First-Principles Investigation of Energetics and Electronic Structures of Ni and Sc Co-Doped MgH₂

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Abstract
First-principles calculations were used to study the energetics and electronic structures of Ni and Sc co-doped MgH₂ 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 MgH₂ 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 MgH₂. 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, MgH₂, 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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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 (MgH₂) 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 MgH₂ [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 MgH₂. Among these two methods, the introduction of transition metals into MgH₂ has played a vital role in the development of Mg-based hydrogen storage materials. The thermodynamic properties and dehydrogenation kinetics of MgH₂ 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 H₂ desorption energies of MgH₂ 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 MgH₂ 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 Mg₁₅Ti₆.₅Ni milled alloys is better than that of Mg₃Ni 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 MgH₂ can weaken Mg-H bonds and promote the desorption of hydrogen. Despite the many experimental and theoretical studies of co-doped MgH₂ hydrogen storage system, there is still a lack of systematic study of the structural, bonding and hydrogen desorption properties of co-doped MgH₂ with Ni and Sc.

Thus in this paper, we conducted a systematic study on the effects of Ni and Sc co-doped on MgH₂ using first-principles calculations. We have studied the preferential sites of Ni and Sc dopants on MgH₂ depending on the minimization of total electronic energy. The dopants’ influence on structural stability and dehydrogenation properties of the MgH₂ 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

MgH₂ has a rutile type tetragonal structure (P42/mmm, group No.136) with experimentally measured lattice parameters of \( a = 4.501 \) Å and \( c = 3.010 \) Å [23]. In the unit cell of MgH₂, 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 MgH₂ 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 MgH₂ system, we simulate a \( 3 \times 3 \times 1 \) 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 MgH₂ \( 3 \times 3 \times 1 \) 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 \( 3 \times 3 \times 3 \) Monkhorst-Pack k-point mesh for geometry optimization and a \( 5 \times 5 \times 9 \) 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]:

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

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](image1.png)

**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](image2.png)

**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 ($\Delta H_{\text{form}}$), 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 ($\Delta H_{\text{form}}$) is calculated in order to recognize the stability of the co-doped system compared to single-doped system, using the follow definition [28] [29]:

$$\Delta H_{\text{form}} = 1/54 \left[ E_t(Mg_{18-x-y}Ni_xSc_yH_{36}) - xE_b(Ni) - yE_b(Sc) - (18-x-y)E_b(Mg) - 18E(H_2) \right]$$

(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. $E(H_2)$ denotes the total energy of free H$_2$ molecule is computed as $-6.77$ eV, which was evaluated via a $8 \times 8 \times 8$ 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 ($\Delta H_{\text{des}}$) are also calculated by using Equation (3) [5] [30]:

$$\Delta H_{\text{des}} = 1/n \left[ E_t(Mg_{18-x-y}Ni_xSc_yH_{36-2n}) + nE(H_2) - E_t(Mg_{18-x-y}Ni_xSc_yH_{36}) \right]$$

(3)

where $E_t(Mg_{18-x-y}Ni_xSc_yH_{36-2n})$ represents the total energy of supercell of hydrides. $E_t(Mg_{18-x-y}Ni_xSc_yH_{36})$ refers to a pseudostructure in which $2n$ H atoms are removed from the relaxed Mg$_{18-x-y}Ni_xSc_yH_{36}$ system. $E(H_2)$ 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 Mg$_{18-x-y}Ni_xSc_yH_{36-2n}$ compound and $n$ is equivalent to 4 for move out H4, H5 and H6 atom with the Mg$_{18-x-y}Ni_xSc_yH_{36-2n}$ compound.

For the Ni single-doped MgH$_2$ system, the hydrogen desorption enthalpies are shown in Figure 3(a). The corresponding $\Delta H_{\text{des}}$ 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 $\Delta H_{\text{des}} = 0.77$ 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 $\Delta H_{\text{des}}$ 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 $\Delta H_{\text{des}}$ 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](https://example.com/figure3.png)

**Figure 3.** The calculated hydrogen desorption enthalpies by moving out H atoms (H1 - H6) for (a) (Mg, Ni)$_2$; (b) (Mg, Ni, Sc)$_2$. 
3.2. Geometrical Feature and Bonding Interactions

Table 1 presents the bond distances between metallic elements of undoped and doped MgH₂ 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 MgH₂ system, which is in good agreement with other theoretical results [20] [31]. In Ni single-doped MgH₂ 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 MgH₂, 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 MgH₂. 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 MgH₂. 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 MgH₂ 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 MgH₂, 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 MgH₂ 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 MgH₂ system are plotted in Figure 4, the Fermi energy.
The (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.

![Total and parital electronic densities of states of the pure MgH2.](image)

![Total and parital electronic densities of states of Ni single-doped MgH2 system.](image)
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$_2$.

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