American Journal of Analytical Chemistry, 2016, 7, 34-42
Published Online January 2016 in SciRes. http://www.scirp.org/journal/ajac
http://dx.doi.org/10.4236/ajac.2016.71004

First-Principles Investigation of Energetics and Electronic Structures of Ni and Sc Co-Doped MgH_2

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Received 10 December 2015; accepted 18 January 2016; published 22 January 2016

Abstract

First-principles calculations were used to study the energetics and electronic structures of Ni and Sc co-doped MgH_2 system. The preferential positions for dopants were determined by the minimal total electronic energy. The results of formation enthalpy indicate that Ni and Sc co-doped MgH_2 system is more stable than Ni single-doped system. The hydrogen desorption enthalpies of these two hydrides are investigated. Ni and Sc co-doping can improve the dehydrogenation properties of MgH_2. The lowest hydrogen desorption enthalpy of 0.30 eV appears in co-doped system, which is significantly lower than that of Ni doping. The electronic structure analysis illustrates that the hybridization of dopants with Mg and H atom together weakens the Mg-H interaction. And the Mg-H bonds are more susceptible to dissociate by Ni and Sc co-doping because of the reduced magnitude of Mg-H hybridization peaks. These behaviors effectively improve the dehydrogenation properties of Ni and Sc co-doped cases.

Keywords

First-Principles Calculation, MgH_2, Stability, Enthalpy, Dehydrogenation Property, Electronic Structure

1. Introduction

Hydrogen energy with high efficiency and pollution-free characteristics [1]-[5], is considered to be one of the most promising candidates to replace fossil fuels. The safe and cost-effective hydrogen storage methods are

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How to cite this paper: Sun, G.L., Li, Y.Y., Zhao, X.X., Mi, Y.M. and Wang, L.L. (2016) First-Principles Investigation of Energetics and Electronic Structures of Ni and Sc Co-Doped MgH_2. *American Journal of Analytical Chemistry*, **7**, 34-42.
http://dx.doi.org/10.4236/ajac.2016.71004

some of the key factors for its practical applications [2]. It is desirable for the hydrogen "container" to have high gravimetric capacities, store and transport hydrogen economically and conveniently [3]-[5]. Storing hydrogen chemically in solid hydrides with atomic state has the potential to fulfill these requirements. Among solid hydrides, magnesium hydride (MgH_2) has been investigated extensively in the last two decades due to its high hydrogen storage capacity (7.6 wt%), good cyclability, cheap cost and lightweight of magnesium [5]-[7]. Unfortunately, a high thermodynamic stability and poor kinetics in the reaction of hydrogenation and dehydrogenation hampered practical applications of MgH_2 [6]-[8].

Over the past several decades, many efforts have been made to overcome these disadvantages. Reducing the grain size [7]-[9], and introducing transition metals (TM) or transition metals oxides [10]-[14], can effectively improve the absorption/desorption kinetics of MgH_2. Among these two methods, the introduction of transition metals into MgH_2 has played a vital role in the development of Mg-based hydrogen storage materials. The thermodynamic properties and dehydrogenation kinetics of MgH_2 can be tuned by doping it with different TM [10] [14]. Larsson *et al*. [14] carried out first-principles calculations based on DFT which showed that Ti, V, Fe, and Ni significantly lowered the H_2 desorption energies of MgH_2 nanoclusters and improved these dehydrogenation properties. Pozzo *et al*. [15] observed that Ni is the best possible choice of the transition metal doped on Mg(0001) surfaces due to low activation barriers for hydrogen dissociation and diffusion processes. More recently, many researchers reported that the hydrogen desorption kinetics of MgH_2 can further be tuned by multi-doping it with different TM [16]-[22]. A computational study carried out by Huang *et al*. [17] showed that the capacity retaining rate of $Mg_{1.5}Ti_{0.5}Ni$ milled alloys is better than that of Mg_2Ni milled alloys. Zhang and the co-workers [16] found that the combined effect of Al and Ni weakens the Mg-Ni and Ni-H interactions and decreases bonding electrons number below Fermi lever. Zhou *et al*. [20] showed that co-doping Y and Al in MgH_2 can weaken Mg-H bonds and promote the desorption of hydrogen. Despite the many experimental and theoretical studies of co-doped MgH_2 hydrogen storage system, there is still a lack of systematic study of the structural, bonding and hydrogen desorption properties of co-doped MgH_2 with Ni and Sc.

