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# Recent advances in hydrogen storage of MgH2 doped by Ni

**Huan Liu\*, Zhenzhong Wang, Jianzhong Zhang, Bin Tao, Quanzhen Liu**

(State Key Laboratory of Safety and Control for Chemicals，SINOPEC Safety Engineering Institute，Qingdao 266000，China)

\*Corresponding author's e-mail: liuh.qday@sinopec.com

**Abstract.** Efficient hydrogen storage remains a tough challenge for the past decades, and $MgH_2$/Mg systems seems as a most promising solution due to its high hydrogen capacity, low cost and universal abundance. However, high sorption temperatures, sluggish kinetics of hydrogen desorption, and poor cycle performances of the $MgH_2$/Mg systems hinder further applications. In this review, both experimental and theoretical researches of Ni doping $MgH_2$ materials are presented aiming at improving the hydrogen desorption/absorption performances, and some realistic perspectives are also provided for further investigations.

## 1. Introduction

Hydrogen is widely regarded as an ultimate energy carrier due to its abundance, sustainability, no pollution, and diverse methods of productions, while highly cost-effective storage of hydrogen remains a tough challenge for several decades[1, 2]. Although hydrogen can be stored in high-pressure gas state (as high as 70 MPa) or low-temperature liquid state (-253 $^{o}$C), low density, expensive costs of equipments, and potential safe hazards hinder its extensive applications [1]. Solid-state storage of hydrogen provides an efficient solution for the challenge. Among them, magnesium hydride, $MgH_2$, is widely regarded as a promising candidate owing to its high hydrogen storage ability (7.6 wt.%), low cost, and abundance on earth[2]. However, further investigations are still required to solve high sorption temperatures, sluggish kinetics of hydrogen desorption, and poor cycle performances of the $MgH_2$/Mg systems. Modifications of $MgH_2$ by means of alloying, doping, and nanotechnology have been proven to lead to enhanced abilities of hydrogen storage, and nickel doping $MgH_2$ system is regarded as an attractive strategy due to the simplicity of synthesis, low extra costs, and efficient performances[2-4]. In this paper, not only experimental investigations, but also theoretical aspects of novel Ni-doping $MgH_2$ materials have been reviewed, and some advices are provided for further researches.

## 2. Experimental progress

Yu and co-workers investigated hydrogen sorption and cycle performances of several transition metals, including Fe, Co, Ni, Cu, and Zn, doping $MgH_2$ materials through a ball-milling synthesis procedure, and the results were exhibited in Table 1[5]. Activation energies and hydrogen adsorbed contents varied on various transition metals, and $MgH_2$ materials doped by Ni, Fe, and Co metals showed enhanced desorption performances, while Cu and Zn metals served as inhibitors rather than promoters. Among them, active energy of the Ni-$MgH_2$ material is 72 kJ/mol, which is much lower than those of other metal-doping $MgH_2$ materials and that of the pure $MgH_2$ (121 kJ/mol), indicating that Ni is a better candidate in improving hydrogen desorption/absorption behaviours.

Table 1 Hydrogen desorption data of doped $MgH_2$ materials

| | Hydrogen released (mL/gMgH$_2$) | Activation energy (kJ/mol) | Hydrogen adsorbed (mL/g MgH$_2$) | | |
| --- | --- | --- | --- | --- | --- |
| | | | 250 ℃ | 300 ℃ | 350 ℃ |
| MgH$_2$-Ni | 653 | 72 | 760 | 764 | 772 |
| MgH$_2$-Co | 739 | 75 | 578 | 608 | 630 |
| MgH$_2$-Fe | 852 | 86 | 484 | 674 | 718 |
| MgH$_2$-Cu | 649 | 73 | 680 | 725 | 783 |
| MgH$_2$-Zn | 690 | 84 | 518 | 635 | 643 |
| MgH$_2$ | 800 | 121 | 831 | 831 | 827 |

Among the synthesis strategies, ball-milling method has been widely chosen as a primary choice for synthesizing a large amount of $MgH_2$-based materials, and effects of ball-milling time and nickel content on the dehydrogen performances on the $MgH_2$/Mg systems were systematically explored by Xie and co-workers[3]. When the ball-milling time increased from 10 min to 30 min, 60 min, and 120 min, the phases attributed to -$MgH_2$ and pure Ni decreased, while the -$MgH_2$ phase gradually enhanced. For the un-doped $MgH_2$ material, the activation energy of dehydrogenation is 168 kJ/mol. After the introduction of Ni, the activation energies dropped to 144 kJ/mol, 124 kJ/mol, 104 kJ/mol, 95 kJ/mol, and 83 kJ/mol, with respect to the nickel contents of 2 wt.%, 4 wt.%, 8 wt.%, 20 wt.%, and 30 wt.%, respectively. The enhancement of dehydrogenation abilities is attributed to nucleation of Mg phase and formation of hydrogen promoted by nickel doping.

