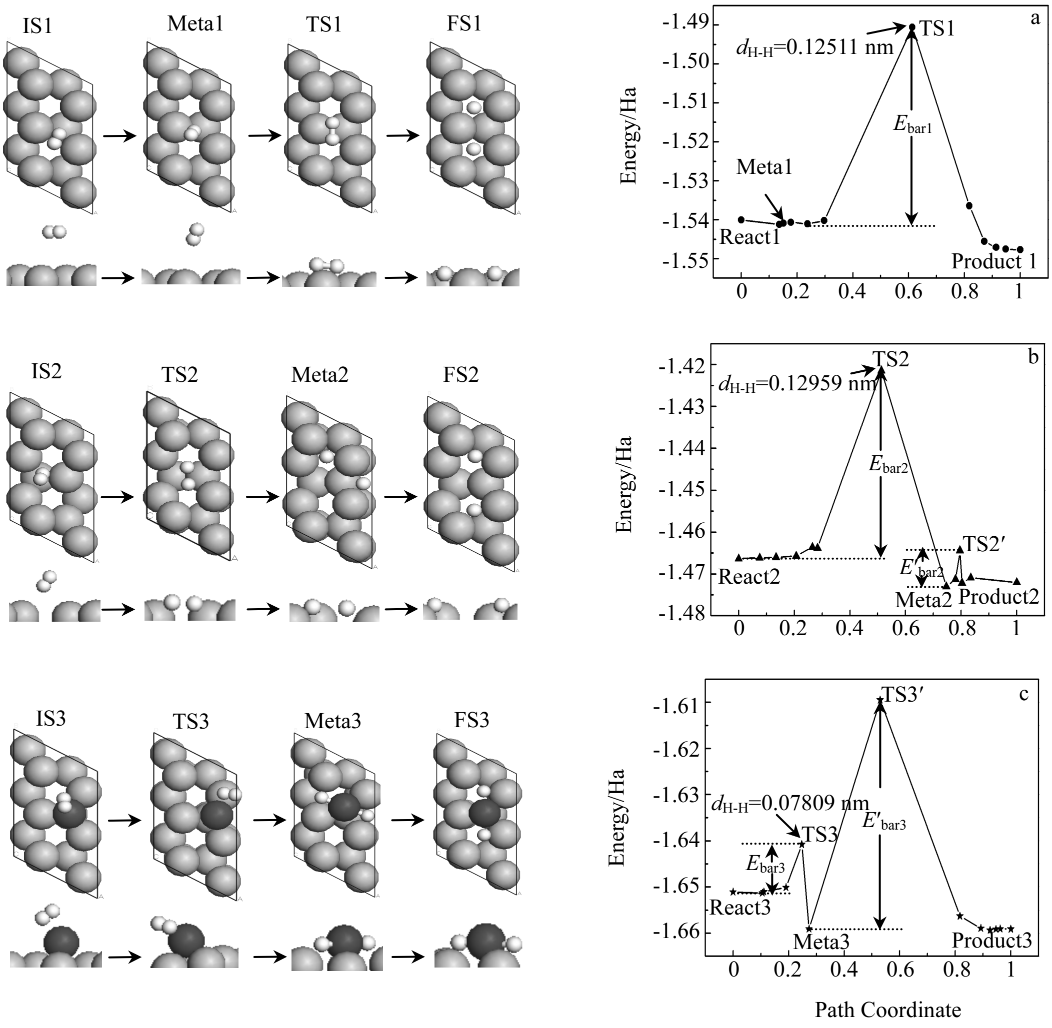

Fig.3 The energy and structural evolution of the systems for H_2 dissociation on clean, vacancy defective and Pd atom adsorption Mg(0001) surfaces: (a) clean surface, (b) vacancy defective surface, and (c) Pd atom adsorption surface