Thus in this paper, we conducted a systematic study on the effects of Ni and Sc co-doped on MgH_2 using first-principles calculations. We have studied the preferential sites of Ni and Sc dopants on MgH_2 depending on the minimization of total electronic energy. The dopants' influence on structural stability and dehydrogenation properties of the MgH_2 were investigated by formation enthalpies and hydrogen desorption enthalpies. Electronic structures were analyzed to identify the intrinsic mechanisms of interactions between Mg and dopants and the desorption of hydrogen on co-doped system.

2. Computational Model and Method

MgH_2 has a rutile type tetragonal structure (P42/mnm, group No.136) with experimentally measured lattice parameters of a = 4.501 Å and c = 3.010 Å [23]. In the unit cell of MgH_2, two Mg atoms occupy the 2a (0, 0, 0) site and four H atoms occupy the 4f (0.303, 0.303, 0) site. Previously, we calculated the lattice parameters of MgH_2 are a = 4.477 Å and c = 2.989 Å, these results are in full agreement with experimental and other theoretical values [12] [20]. For Ni and Sc co-doped on MgH_2 system, we simulate a 3 × 3 × 1 supercell model (see **Figure 1**) that contained a total of 54 atoms with four non-equivalent positions for Mg and six non-equivalent positions for H. The MgH_2 3 × 3 × 1 supercell is computed using the bulk parameters. Relaxations of the atomic coordinates were carried out, the optimal atomic positions of Mg and H atoms are good agreement with other theoretical data [20].

All energy and electronic structure calculations were performed under the framework of the density functional theory (DFT) via the Vienna *ab initio* Simulation Package (VASP) [24]. The electron-ion core interactions were described by the projector augmented wave (PAW) method [25]. The Perdew-Wang 91 (PW91) functional as generalized gradient approximation (GGA) was adopted for the exchange-correlation term [26]. For the plane-wave basis set a cutoff energy of 350 eV was used. A Gaussian smearing method for geometry optimization and a tetrahedron method with Blöchl corrections for electronic structures with an energy broadening of 0.05 eV were used throughout. Dependence of total energy on k-mesh was checked, a 3 × 3 × 7 Monkhorst-Pack k-point mesh for geometry optimization and a 5 × 5 × 9 Monkhorst-Pack k-point mesh for electronic structures were used to save the computing cost. The total energy convergence was chosen to be 10^{-7} eV and the absolute magnitude of force on each atom was below 0.01 eV/Å.

3. Results and Discussion

3.1. Dopant Site Preference and Substitution Energy

In order to find the optimum geometry and doped sites of dopants (Ni and Sc) in MgH_2, the total electronic energies of dopants in every non-equivalent position need to be calculated. In the Ni-doped system, each of the four non-equivalent positions of Mg is substituted by Ni in order. The calculated total electronic energies are shown in **Figure 2(a)**. Due to the minimal total electronic energy, Ni prefers to substitute for the Mg3 position, and the new compound is denoted as (Mg, Ni)H_2. Then, Mg is substituted by Sc in other three non-equivalent positions (Mg1, Mg2 and Mg4) of (Mg, Ni)H_2 compound. The calculated total electronic energies are shown in **Figure 2(b)**. It can be seen that Sc prefers to substitute for the Mg4 position due to its lowest total electronic energy, and the new compound is denoted as (Mg, Ni, Sc)H_2. Hence, in co-doped system, the Mg3 and Mg4 would be simultaneously substituted by Ni and Sc, respectively.

To identify the favorability of Ni and Y co-doping in MgH_2 comparing to Ni single-doping, the substitution energies (E_{sub}) of (Mg, Ni)H_2 and (Mg, Ni, Sc)H_2 are estimated via the definition [21] [27]:

$$E_{sub} = 1/54\left[E_t\left(Mg_{18-x-y}Ni_xSc_yH_{36}\right) - E_t\left(Mg_{18}H_{36}\right) - xE_b\left(Ni\right) - yE_b\left(Sc\right) + \left(x+y\right)E_b\left(Mg\right)\right] \quad (1)$$

where E_t(M) refer to the total energies of supercell of hydrides. E_b represents the total energies per atom in the bulk structure. The x and y are the number of dopants in the supercell. The obtained substitution energies of (Mg, Ni)H_2 and (Mg, Ni, Sc)H_2 are 0.16 and 0.12 eV/atom, respectively. From energy point of view, the smaller substitution energy corresponds to the more favorable substitution doping. Therefore, the co-doping Ni and Sc into MgH_2 is most energetically favorable than the single-doping Ni into MgH_2.