Except the ball-milling time and nickel contents, effects of nickel based compounds, including $Ni_3C$, $Ni_3N$, NiO, and $Ni_2P$, on the dehydrogenation abilities of $MgH_2$ materials were fully investigated by Zhang et al[6], and the nickel doping $MgH_2$ materials were also synthesized through a ball-milling method. Activation energies of dehydrogenation increased in the following order (Figure 1): 97.8 kJ/mol (MgH$_2$-Ni$_3$C) < 100.0 kJ/mol (MgH$_2$-Ni$_3$N) < 119.7 kJ/mol (MgH$_2$-NiO) < 132.5 kJ/mol (MgH$_2$-Ni$_2$P), and the onset dehydrogenation temperatures of the Ni$_3$C-, Ni$_3$N-, NiO-, and Ni$_2$P-doping $MgH_2$ composites were 160 ℃, 180 ℃, 205 ℃, and 248 ℃, respectively. Therefore, Ni$_3$C-doping $MgH_2$ composite exhibited an enhanced dehydrogenation performance than the other nickel-doping $MgH_2$ materials. Besides, the nickel-containing compounds exhibited a higher affinity to electrons than to the $MgH_2$ materials, which served as medium for electron transfer in dehydrogenation process.
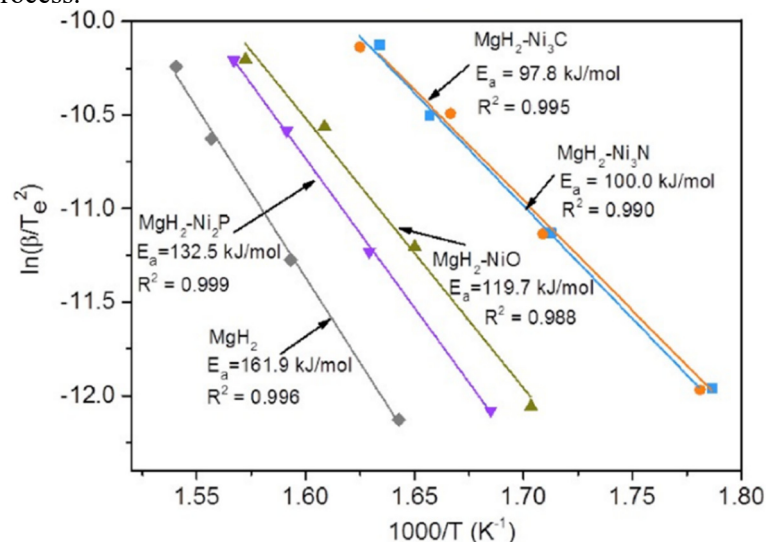


Figure 1. Kissinger plots of Ni-doping $MgH_2$ composites

Researches led by Chen and An extended the scopes of Ni-based compounds[7, 8]. Chen et al. synthesized porous nickel nanofiber through electrospinning technique, then the nickel-doping $MgH_2$ material were obtained through ball-milling the nickel nanofiber with $MgH_2$ [7]. For the pure $MgH_2$

material, the onset temperature of hydrogen desorption was 340 $^{\circ}$C, while for the nickel doped MgH$_2$ material (4 %), the temperature decreased to 143 $^{\circ}$C, with an activation energy of 81.5 kJ/mol. The Ni-MgH$_2$ material performed an enhanced desorption ability, which released 7.02 wt.% hydrogen in 11 min at 325 $^{\circ}$C. The nickel nanofiber homogenously dispersed on the surface of MgH$_2$ material, leading to the formation of an active interface between the nickel nanofiber and the MgH$_2$, which promoted the enhancements of dehydrogenation performances.

