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Theoretical study of hydrogen dissociation and diffusion on Nb and Ni co-doped Mg(0001): A synergistic effect

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ABSTRACT

The interaction of H_2 with clean, Ni and Nb doped Mg(0001) surface are investigated by first-principles calculations. Individual Ni and Nb atoms within the outermost surface can reduce the dissociation barrier of the hydrogen molecule. They, however, prefers to substitute for the Mg atoms within the second layer, leading to a weaker catalytic effect for the dissociation of H_2, a bottleneck for the hydriding of MgH_2. Interestingly, co-doping of Ni and Nb stabilizes Ni at the first layer, and results in a significant reduction of the dissociation barrier of H_2 on the Mg surface, coupled with an increase of the diffusion barrier of H. Although codoped Ni and Nb shows no remarkable advantage over single Nb here, it implies that the catalytic effect could be optimized by co-doping of "modest" transition metals with balanced barriers for dissociation of H_2 and diffusion of H on Mg surfaces.

1. Introduction

The availability of an economical, safe, and practical hydrogen storage mechanism is critical for the environment and energy friendly hydrogen economy. Mg is an attractive option due to its light weight, low cost, abundance and high hydrogen storage capacity up to 7.6% [1]. Unfortunately, high thermodynamic stability and slow kinetics of dehydrogenation and hydrogenation have hindered its practical applications [2,3].

Transition metals (TMs) doping is a widely used processing technique to improve the hydrogen storage materials. In the Mg system, it is expected to weaken the Mg–H bond and reduce the stability of the hydride. There are many literatures reported that the catalytic effect of Nb_2O_5 is superior in absorption as well as desorption [4–6]. Huot et al. have shown that MgH_2 with 5% of Nb leaded to the formation of a new bcc phase and improved the kinetics of MgH_2 during both adsorption/desorption [7,8]. Because niobium does not alloy with Mg nor form intermetallic compounds, these will be heterogeneously catalyzed materials [9]. Nb acts as a very efficient catalyst in the desorption of H_2 from MgH_2 [10].

Interestingly, *multiple* additions are often found to have a more remarkable effect in improving desorption kinetics of MgH_2 than that of a *single* addition in general, such as V + Zr or Mn + Zr [11], Zr + Ni [12], Ni + Y [13] and $Cr_2O_3 + Nb_2O_5$ [14].

From the theoretical point of view, there are some literatures on TM elements acting as a catalyst for hydrogen absorption on the Mg surface to improve its kinetics. Ni doped Mg(0001) surface are investigated by Pozzo et al. [15]. It was shown that the alloying of Ni and Nb with MgH_2 lower the heat of formation [16]. Most of these theoretical studies, however, were based on an assumption that TMs (or vacancies) are located at the outmost layer of Mg. Banerjee et al. reported that Ti, V, and Ni preferred to substitute one of the Mg atoms from the second layer than the top and thus reduced their catalyst effect [17]. Meanwhile, a co-doping of V and Ni could stabilize Ni at the first layer and thus maintained the high catalytic effect of Ni for the dissociation of H_2 [18]. In our earlier study, the stability of a series of TMs (Ti, V, Zr, Fe, Ru, Co, Rh, Ni, Pd, Cu, Ag) on Mg(0001) surface was investigated systemically, and found that all the single TM prefers to the second layer, while some TMs could be stabilized at the outmost layer by co-doping [19]. For instance, Ni and Co are easy to be pushed to the first layer when co-doped with Ti, V, and Nb.

Meanwhile, hydrogen dissociation and diffusion on the surface are critical for the kinetic process of Mg based materials of hydrogen storage. In this paper, we have conducted a systematic investigation of Ni and Nb-doped Mg surface, focusing on the dissociation and diffusion of hydrogen. It is found that the dissociation barrier is significantly lowered when Ni is located at the first layer, but the barrier is hardly reduced in the case of Ni at the energetically favored second layer. For Nb doped cases, the dissociation barrier is reduced for Nb at both first and second layers, in particular at the first layer. When Ni and Nb are co-doped on the Mg(0001) surface, it significantly

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reduces the dissociation barrier of the hydrogen molecule as the earlier reported Ni and V co-doped system. Our finding might be useful for the design of hydrogen storage media with high efficiency.