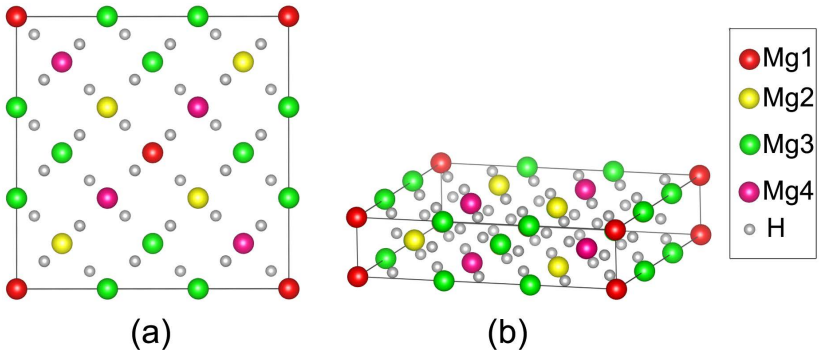

Figure 1. Top (a) and side (b) views of MgH_2 3 × 3 × 1 supercell model. Mg1, Mg2, Mg3 and Mg4 denote four non-equivalent position for Mg, respectively.

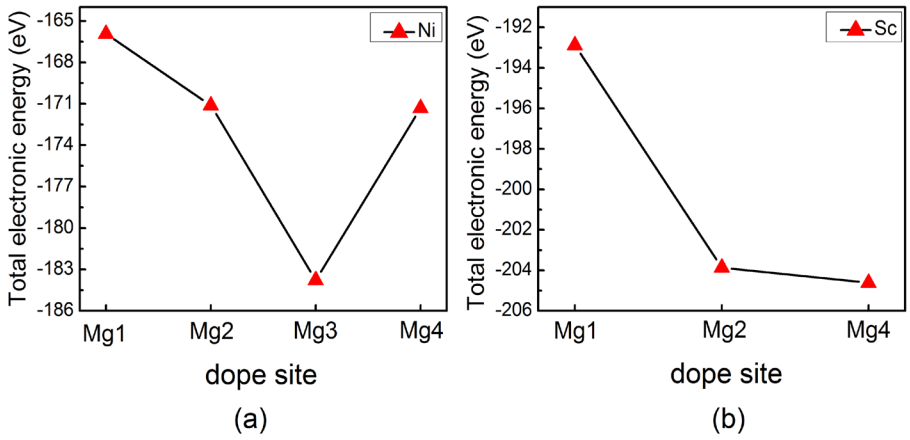

Figure 2. The total electronic energy of (a) doped $Mg_{18}H_{36}$ with Ni in four non-equivalent positions of Mg; (b) doped (Mg, Ni)H_2 with Sc in the other non-equivalent positions of Mg.

3.2. Stability and Dehydrogenation Properties

In general, the structural stability of crystal is closely related to the formation enthalpy (ΔH_{form}), negative formation enthalpy indicates that the crystal can exist stably. Furthermore, the more negative formation enthalpy suggests the higher stability of crystal [28]. The formation enthalpy (ΔH_{form}) is calculated in order to recognize the stability of the co-doped system compared to single-doped system, using the follow definition [28] [29]:

$$\Delta H_{\text{form}} = 1/54\left[E_{\text{t}}\left(\text{Mg}_{18-x-y}\text{Ni}_x\text{Sc}_y\text{H}_{36}\right) - xE_{\text{b}}\left(\text{Ni}\right) - yE_{\text{b}}\left(\text{Sc}\right) - \left(18-x-y\right)E_{\text{b}}\left(\text{Mg}\right) - 18E\left(\text{H}_2\right)\right] \quad (2)$$

where E_{t} represents the total energies of supercell of hydrides. E_{b} is the total energies per atom in the bulk structure. The x and y are the number of dopants in the supercell. $E(\text{H}_2)$ denotes the total energy of free H_2 molecule is computed as −6.77 eV, which was evaluated via a 8 × 8 × 8 Å supercell in full agreement with experimental [5] and other theoretical data [12] [18]. The calculated formation enthalpies of (Mg, Ni)H_2 and (Mg, Ni, Sc)H_2 are −0.06 and −0.10 eV/atom, respectively. It can be seen that the formation enthalpies of these two compounds are both negative, which means that these compounds can exist stably. Besides, Ni and Sc co-doped system has lower enthalpy value, which means co-doped system exhibits higher stability compared to Ni single-doping.

