

## Effects of highly dispersed Ni nanoparticles on the hydrogen storage performance of MgH<sub>2</sub>

Nuo Xu, Zirui Yuan, Zhihong Ma, Xinli Guo, Yunfeng Zhu, Yongjin Zou, and Yao Zhang

Cite this article as:

Nuo Xu, Zirui Yuan, Zhihong Ma, Xinli Guo, Yunfeng Zhu, Yongjin Zou, and Yao Zhang, Effects of highly dispersed Ni nanoparticles on the hydrogen storage performance of MgH<sub>2</sub>, *Int. J. Miner. Metall. Mater.*, 30(2023), No. 1, pp. 54-62. <https://doi.org/10.1007/s12613-022-2510-8>

View the article online at [SpringerLink](#) or [IJMMM Webpage](#).

### Articles you may be interested in

Jian-zheng Song, Zi-yang Zhao, Xin Zhao, Rui-dong Fu, and Shu-min Han, [Hydrogen storage properties of MgH<sub>2</sub> co-catalyzed by LaH<sub>3</sub> and NbH<sub>3</sub>](#), *Int. J. Miner. Metall. Mater.*, 24(2017), No. 10, pp. 1183-1191. <https://doi.org/10.1007/s12613-017-1509-z>

Wan-liang Mi, Zhao-sen Liu, Toru Kimura, Atsunori Kamegawa, and Hai-liang Wang, [Crystal structure and hydrogen storage properties of \(La,Ce\)Ni<sub>5-x</sub>M<sub>x</sub> \(M=Al, Fe, or Co\) alloys](#), *Int. J. Miner. Metall. Mater.*, 26(2019), No. 1, pp. 108-113. <https://doi.org/10.1007/s12613-019-1714-z>

Revanna Kullaiah, Liju Elias, and Ampar Chitharanjan Hegde, [Effect of TiO<sub>2</sub> nanoparticles on hydrogen evolution reaction activity of Ni coatings](#), *Int. J. Miner. Metall. Mater.*, 25(2018), No. 4, pp. 472-479. <https://doi.org/10.1007/s12613-018-1593-8>

Yuan Li, Li-na Cheng, Wen-kang Miao, Chun-xiao Wang, De-zhi Kuang, and Shu-min Han, [Nd–Mg–Ni alloy electrodes modified by reduced graphene oxide with improved electrochemical kinetics](#), *Int. J. Miner. Metall. Mater.*, 27(2020), No. 3, pp. 391-400. <https://doi.org/10.1007/s12613-019-1880-z>

Thongsuk Sichumsaeng, Nutthakritta Phromviyo, and Santi Maensiri, [Influence of gas-diffusion-layer current collector on electrochemical performance of Ni\(OH\)<sub>2</sub> nanostructures](#), *Int. J. Miner. Metall. Mater.*, 28(2021), No. 6, pp. 1038-1047. <https://doi.org/10.1007/s12613-020-2174-1>

Tian Qiu, Jian-guo Yang, and Xue-jie Bai, [Insight into the change in carbon structure and thermodynamics during anthracite transformation into graphite](#), *Int. J. Miner. Metall. Mater.*, 27(2020), No. 2, pp. 162-172. <https://doi.org/10.1007/s12613-019-1859-9>



IJMMM WeChat



QQ author group

# Effects of highly dispersed Ni nanoparticles on the hydrogen storage performance of MgH<sub>2</sub>

Nuo Xu<sup>1)\*</sup>, Zirui Yuan<sup>1)\*</sup>, Zhihong Ma<sup>2)\*</sup>, Xinli Guo<sup>1)</sup>, Yunfeng Zhu<sup>3)</sup>, Yongjin Zou<sup>4)</sup>, and Yao Zhang<sup>1),✉</sup>

1) School of Materials Science and Engineering, Jiangsu Key Laboratory of Advanced Metallic Materials, Southeast University, Nanjing 211189, China

2) School of Materials Science and Engineering, Baise University, Baise 533000, China

3) College of Materials Science and Engineering, Jiangsu Collaborative Innovation Centre for Advanced Inorganic Function Composites, Nanjing Tech University, Nanjing 211816, China

4) Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin 541004, China

(Received: 4 January 2022; revised: 25 April 2022; accepted: 28 April 2022)