2. Computational method

Our calculations were performed with the *ab initio* simulation package VASP [20]. Perdew–Burke–Ernzerhof functional was used for the calculation of the exchange-correlation energy [21]. The electron-ion interactions are described with projector augmented wave (PAW) method [22]. For all the calculations, the plane wave cutoff energy was set to be 400 eV. For all the relaxation, the energy difference of 10^{-4} eV was set as the convergence criterion between successive ionic steps and the forces on each atom were minimized up to 0.01 eV/Å.

The optimized lattice constants of bulk Mg(a, c) are 3.19 Å, 5.19 Å and the cohesive energy (E_{coh}) is 1.51 eV/atom in our calculations, which are in agreement with the experimental values ($a = 3.21$ Å, $c = 5.21$ Å, $E_{coh} = 1.51$ eV/atom) [23,24] The clean, and single TM-doped Mg(0001) surfaces were modeled by a five-layer 3×3 slab, while the surfaces of two TM-doped Mg(0001) surfaces were modeled by a five-layer 3×4 slab. Monkhorst-Pack grids of (5×5×1) is used in the Brillouin zone sampling [25] for 3×3 and 3×4 slabs. The top three layers in each slab are full relaxed in the calculations, while the bottom two layers are fixed at their bulk configurations. The vacuum space was set to 15 Å to guarantee a sufficient separation between the periodic images. The surface energies are calculated to be 0.29 eV/atom, which is in good agreement with previous reports [17].

To determine activation barriers for dissociation and diffusion of hydrogen on the doped surfaces, the nudged elastic band (NEB) method [26] was used.

3. Results and discussion

3.1. Hydrogen dissociation and diffusion on Nb and Ni individually doped Mg(0001)

Before discussing the dissociation and diffusion of hydrogen on single Nb or Ni doped Mg(0001) surface, we briefly describe the stability of individual Nb or Ni atom on Mg surface. Ni and Nb are thermodynamically favorable to substitute one of the Mg atoms from the second layer than that from first layer. The differences in energy between the first and second layer for Ni and Nb are 0.143 and 0.707 eV, respectively. More details on the stability of TMs on Mg(0001) surface could be found in Ref. [19].

Subsequently, we have calculated the activation barrier for the dissociation and diffusion of hydrogen molecule on the clean Mg surface. The hydrogen molecule preferably dissociates over a bridge site than the top site [17], and the hydrogen atoms preferably occupy the face center cubic (fcc) and hexagonal closed packed (hcp) holes after dissociation, respectively. The activation barrier for the dissociation of hydrogen molecule on the clean Mg(0001) surface is calculated to be 0.882 eV, which is in good agreement with previously reported values (listed Table 1). The minor differences between our calculated data and the literature could be due to the difference of the plane wave cutoff energy and H positions adopted in the simulations. The barrier height for the diffusion of hydrogen atoms is estimated to be 0.105 eV. This suggests that in the case of the clean Mg surface, the dissociation of hydrogen will govern the rate limiting step in the hydriding process of Mg.

The dissociation of hydrogen molecule on single Ni and Nb doped Mg(0001) surface is also studied by placing the TM atoms in the outmost and the second layers of the surface. For the cases with TM on the outmost layer, H_2 is initially placed about 3.5 Å over the Mg surface parallel. Then H_2 is dissociated to two hollow sites before one H moves to the next hollow site (c.f Fig. 1) to stabilize the adsorption. It has been found that the dissociation of hydrogen molecule requires small activation energy. The activation barrier for dissociation is found to be 0.137 eV and 0 for the Ni and Nb cases, respectively. We also have calculated the diffusion behavior of hydrogen atoms on the doped Mg surface. The diffusion barriers of hydrogen atom from the adsorption site to the next hollow site (in the Fig. 1) are estimated to be 0.433 and 0.811 eV for Ni and Nb doped cases, respectively. The difference in the barrier energy is consistent to the M–H bond energy. Moreover, the lower diffusion barrier for the Ni doped Mg surface suggests its better catalytic performance than Nb.