As far as the energy barriers of H_2 dissociation on three different Mg(0001) surfaces are concerned, a tendency of $E_{\mathrm{bar1}} > E_{\mathrm{bar2}} > E_{\mathrm{bar3}}$ can be found, which is suggested that the catalytic activities for H_2 dissociation on clean, vacancy defective and Pd atom coadsorption Mg(0001) surfaces are progressively enhanced. This is in good agreement with the results of the weakened degree of H-H bond strength in three stable adsorption configurations represented in the segment 2.1. Grounded on this, it can be concluded that vacancy defect and Pd atom not only enhance the physisorption or chemisorption interactions between H_2 and Mg surface, but also decrease significantly the energy barriers of H_2 dissociation, which may be the main reason of nanocrystalline magnesium with Pd catalyst possesses with fast hydrogenation kinetics [1]. Comparatively, the catalytic role of vacancy defect on H_2 dissociation is not as remarkable as that of Pd atom, and it is more likely to facilitate the diffusion of dissociated H atoms into Mg bulk [17].

2.3 The mechanism of vacancy defect and Pd atom favoring H_2 adsorption and dissociation on Mg (0001) surface

In order to investigate the underlying microscopic mechanism of vacancy defect and Pd atom benefiting H_2 adsorption and dissociation on Mg(0001) surface, the total and partial densities of states (DOS) of three different Mg (0001) surfaces with and without H_2 adsorption are both calculated, shown in Fig.4. From Fig.4a, it is found that the bonding peaks of per Mg atom on the topmost layer of clean Mg (0001) surface without H_2 adsorption are mainly located at the energy range between Fermi level E_F and -7 eV. The bonding electrons between -6 and 0 eV are mainly dominated by the valence electrons of Mg(s) and Mg(p) orbits of the topmost layer Mg atoms. The bonding electrons between -7 and-6 eV are contributed by the Mg(s) orbits of the topmost layer Mg atoms. Compared with the case of clean Mg(0001) surface, no evident change for the altitude of bonding peaks, and the energy ranges of per Mg atom on the topmost layer of vacancy defective Mg(0001) surface without H_2 adsorption can be observed as shown in Fig.4b. For the case of Pd atom coadsorption Mg(0001) surface, the bonding peaks of Pd atom adsorbed are mainly located at the energy range between