In order to further assess the dehydrogenation abilities of (Mg, Ni)H_2 and (Mg, Ni, Sc)H_2, their hydrogen desorption enthalpies (ΔH_{des}) are also calculated by using Equation (3) [5] [30]:

$$\Delta H_{\text{des}} = 1/n\left[E_{\text{t}}\left(\text{Mg}_{18-x-y}\text{Ni}_x\text{Sc}_y\text{H}_{36-2n}\right) + nE\left(\text{H}_2\right) - E_{\text{t}}\left(\text{Mg}_{18-x-y}\text{Ni}_x\text{Sc}_y\text{H}_{36}\right)\right] \quad (3)$$

where $E_{\text{t}}(\text{Mg}_{18-x-y}\text{Ni}_x\text{Sc}_y\text{H}_{36})$ represents the total energy of supercell of hydrides. $E_{\text{t}}(\text{Mg}_{18-x-y}\text{Ni}_x\text{Sc}_y\text{H}_{36-2n})$ refers to a pseudostructure in which $2n$ H atoms are removed from the relaxed $\text{Mg}_{18-x-y}\text{Ni}_x\text{Sc}_y\text{H}_{36}$ system. $E(\text{H}_2)$ is the same as that used in Equation (2). In the dehydrogenation process, n is equivalent to 2 for move out H1, H2 and H3 atom with the $\text{Mg}_{18-x-y}\text{Ni}_x\text{Sc}_y\text{H}_{36-2n}$ compound and n is equivalent to 4 for move out H4, H5 and H6 atom with the $\text{Mg}_{18-x-y}\text{Ni}_x\text{Sc}_y\text{H}_{36-2n}$ compound.

For the Ni single-doped MgH_2 system, the hydrogen desorption enthalpies are shown in **Figure 3(a)**. The corresponding ΔH_{des} values are 1.86, 1.67, 1.72, 0.52, 1.02 and 0.57 eV/H_2 for H1 - H6 respectively. Compare with the hydrogen desorption enthalpy of ΔH_{des} = 0.77 eV/H_2 results for MgH_2 in 570 K [16], part desorption enthalpies of Ni-doped MgH_2 are decreased. Therefore, the H (H4, H6) around dopant Ni would be released easily, due to the smaller hydrogen desorption enthalpy. For the Ni and Sc co-doped MgH_2 system, the hydrogen desorption enthalpies of Ni and Sc co-doped are shown in **Figure 3(b)**. The corresponding ΔH_{des} values are 0.75, 1.35, 0.67, 0.34, 1.09 and 0.30 eV/H_2 for H1 - H6, respectively. It can be observed that most of the hydrogen desorption enthalpies for this hydride are significantly decreased in comparison with Ni doping, except for the ΔH_{des} value of H5 around Mg. Thus most hydrogen dissociation is much easier than single-doped case, which indicates the Ni and Sc co-doped system has more promising dehydrogenation properties. Although the partial substitution of Mg by Ni and Sc has significant effects on MgH_2, the detailed understanding of the effect of co-doping of Ni and Sc on the hydrogen desorption process and kinetics of MgH_2 requires a further investigated, which will be the subject of our future work.