**Abstract:** MgH<sub>2</sub> with a large hydrogen capacity is regarded as a promising hydrogen storage material. However, it still suffers from high thermal stability and sluggish kinetics. In this paper, highly dispersed nano-Ni has been successfully prepared by using the polyol reduction method with an average size of 2.14 nm, which significantly improves the de/rehydrogenation properties of MgH<sub>2</sub>. The MgH<sub>2</sub>-10wt% nano-Ni sample starts releasing H<sub>2</sub> at 497 K, and roughly 6.2wt% H<sub>2</sub> has been liberated at 583 K. The rehydrogenation kinetics of the sample are also greatly improved, and the adsorption capacity reaches 5.3wt% H<sub>2</sub> in 1000 s at 482 K and under 3 MPa hydrogen pressure. Moreover, the activation energies of de/rehydrogenation of the MgH<sub>2</sub>-10wt% nano-Ni sample are reduced to (88 ± 2) and (87 ± 1) kJ·mol<sup>-1</sup>, respectively. In addition, the thermal stability of the MgH<sub>2</sub>-10wt% nano-Ni system is reduced by 5.5 kJ per mol H<sub>2</sub> from that of pristine MgH<sub>2</sub>. This finding indicates that nano-Ni significantly improves both the thermodynamic and kinetic performances of the de/rehydrogenation of MgH<sub>2</sub>, serving as a bi-functional additive of both reagent and catalyst.

**Keywords:** Ni nanoparticle; kinetics; thermodynamics; MgH<sub>2</sub>; hydrogen storage performance

## 1. Introduction

Currently, fossil fuels provide 80% of the global energy demand. Unfortunately, they also cause environmental pollution and greenhouse effects [1]. The need to find renewable and clean energy to replace fossil energy has become a global consensus [2]. Hydrogen has attracted extensive interest from all over the world as an efficient and sustainable secondary energy. The so-called hydrogen economy consists of the production, storage, and transportation of hydrogen, as well as hydrogen energy applications. However, hydrogen storage has always been a bottleneck that hampers the application of hydrogen [3–7].

During the past decade, many hydrogen storage materials and technologies have been developed [8]. MgH<sub>2</sub> has received much attention among these solid-state hydrogen storage materials because of its light weight, abundant reserves, non-toxic nature, and large hydrogen storage capacity, which has considerable potential for use in hydrogen fuel cells [9–12]. Excellent solid-state hydrogen storage materials should be capable of absorbing or releasing a large amount of hydrogen rapidly under low pressure and ambient temperature [13]. However, due to the high thermodynamic stability

and retarded reaction kinetics of MgH<sub>2</sub>, the system delivers a high operating temperature and sluggish hydrogen absorption/desorption rate, making it difficult to meet the requirements of practical applications [14–18]. Many efforts, such as alloying, nanosizing, and catalyst doping, have been made to overcome these issues [19–25]. Zhang *et al.* [26] successfully synthesized ultrafine MgH<sub>2</sub> nanoparticles of 4–5 nm, which can achieve a reversible hydrogen storage of 6.7wt% at room temperature. Adding catalysts could effectively lower the working temperature of hydrogen storage, enhance the desorption, and increase the reversible absorption rate of hydrogen [27–30]. Theoretically, the doped catalyst can provide favorable charge transfer and promote heat transfer in the MgH<sub>2</sub> system by generating many defects on the surface of MgH<sub>2</sub> [31–32].

In general, nanoscale catalysts can be in close contact with MgH<sub>2</sub> to create more active sites. Therefore, nanoscale catalysts can improve the hydrogen storage performance of MgH<sub>2</sub> [33]. Many studies have been conducted on transition metal catalysts in recent years [34–35]. Specifically, the transition metals Fe, Co, Ni, and Cu, for example, have been proven to play an important role in enhancing the hydrogen storage properties of MgH<sub>2</sub> [36]. The Ni-doped MgH<sub>2</sub> com-

\* These authors contributed equally to this work.