An et al. developed another novel procedure for synthesizing one-dimensional porous Ni@C materials through a combination of solvothermal and annealing processes [8]. The Ni@C nanorods exhibited an interconnected mesoporous structure, and the surface areas were 161.4 m$^2$/g, with a pore diameter around 12.5 nm. After ball-milling the Ni@C nanorod with MgH$_2$, the nickel doping Ni@C-MgH$_2$ composite was obtained. The on-set dehydrogenation temperature of the nickel doping composite was 57 $^{\circ}$C lower than that of the undoped material. The Ni@C-MgH$_2$ composite also exhibited a better hydrogenation performance, which could adsorb 6.4 wt.% hydrogen at 300 $^{\circ}$C in 10 min. For comparison, only 2.3 wt.% of hydrogen was adsorbed at the same temperature on the pure MgH$_2$ material even at a adsorbing time of 100 min. The intense interaction between Ni@C nanorods and MgH$_2$ provided active sites for dehydrogenation and diffusion channels, which was the main cause for the lower dehydrogenation temperature and improved dehydrogenation kinetics of the nickel doping MgH$_2$.

## 3. Theoretical progress
Experimental investigations provided inspiring improvements of the MgH$_2$/Mg systems, and theoretical calculations also shed light on the structure modifications of MgH$_2$ deriving from Ni doping. AlMatrouk and Chihaia investigated the doping effects of nickel and cobalt on the surface and bulk structures of MgH$_2$ based on the Density Functional Theory (DFT) calculations[9]. Results revealed that substitution of the bulk magnesium with nickel or cobalt led to the formation of hydrogen vacancy, and that apparent changes of MgH$_2$ (0 0 1) surface were also observed after doping (Figure 2). Relative residence time of hydrogen on the surface were shortened, therefore promoting the dehydrogenation ability. Nickel exhibited a more efficient ability (69.34%) than cobalt (83.04) in releasing the hydrogen from the surface.
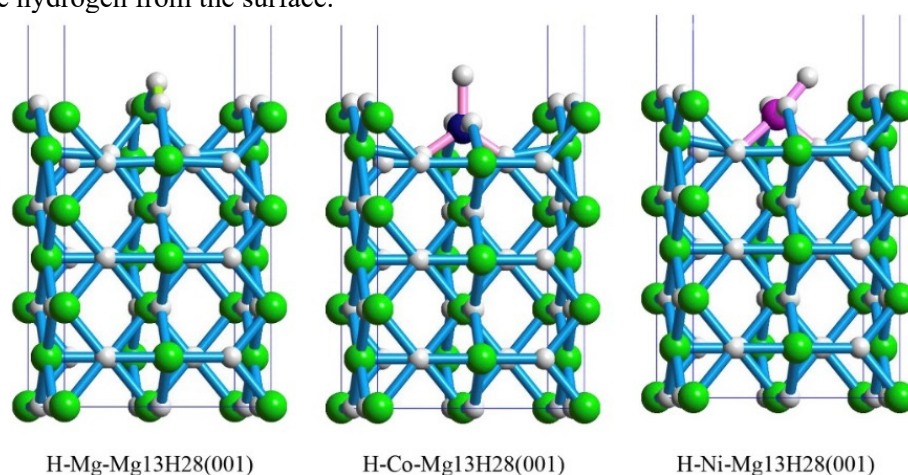


H-Mg-Mg13H28(001)          H-Co-Mg13H28(001)          H-Ni-Mg13H28(001)

**Figure 2.** Side view of the slab structures H-M-Mg13H28(001), where M¼Mg (left column), Co (central column) and Ni (right column)

Dai and co-workers investigated the structural and electronic effects of (0 0 1) metal surface of MgH$_2$ doping by a series of metals, including Al, Ti, Mg, and Ni, in dehydrogenation reactions based on the first principle calculations[10]. Results revealed that Al and Ti preferred to replace Mg atoms, while Mn and Ni tended to occupy interstitial sites. An Al-Mg nanocluster would form after Al doping, weakening the interactions between Mg and H, thus leading to an enhanced dehydrogenation activity. Ti distorted the positions of hydrogen atoms by forming a TiH$_2$ phase through interacting with

neighboring H atoms. Surface structure was distorted after Mn doping, leading to a remarkable decrease of the dehydrogenation active energy. As for the Ni-doping $MgH_2$ system, a $Mg_2NiH_4$ phase was formed, which was thermodynamically less stable than $MgH_2$, and led to the enhanced dehydrogenation ability.

## 4. Conclusion

Improvements of the $MgH_2$/Mg systems by Ni doping provide remarkable effects in decrease of the active energies, better hydrogen sorption abilities and enhanced cycle performances from both experimental and theoretical aspects. Especially the introduction of nickel-based compounds synthesized with highly dispersed Ni and interconnected porous structure coupled with theoretical calculations might provide more efficient options.

## Acknowledgments

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