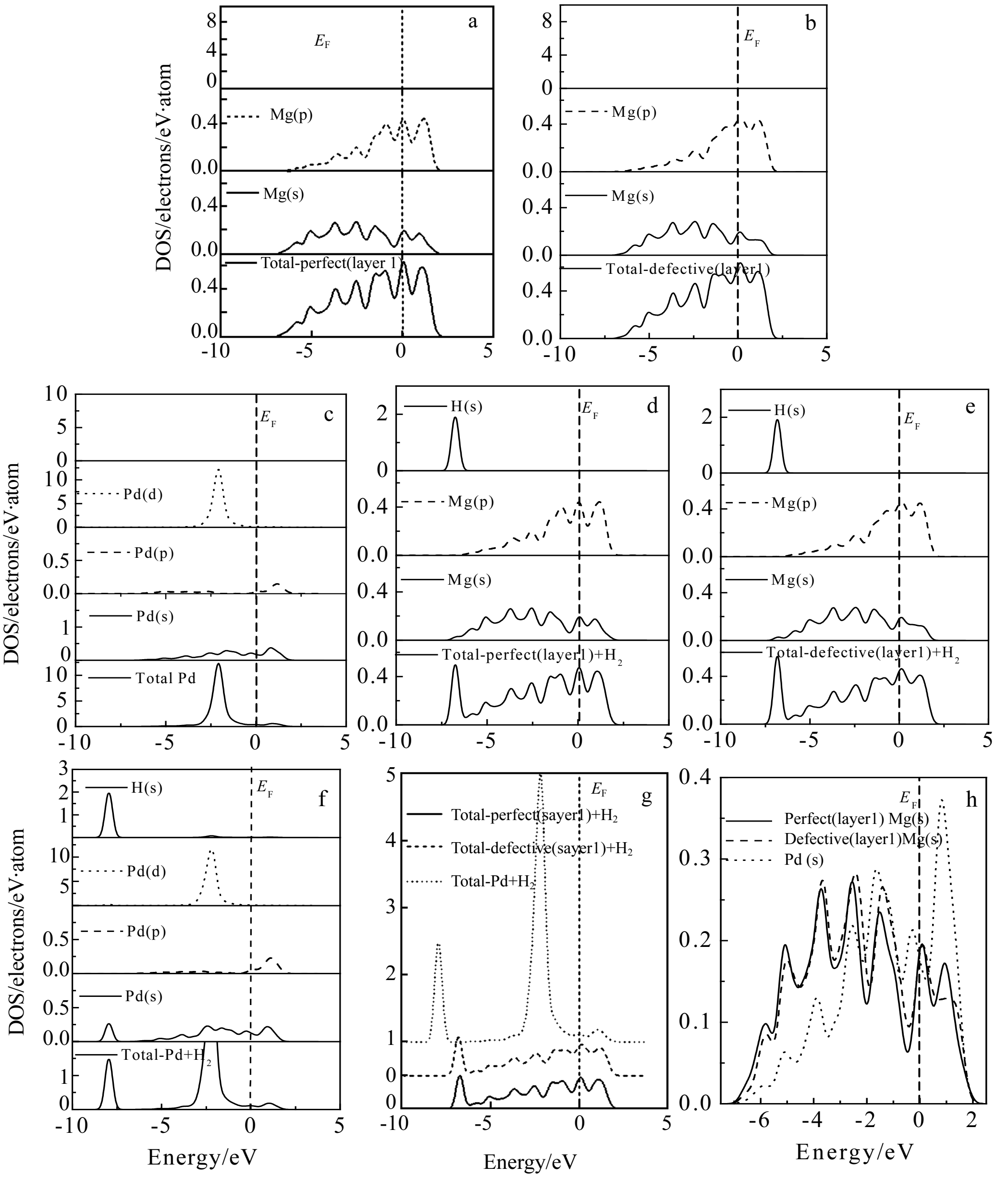

Fig.4 Total and partial density of states of average per Mg or Pd atom interacting directly with H_2 before and after H_2 adsorption on clean, vacancy defective and Pd atom coadsorption Mg(0001) surfaces: (a), (b), (c) density of states of metal atoms interacting directly with H_2 before H_2 adsorption on three surfaces;(d)，(e)，(f) density of states of metal atoms interacting directly with H_2 after H_2 adsorption on three surfaces, (g) the comparison of total density of states of metal atoms interacting directly with H_2 after H_2 adsorption on three surfaces; (h) the comparison of partial density of states of *s* orbital of metal atoms interacting directly with H_2 before H_2 adsorption on three surfaces

E_F and -6.5 eV. The bonding electrons between -2.5 and 0 eV mainly come from the valence electrons of Pd (s) and Pd (d) orbitals. The bonding electrons between -6.5 and -2.5 eV mainly originate from the contribution of valence electrons of Pd (s) and a few Pd(p) orbits. After H_2 adsorption, the total and partial densities of states (DOS) of Mg and Pd atoms interacting directly with H_2 present significant change as shown in Fig.4d-4f. For the case of clean and vacancy defective Mg (0001) surfaces with H_2 adsorption, as shown in Fig.4d and 4e, a new bonding peak appears at the low energy region between -7.5 and -6.3 eV, which are the interactions H(s) and a few Mg (s) electrons. This is suggested that there is a weak physisorption interaction between H_2 and Mg atoms of the topmost layer on clean and vacancy defective Mg(0001) surfaces. Besides, the partial densities of states of Mg(s) of the topmost layer shift slightly to the low energy region due to the influence of H_2 adsorbed, whereas the change of partial densities of states of Mg(p) is not so apparent. For the case of Pd atom coadsorption Mg(0001) surface with H_2 adsorption, as shown in Fig.4f, it is found that there is a new bonding peak appearing at the low energy region between –8.5 and –7.5 eV after H_2 adsorption, which are mainly from the contributions of H(s) and Pd(s) orbits. This means that there exists a strong chemisorption interaction between H_2 and Pd. Meanwhile, a new bonding peak can also be seen between –8.5 and –7.5 eV for the partial densities of states of Pd(s). Further analysis of the total densities of states of Mg or Pd atoms interacting directly with H_2 after H_2 adsorption is performed as shown in Fig. 4(g). It is noticed that these densities of states shift to the low energy region and the altitude of bonding peaks below E_F is elevated progressively in the order of clean, vacancy defective and Pd atom coadsorption Mg(0001) surfaces, which may be the main reason for increasing of adsorption abilities of H_2 on three different surfaces.