✉ Corresponding author: Yao Zhang E-mail: zhangyao@seu.edu.cn

© University of Science and Technology Beijing 2023

posite, in particular, exhibits exceptional catalytic performance [37]. Yu *et al.* [38] and Xie *et al.* [39] found that introducing the transition metals Fe, Co, Ni, Cu, and Zn into MgH<sub>2</sub> during the ball milling or dehydrogenation/absorption cycle processes will form numerous defects at the interfaces of Fe/MgH<sub>2</sub>, Co/MgH<sub>2</sub>, Ni/MgH<sub>2</sub>, etc., respectively. Such defects considerably aid the splitting of H<sub>2</sub> molecules and the recombination of hydrogen atoms. Moreover, Chen *et al.* [40] investigated the hydrogen storage performance of the MgH<sub>2</sub>-Ni/TiO<sub>2</sub> system and found that metallic Ni particles could easily react with Mg to yield Mg<sub>2</sub>Ni compound during the dehydrogenation process, and the *in-situ* produced Mg<sub>2</sub>Ni is converted into Mg<sub>2</sub>NiH<sub>4</sub> during the subsequent rehydrogenation, acting as a hydrogen pump. Shao *et al.* [41] prepared a stable Ni-metal organic framework (MOFs) catalyst with uniform and dispersed Ni atoms that can improve the hydrogen storage performance of the MgH<sub>2</sub> system. Huang *et al.* [42] created highly dispersed metal-supported catalysts, including a series of 3d transition elements, La and Ce, on N-doped carbon (M-N-C). The kinetics of MgH<sub>2</sub>-M-N-Cs were correlated with the electronegativity of M in M-N-Cs (V, Cr, Fe, Co, Ni, Cu, Zn), indicating that M-N-Cs with high electronegativity core elements can enhance the kinetics. In addition, MgH<sub>2</sub>-Ni-N-C500 with the highest electronegativity (Ni, 1.91) was demonstrated remarkable kinetic performance. Zhang *et al.* [43] synthesized a series of nickel-based compounds (Ni<sub>3</sub>C, Ni<sub>3</sub>N, NiO, and Ni<sub>2</sub>P) and found that the catalyst obtained by combining Ni with low electronegativity elements (Ni<sub>3</sub>C) better enhanced the hydrogen storage performance of the MgH<sub>2</sub> system. In addition, El-Eskandarany *et al.* [44] employed Ni spheres as a grinding medium, progressively doping Ni spheres into MgH<sub>2</sub> powder. Their samples after ball milling exhibited a low dehydrogenation temperature (491 K) and a dehydrogenation activation energy (75 kJ·mol<sup>-1</sup>). Recent research has found that the size of the Ni particles has a major impact on the adsorption and dehydrogenation kinetics of MgH<sub>2</sub>. Si *et al.* [45] discovered that the initial dehydrogenation temperature of the MgH<sub>2</sub>-5wt% nano-Ni/C system was significantly reduced by 453 K, and the hydrogen absorption kinetics of the system was noticeably increased by 16-fold compared with that of the original MgH<sub>2</sub>. Gao *et al.* [46] created Ni/Ti<sub>3</sub>C<sub>2</sub> catalysts

with interfacial differences and discovered that when Ni had the smallest particle size and best dispersibility at the Ti<sub>3</sub>C<sub>2</sub> matrix interface, the most effective catalytic activity was produced. Chen *et al.* [47] synthesized Ni nanofibers with a uniform diameter of 50 nm and a porous structure composed of many Ni nano-crystallites, which were easily broken into superfine Ni nanoparticles with an average diameter of 17 nm by ball milling and uniformly dispersed on the surface of MgH<sub>2</sub>. The hydrogen storage significantly improves the performance of MgH<sub>2</sub>. Zhu *et al.* [48] designed a self-assembled two-dimensional MXene-based catalyst (2D-Ni@Ti<sub>3</sub>C<sub>2</sub>) whose Ni particles had an average size of less than 50 nm, and smaller particles were in the range of 5 nm. The MgH<sub>2</sub> + Ni@Ti-MX composite absorbed 5.4wt% H<sub>2</sub> in 25 s at 398 K and released 5.2wt% H<sub>2</sub> in 15 min at 523 K, demonstrating enhanced hydrogen storage performance. Therefore, the particle size of the catalyst and its close contact with MgH<sub>2</sub> determine its catalytic performance. Rahmalina *et al.* [49] also proved that reducing the size of Ni particles is the best approach to enhance the thermodynamic and kinetic performance of MgH<sub>2</sub>. However, the best size of Ni and its size effect on the de/rehydrogenation performance still remain unclear.

In this paper, we focus on the effect and mechanism of nano-Ni particles on the thermal stability and catalytic performance of MgH<sub>2</sub>. Ni particles with size of 1.5–2.5 nm have been successfully synthesized in this work. The effect of nano-Ni particle size on the MgH<sub>2</sub> system has been systematically studied, along with the catalytic mechanism of nano-Ni on the MgH<sub>2</sub> system.