When the TM atoms are placed in the second layer of the surface (in Fig. 1), similar processes are simulated. The activation barriers for dissociation are found to be 0.861 and 0.300 eV for the cases of Ni and Nb, respectively. The diffusion barriers of hydrogen atom from the adsorption site to the next hollow site (in the Fig. 1) are estimated to be 0.204 eV for Ni and 0.082 eV for Nb, respectively. Obviously, the reduction of rate limiting dissociation barrier is more remarkable when the TMs at the outmost layer.

We also investigated the relation between the d-band centre of Ni and Nb and the dissociation (diffusion) barriers. The d-band centers are found to be −1.018, −0.143, and 0.08 eV for Ni ,Nb, and V, respectively, when they are in the first layer. It is found that the higher

Table 1
Calculated adsorption energy, activation and diffusion barriers for H, with a comparison to available the theoretical and experimental data.

	Hydrogen absorption energy (eV)	Activation barrier for dissociation (eV)	Activation barrier for diffusion (eV)	Hydrogen absorption energy (eV)	Activation barrier for dissociation (eV)	Activation barrier for diffusion (eV)
Pure Mg surface (Expt.)	-0.056^{a} -0.066^{b} -0.05^{c}	0.882^{a} 0.97^{b} 0.87^{c} 1.05^{d} 0.75 ± 0.15^{e}	0.105^{a} 0.26^{b} 0.18^{c} 0.182^{d}	…	…	…
	Substitution surface	TM at the first layer		Substitution surface	TM at the second layer	
Nb doped Mg surface	-0.658^{a}	0^{a}	0.811^{a}	-0.074^{a}	0.300^{a}	0.082^{a}
V doped Mg surface	-0.67^{b}	0^{b}	0.73^{b}	-0.132^{b}	0.56^{b}	0.12^{b}
Ni doped Mg surface	-0.398^{a} -0.37^{b}	0.137^{a} 0.124^{b} 0.06^{c}	0.433^{a} 0.45^{b} 0.27^{c}	-0.136^{a} -0.092^{b}	0.861^{a} 0.78^{b}	0.204^{a} 0.22^{b}

[a] This work.
[b] Reference [18].
[c] Reference [16].
[d] Reference [30].
[e] Reference [31].