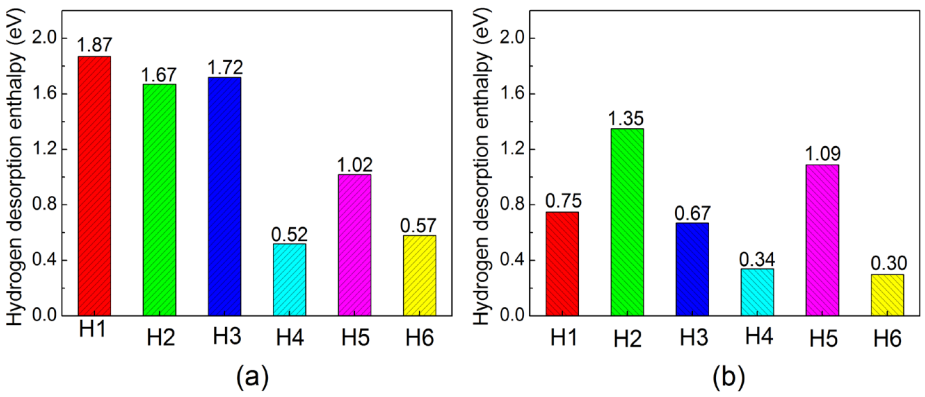

Figure 3. The calculated hydrogen desorption enthalpies by moving out H atoms (H1 - H6) for (a) (Mg, Ni)H_2; (b) (Mg, Ni, Sc)H_2.

3.2. Geometrical Feature and Bonding Interactions

Table 1 presents the bond distances between metallic elements of undoped and doped MgH_2 systems. The bond length of Mg-Mg range from 3.500 Å to 4.476 Å with an average of 3.663 Å in pure MgH_2 system, which is in good agreement with other theoretical results [20] [31]. In Ni single-doped MgH_2 system, Mg2 and Mg4 are the nearest neighboring metallic atoms of the dopant Ni. The average of Mg-Ni bond length is 3.692 Å, shorter than that of Mg-Mg bond in pure MgH_2, which implies the bond strength of Mg-Ni is enhanced. The bond length of Mg-Mg is also decreased, thus the strength of Mg-Mg bond is enhanced in comparison with that of the pure MgH_2. For Ni and Sc co-doped system, the bond length of Mg-Mg is further decreased, enhancing the strength of Mg-Mg bond. The distances between the Mg and Ni atoms are longer than that of the single-doped system, indicates that its bond strength are weakened. Furthermore, the length of Mg2-Sc bond and the Ni-Sc bond are shorter than the Ni-doped system, thus the bond strength of Mg2-Sc and Ni-Sc are enhanced. These can be inferred that the dopant Sc has alloying trend with Mg and Ni atoms, which would be weakened the strength of Mg-H and Ni-H bonds.

Table 2 lists the interaction of metallic and H atoms of doped MgH_2. In this calculation, the bond length of Mg-H ranges from 1.926 Å to 1.941 Å with an average of 1.934 Å, consistent with the experimental [29] and other theoretical results [32] [33]. For the MgH_2 single-doped with Ni, H4, H5 and H6 atoms are the nearest neighboring atoms of dopant Ni and these atoms move towards Ni, thus the bond length of Mg-H (H4 - H6) are increased. Compared with undoped MgH_2, the bond lengths of Mg-H5 and Mg-H6 are increased with 0.008 Å and 0.304 Å, receptively. Therefore, the bond strength of Mg-H is weakened by Ni doping. For the MgH_2 co-doped with Ni and Sc, the bond length of Ni-H (H4, H6) is longer than that of Ni single-doped system, thus the strength of Mg-H (H4, H6) bond is weakened. H2, H3 and H5 atoms are the nearest neighboring atoms of the dopant Sc and the length of Sc-H is increased compared with Mg4-H bond, and then the strength of Sc-H bond is weaened. Comparing with Ni single-doped system, the bond length of Ni-H (H4, H6) and Mg-H (H2, H6) are increased, so the dopant Sc can further weaken the Mg-H and Ni-H bond.

3.3. Electronic Structure

The total and partial density of states (DOS) of the pure MgH_2 system are plotted in **Figure 4**, the Fermi energy

Table 1. Calculated the bond distance (Å) between metallic elements in the hydrides.

MgH_2	Mg1-Mg2	Mg1-Mg3	Mg1-Mg4	Mg2-Mg3	Mg2-Mg4	Mg3-Mg4
	3.501	4.476	3.501	3.500	3.500	3.500
(Mg, Ni)H_2	Mg1-Mg2	Mg1-Ni	Mg1-Mg4	Mg2-Ni	Mg2-Mg4	Ni-Mg4
	3.272	4.322	3.269	3.445	3.203	3.300
(Mg, Ni, Sc)H_2	Mg1-Mg2	Mg1-Ni	Mg1-Sc	Mg2-Ni	Mg2-Sc	Ni-Sc
	3.208	4.350	3.381	3.684	3.170	3.106

Table 2. Calculated the bond distance (Å) between H and metallic atoms in the hydrides.