Based on the analysis above-mentioned, it can be found that the changes of densities of states of Mg or Pd atoms interacting directly with H_2 are mainly caused by the changes of partial densities of states of their respective *s* orbits, meaning that the electrons of Mg(s) or Pd(s) orbits play a significant role on H_2 adsorption and dissociation. Therefore, further comparison of the partial densities of states of *s* orbits of Mg or Pd atoms on the topmost layer is done as shown in Fig.4h. It is found that the partial densities of states of Mg(s) between –7 and –4 eV for clean Mg(0001) surface are significantly higher than that for vacancy defective Mg(0001) surface, whereas the one between –4 and 0 eV is just reverse. For the vacancy defective Mg(0001) surface, more bonding electrons happen to shift from low energy region to E_F, which benefits increasing of the bonding electrons around E_F and improving of the catalytic activity of Mg surface [18]. This may be the main reason for vacancy defect enhancing the adsorption and dissociation abilities of H_2 on Mg (0001) surface. For Pd atom coadsorption Mg (0001) surface, the partial densities of states of Pd(s) between -7 and -2 eV are evidently lower than that of Mg(s) of clean and vacancy defective Mg(0001) surfaces, whereas the one between -2 and 0 eV is just reverse. More bonding electrons around E_F are favoring in improving of the catalytic activity of H_2 adsorption and dissociation of Pd atom coadsorption Mg(0001) surface.

3 Conclusions

1) Model of H_2 adsorption on clean Mg(0001) surface is weak physisorption, and minute quantity of charges are transferred from Mg surface to H_2. Meanwhile, there is a high energy barrier, i.e., 1.3774 eV, when H_2 is dissociated into two separate hydrogen atoms.

2) Vacancy defect benefits enhancing of the physisorption interaction between H_2 and Mg surface, which makes the quantity of the charges transferred from Mg surface to H_2 adsorbed be increased significantly; the energy barrier, i.e., 1.2221 eV, of H_2 dissociation is reduced to some extent, too.

3) For the Mg(0001) surface with Pd atom coadsorption, there is a strong chemisorption interaction between the Pd atom and H_2 adsorbed, and the charges are reversely transferred from H_2 to Pd atom. Due to the excellent catalytic effect of Pd, the energy barrier, i.e. 0.2860 eV, of H_2 dissociationis reduced remarkably.

4) The catalytic activity for H_2 adsorption and dissociation on three different surfaces is closely related to the bonding electrons number of *s* orbital of the topmost layer metal atoms which interact directly with H_2 around Fermi level.

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氢分子在 Mg(0001)表面的吸附与解离性能研究

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摘 要：采用基于密度泛函理论的第一原理计算方法，研究了氢分子(H_2)在清洁、空位缺陷及 Pd 原子吸附的 Mg(0001)表面的吸附与解离性能。结果显示：H_2在清洁 Mg(0001)表面呈较弱的物理吸附，H_2解离需克服较高的能垒(1.3774 eV)；空位缺陷的存在增强了 Mg 表面对H_2的物理吸附能力，且使H_2的解离能垒(1.2221 eV)有所降低；而清洁表面吸附的 Pd 原子则会与H_2产生强烈的化学吸附作用，极大地降低了H_2的解离能垒(0.2860 eV)。电子结构分析发现：3 种表面对H_2吸附与解离的催化活性与 Mg(0001)表面最上层与H_2直接产生吸附作用的金属原子在费米能级(E_F)附近 s 轨道的成键电子数密切相关。

关键词：Mg(0001)表面；吸附；解离；能垒

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