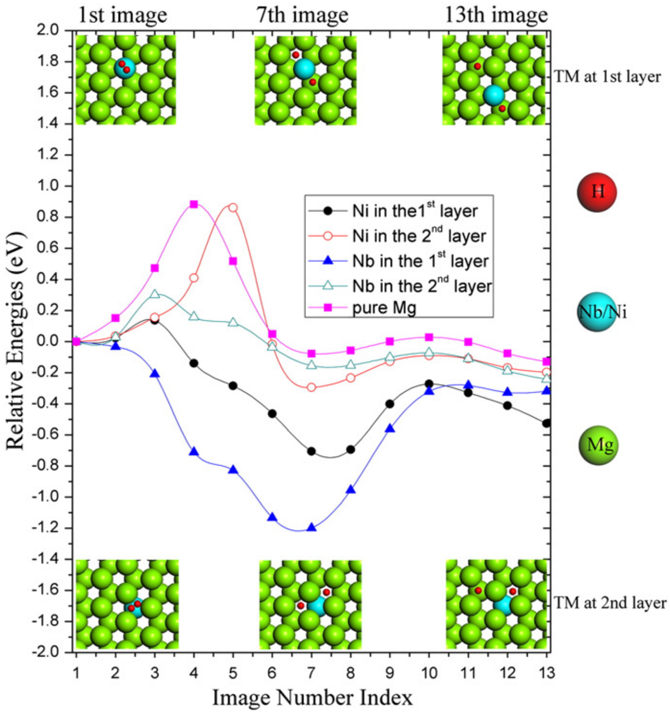

Fig. 1. NEB profiles for the dissociation and diffusion of hydrogen molecule on clean and Nb/Ni doped Mg surfaces. Solid squares are corresponding to the clean Mg surfaces, while solid (open) circles, solid (open) triangles are corresponding to the Ni and Nb doped in the first (second) layer of Mg(0001) surfaces, respectively. The corresponding configurations of the initial, final state of dissociation, and final states of the diffusion are shown in the upper and lower panels.

d-band centre of Nb is accompanied by a lower dissociation barrier and a higher diffusion barrier than those of Ni, in good agreement with the earlier reported results [27]. The d-band centers are found to be −1.027, −0.251, and 0.06 eV for Ni, Nb, and V located in the second layer, respectively. However, their relations to the barriers are changed as the higher d-band centre (Nb) is accompanied by a lower dissociation and diffusion barriers. This indicates that the dissociation of H_2 is dominated by Mg atoms when Ni and Nb are located at the second layer.

3.2. Hydrogen dissociation and diffusion with the Nb, Ni co-doped Mg surface

The single doped metals in the second layer of Mg surface are energetically preferable, leading to a significantly reduced catalyst effects for the dissociation of H_2. It is crucial to stabilize the doped metals at the first layer of Mg surface to enhance their catalyst effect. In literature, it was reported that Ni could be stabilized at the first layer with co-doping of V [18]. According to our earlier investigation [19], Ni and Nb prefer to be adjacent with Nb and Ni staying in the second and first layer, respectively, when they are co-doped on the Mg surface. In particular, there is a dip around the local structure of Ni in the co-doped configuration, which might improve the adsorption as mentioned in Ref. [18].

The interaction of hydrogen molecule with the Nb and Ni co-doped Mg surface is then studied in two steps. In the first step, the hydrogen molecule approaches the Mg surface and dissociates into two H atoms, and in the second step the hydrogen atoms are diffused on the surface to stabilize their adsorption.

Here we find that the hydrogen atoms prefer on the top of Ni atom as a meta-stable state after the dissociation, although they are energetically favored at the three-fold hollow sites. The possible final configurations for the two H atoms after diffusion could be as following (c.f. Fig. 2): (1) Two hydrogen atoms occupy two hcp site with one H atom above the Nb atom (S1); (2) two hydrogen atoms occupy two hcp sites above Mg atoms (S2); (3) two hydrogen atoms occupy fcc sites near the Nb atom (S3); (4) two hydrogen atoms occupy the fcc sites with one near the Nb atom and one away from it (S4); (5) the H atoms are located at the fcc site away from Nb and the hcp sites above Nb (S5); and (6) the H atoms occupy the fcc and the hcp site away from the Nb atom (S6).

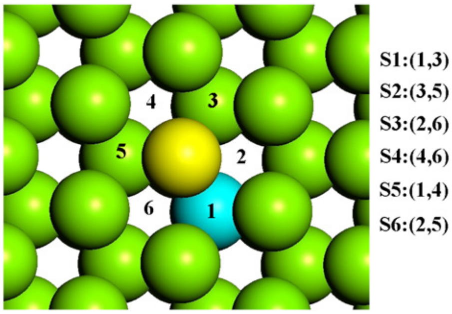

Fig. 2. Possible absorption configurations of the dissociated H on the Nb and Ni co-doped Mg(0001) surface. Mg, Ni, Nb, and H atoms are denoted by green, yellow, blue, and red balls., and numbers 1, 2, 3, 4, 5, and 6 represent various possible H adsorption sites.