(Mg, Ni)H_2	Mg1-H1	1.789	Mg2-H1	1.833	Ni-H4(1)	1.760	Mg4-H2	1.781
	Mg1-H2	1.836	Mg2-H3	1.800	Ni-H4(2)	1.623	Mg4-H3	1.765
			Mg2-H6	2.238	Ni-H5	1.656	Mg4-H5	1.942
					Ni-H6	1.683		
(Mg, Ni, Sc)H_2	Mg1-H1	1.746	Mg2-H1	1.826	Ni-H4(1)	1.780	Sc-H2	1.913
	Mg1-H2	1.842	Mg2-H3	1.749	Ni-H4(2)	1.669	Sc-H3	1.835
			Mg2-H6	2.544	Ni-H5	1.639	Sc-H5	1.970
					Ni-H6	1.735		

(E_F) level is set at zero and used as a reference. The energy gap between the valence band (VB) and conduction band (CB) is 3.82 eV. The value is in good agreement with other theoretical calculations reported previously [20] [34]. The relatively large energy gap of MgH_2 leads to a high formation enthalpy and poor hydrogen sorption kinetics of MgH_2 [35]. The DOSs plot corresponding to MgH_2 shows a large dispersion of the bands signaling the s-like character. The VB is mainly dominated by H s orbitals and the CB mainly by Mg s and Mg p orbitals. The amplitude of the partial DOS of the H s orbital is a result of the weight of H in the structure, and also of the transfer of electronics from Mg to H leading to an ionic hydride.

The total and partial DOS of Ni-doped MgH_2 system are plotted in **Figure 5**. The amplitude of the partial DOS of the Ni d orbital was minimized by 10 in order to plot the partial DOSs of all atoms in the same panel with the same scale. The total DOS curve shows a remarkable decrease in the band gap of 0 eV, show clearly metallic characteristics. Ni doping leads to the appearance of a narrow d-band in the middle of the band gap.

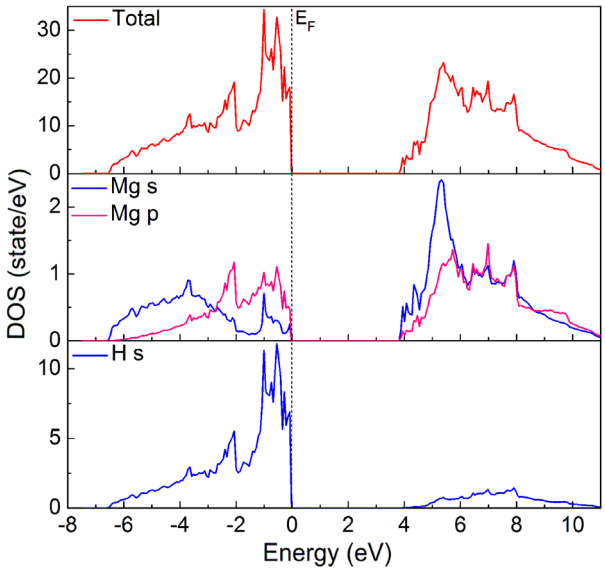

Figure 4. Total and parital electronic densities of states of the pure MgH_2.

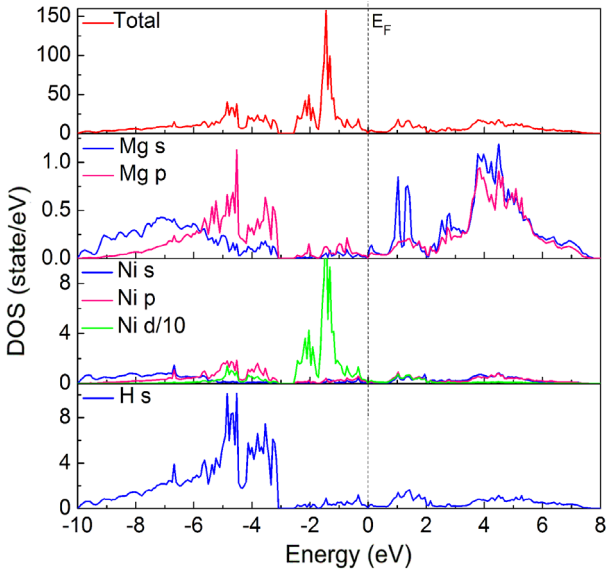

Figure 5. Total and parital electronic densities of states of Ni single-doped MgH_2 system.