The average binding energy is defined as:

$$E_b = \left(E_{\mathrm{NiNb/Mg(0001)+2H}} - E_{\mathrm{H_2}} - E_{\mathrm{NiNb/Mg(0001)}} \right) / 2 \tag{3}$$

Where $E_{\mathrm{NiNb/Mg(0001)\,+\,2H}}$ is the total energy of the system with the adsorption of two hydrogen atoms, $E_{\mathrm{NiNb/Mg(0001)}}$ is the energy of the Nb and Ni co-doped Mg(0001) surface., $E_{H_2}$is the energy of H_2. The average binding energies are listed in Table 2.

We find that configuration S5 is energetically favored (c.f. Table 2). Theoretically, the TM elements act as good catalysts because of the availability of *d* electrons for donation and vacant *d* states for back donation. In Fig. 3, we depicted the PDOS of H, Ni, and Nb before and after dissociation (configuration S5) for comparison. In Fig. 3(a) and (c), there is no overlap between the Ni *d* and H *s* levels and a peak of hydrogen appears at −6.99 eV below the Fermi level. The *d* levels of Ni and Nb (Figure (c)) show a broad peak for the *d* levels and it shows little magnetism as the DOS spin up and down channels are nearly symmetrical. After the interaction with hydrogen, two distinct features are observed: (1) the new peak of H is blue-shifted with respect to that of pure hydrogen; (2) the appearance of a small new peak of s levels of Ni and Nb (Fig. 3(b)). Moreover, the PDOS of Nb (Fig. 3(d)) has changed remarkably after the interaction with hydrogen, indicating a strong influence on Nb atom even at the second layer by the dissociated hydrogen atoms.

After the favorable adsorption configuration for the dissociated H atoms on the Ni-Nb co-doped Mg surface was obtained, we investigated the activation barrier for the dissociation of hydrogen molecule along the minimum energy path by NEB method. It is found that the dissociation of hydrogen molecule on the Ni site requires an activa-

Table 2
The average binding energy of the dissociated H atoms at various adsorption configurations on the Mg(0001) surface (c.f. Fig. 2).

Configuration	Binding energy (eV/H)
S1	−0.343
S2	−0.183
S3	−0.052
S4	−0.130
S5	−0.398
S6	−0.126

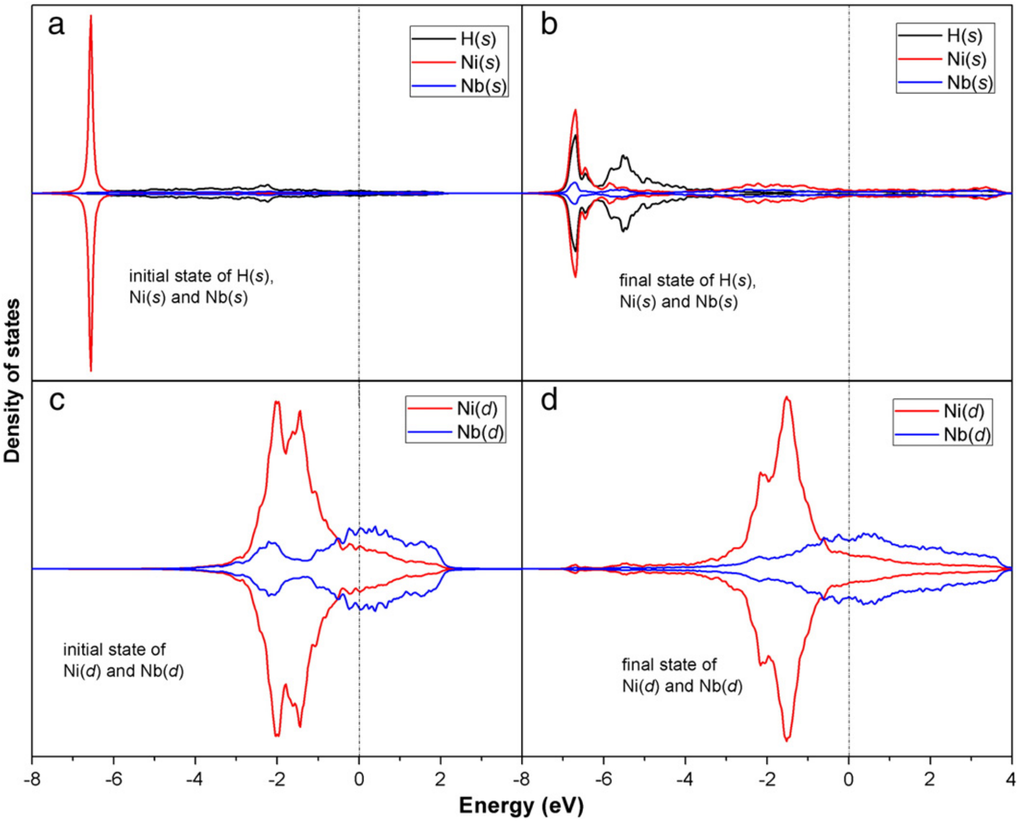

Fig. 3. Projected densities of states for H, Ni, and Nb before and after H_2 dissociation on Mg(0001) surface. Subplots (a) and (c) are corresponding to the PDOS of H(*s*), Ni(*s*,*d*), and Nb(*s*,*d*) of initial states (before dissociation), while (b) and (d) are corresponding to that after dissociation (final state). The H, Ni and Nb are represented by black, red and blue lines, respectively.

tion barrier of 0.117 eV as shown in Fig. 4, followed by a migration toward the most stable hollow sites. This is significantly lower than that of the clean Mg surface, where the activation barrier is found to be 0.882 eV.

The activation barrier for the diffusion of hydrogen atom has been calculated with 5 replicas for two possible *surface* migration ways. One possible path is that the hydrogen moves from the fcc site near Ni (distance of Ni-H is 1.62 Å) to a hcp site (distance of Ni-H is 3.03 Å). The corresponding reaction path is shown in Fig. 4, with a calculated barrier of diffusion of 0. 634 eV. The barrier of diffusion is higher than that of pure Mg, which is 0.26 eV [17]. An alternative way is that the hydrogen atom moves from the hcp site near Ni (distance of Ni-H is 1.69 Å) to a fcc site (distance of Ni-H is 4.19 Å). The barrier of diffusion is 1.026 eV, which is even higher than the first case. It indicates that the diffusion barrier could be raised up, although the co-doping of Ni and Nb reduces the rate limiting dissociation barrier significantly. Meanwhile, we notice that single doped Nb could diffuse into bulk from the 2nd layer since its stability inside the bulk is expected to be comparable to that at the 2nd layer [28]. While the co-doped Ni and Nb pair could be also diffuse into bulk, it is expected much more difficult than that for single Nb as the adjacent Ni and Nb configuration is the most stable one among the studied cases.

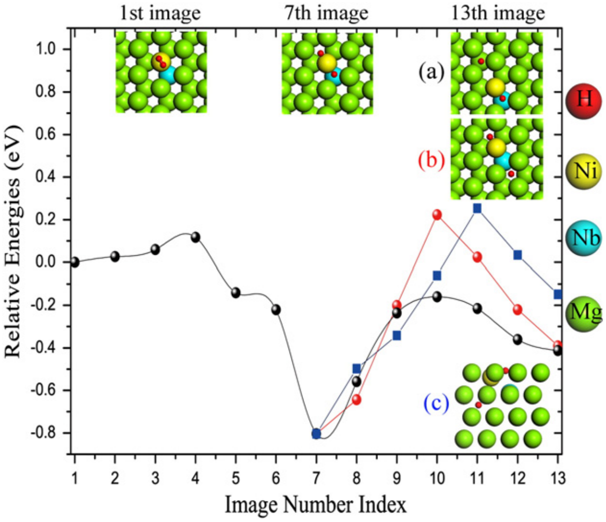

Fig. 4. NEB profiles for the dissociation and diffusion of hydrogen on the Ni and Nb co-doped Mg surface with Ni and Nb atoms located at the first and second layers, respectively. The structures of Nb and Ni co-doping in Mg surface for the initial, final state of dissociation, and final states of the diffusion are shown in the insets, with three possible final states of the diffusion considered, (a), (b), and (c).