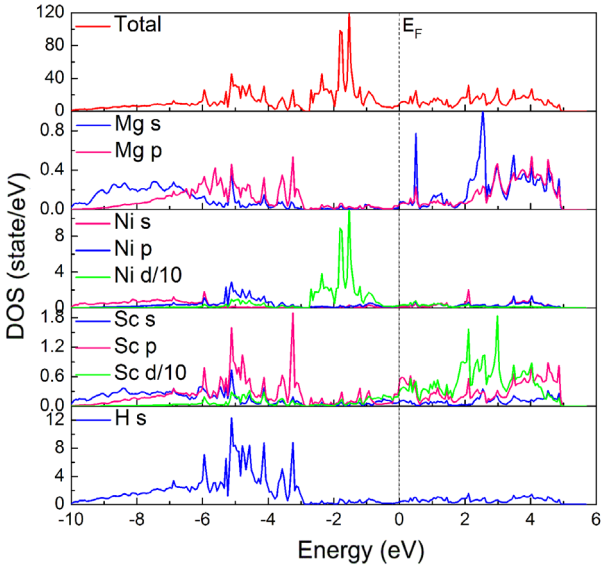

Figure 6. Total and parital electronic densities of states of Ni and Sc co-doped MgH_2.

This d orbital is strongly hybridized with Mg p and H s orbitals giving the strongly Mg-Ni and Ni-H bonding. Furthermore, the H s orbitals distributed in the region of −5.5 to −3.1 eV are less overlapped with Mg s p orbitals comparing to pure MgH_2, and the amplitude of the valence band is decreased, which can help to weaken the hybridization of Mg-H bond. These weak bonding interactions between Mg and H in Ni doped system are the reasons why this system has better dehydrogenation property.

The total and partial DOS of the Ni and Sc co-doped MgH_2 system are plotted in **Figure 6**. Similar to the Ni single-doped system, the amplitude of the partial DOS of the Ni and Sc d orbitals were minimized by 10 in order to plot the partial DOSs of all atoms in the same panel with the same scale. The similar lowered bonding peaks of H s, Mg s and p orbitals can also be observed, indicating the Mg-H bond is further weakened after Sc doping. The Sc p and d orbitals overlap with H s, Mg p, Ni p and d orbitals in the energy region of −3.2 to 6.1 eV. And the distributions of bonding peaks of Sc d orbitals are mainly concentrated in the energy region of 1.8 to 4.2 eV and overlap well with Mg s and p orbitals. These behaviors indicate that Sc atom has strong bonding interaction with H, Mg and Ni atoms and decreases Mg-H p-s mixing. Therefore, the Mg-H hybridizations are significantly weakened in Ni and Sc co-doped system, and this system exhibits more promising dehydrogenation property.

4. Conclusion

In summary, the Ni and Sc co-doping effects on the energetics and electronic structures of MgH_2 were studied by the first-principles calculations based on DFT. Due to the minimal total electronic energy, Ni and M dopants prefer to substitute the Mg3 and Mg4 positions, respectively. The substitution energy and formation enthalpy are used to estimate the energetic stability of the doped MgH_2 system. Ni and Sc co-doped MgH_2 system are more stable than Ni single-doped system. The hydrogen desorption enthalpies of these three systems were also studied. According to the relatively lower hydrogen desorption enthalpies, the co-doped systems possess more promising dehydrogenation properties compared with pure Ni doping. And the lowest hydrogen desorption enthalpy of 0.30 eV appears in co-doped system. The electronic structure analysis illustrates that the hybridization of dopants with Mg and H atom together weakens the Mg-H interaction. The decrease in hybridization peaks of Mg-H and band gaps leads to an easier Mg-H dissociation and lower hydrogen desorption enthalpy when the MgH_2 is co-doped with Ni and Sc. Therefore, the co-doping with Ni and Sc effectively improves the dehydrogenation properties of destabilized MgH_2.

Acknowledgements

The work was supported by the National Natural Science Fund (No. 11504228) and the Graduated Innovative

Research Project of Shanghai University of Engineering Science (No. E1-0903-14-01107-14KY0411) and the Innovation Program of Shanghai Municipal Education Commission, China (10YZ172).

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