We also investigated the possible hydrogen diffuse into *bulk*. The diffusion barrier and the configuration of final state are illustrated in Fig. 4. The calculated barrier on Ni and Nb co-doped Mg (0001) surface is 1.05 eV, which is greater than that of pure Mg, 0.58 eV as we calculated or 0.45 eV from Ref. [29]. The configuration of the transition state on Ni and Nb co-doped surface and corresponding projected DOS's of Ni 4s, 3d, and H 1s are illustrated in Fig. 5. The hybridization of H 1s and Ni 4s, 3d indicates that the interaction between H and Ni is rather strong even at the transition state. In fact, the adsorption of H at the transition state is stronger than that on clean Mg surface (0.131 eV vs. 0.263 eV, with respect to the energy of H in its molecule). However, the strong interaction of H with Ni, with −0.399 eV of H adsorption energy, at the initial state of the *diffusion* results in an increased diffusion barrier, coupled with the decrease of the dissociation barrier of H_2. It implies that “modest” transition metal catalysts are required to optimize the hydriding of Mg with balanced barriers for dissociation of H_2 and diffusion of H on Mg surfaces.

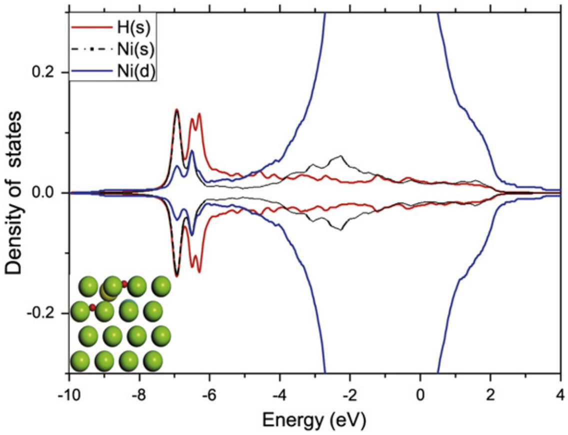

Fig. 5. The PDOS of H and Ni at the transitional state of H diffusion towards bulk on the favorable Ni and Nb co-doped Mg surface. The structure of the transitional state is illustrated in the inset.

We noticed that the dissociation barrier and diffusion barrier of (V, Ni) were reported to be 0.098 and 0.41 eV, respectively [18]. Since the catalytic effect of (Nb, Ni) co-doping is rather similar to that of (V, Ni) co-doped Mg–H systems, we further investigated the d-band center of Ni in both co-doped systems, which were calculated to be −1.52 and −1.46 eV for Ni in (V, Ni) and (Nb, Ni) cases, respectively. According to Ref. [27], the diffusion barriers of H on TMs on the Mg surface increase as the d-band center increases, while the dissociation barrier of H_2 changes reversely. Here, our calculated diffusion barrier of (Nb, Ni) is greater than that of (V, Ni) case, in line with the rule summarized in Ref. [27].

4. Conclusion

We have performed a systematic theoretical investigation of hydrogen dissociation and diffusion on the Nb and Ni individually and co-doped Mg(0001) surface. We find: (i) when Nb and Ni are located at the outermost layer, they can significantly reduce the rate limiting dissociation barrier in the hydriding process of Mg, though it is accompanied by a slightly increased barrier for diffusion. (ii) Nb and Ni prefer to stay in the second layer, and thus that their catalytic effect for the dissociation is weakened. (iii) On the most stable Ni and Nb co-doped Mg(0001) surface, we found that the rate limiting dissociation barrier of H_2 is significantly reduced by the co-doping of Ni and Nb, while the diffusion barrier of H atoms gets higher with respect to that of pure Mg surface.

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