## 2. Experimental

### 2.1. Preparation of the MgH<sub>2</sub>-nano-Ni

The overall synthesis process of nano-Ni particles is shown in Fig. 1. First, 1.8 g sodium hydroxide (97%, Aladdin), 0.2241 g nickel acetate tetrahydrate (99%, Aladdin), 2.05 g oleic acid (analytical reagent (AR), Macklin), 0.5 g polyvinylpyrrolidone (PVP, guaranteed reagent (GR), Sino-pharm), and 150 mL of 1,2-propylene glycol (AR, Sino-pharm) were placed in a round-bottom flask. The temperature was increased to 389 K, and the reagents completely dis-

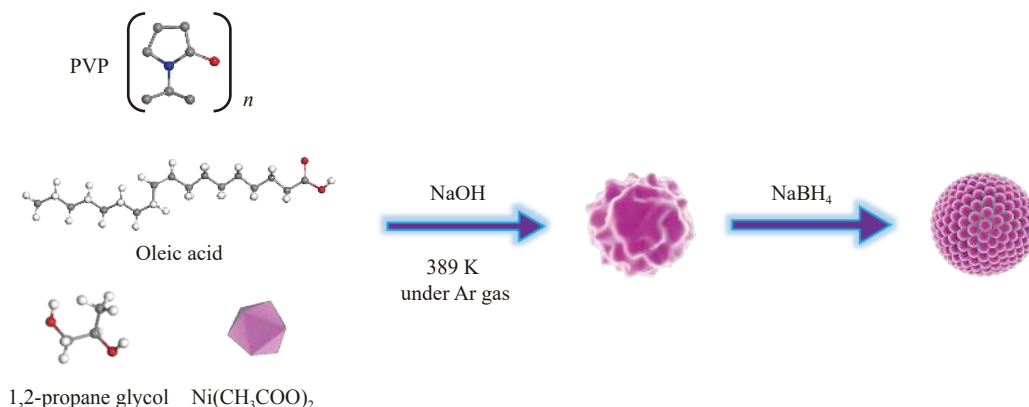


Fig. 1. Illustration of the synthesis of the nano-Ni composite.

solved with continuous magnetic stirring. The semi-products were obtained by dropping 30 mL of 1,2-propylene glycol solution containing 0.486 g of potassium borohydride (98%, Aladdin) into the solution in a glove box filled with high-purity argon. Finally, the Ni nanoparticles were collected by centrifugation and vacuum drying at 353 K for 10 h.

The purchased  $\text{MgH}_2$  (95%, Alfa Aesar) was mixed (QM-1SP, Nanjing) with the prepared  $x\text{wt}\%$  nano-Ni ( $x = 0, 3, 5, 10, 15$ ) at 450 r/min with a 40:1 ball-to-powder ratio for 5 h. All samples were treated in a glovebox (Mikrouna Super 1220/750), and their  $\text{H}_2\text{O}$  and  $\text{O}_2$  levels were below 0.0001%.

## 2.2. Structural and morphology characterization

The phase structure of the composite system was determined by X-ray diffraction (XRD) and *in-situ* XRD (Rigaku) patterns. The morphology was characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM), respectively. High-magnification images were obtained by using a high-resolution transmission electron microscope (HRTEM, FEI Tecnai G2 T20). The microstructure of the phases was analyzed by selected area electron diffraction (SAED).

## 2.3. De/rehydrogenation performances

The non-isothermal dehydrogenation performance was evaluated by using the volume release method (VR), from which the initial dehydrogenation temperature, the final dehydrogenation temperature, and the dehydrogenation capacity of the samples were identified. Dehydrogenation onset,

peak, and cut-off temperatures were determined by temperature-programmed desorption (TPD) with online mass spectrometry (MS, Hiden, UK). The isothermal hydrogenation curves of the  $\text{MgH}_2$ -nano-Ni system were measured at 394, 421, 450, and 482 K, respectively, under 3 MPa. The pressure-composition isotherm curves (PCI) of  $\text{MgH}_2$  and  $\text{MgH}_2$ -nano-Ni were tested at different temperatures. Differential scanning calorimetry (DSC) was performed on a TA Q2000 instrument, and approximately 5 mg of each sample was heated from room temperature to 773 K at 5, 10, 15, and 20  $\text{K}\cdot\text{min}^{-1}$ , respectively.

## 3. Results and discussion

### 3.1. Characterization of nano-Ni

The TEM images in Fig. 2(a) and (b) show that the prepared catalyst powders are nanoclusters of extremely fine particles formed by agglomeration. The calculated average particle size is 2.14 nm, as indicated by the Nano Measure software, and the particle size is concentrated at 1.5–2.5 nm. This finding indicates that the particle size is relatively uniform, much smaller than that reported in many previous works [44–45,49–50], which should benefit the catalytic activity of the catalyst. The XRD pattern of the nanoparticles is displayed in Fig. 2(c), and all diffraction peaks correspond to Ni (111), Ni (200), and Ni (220), respectively. This finding demonstrates that the Ni precursor is completely reduced to metallic Ni after preparation. In addition, the diffraction peaks broaden while their intensities weaken, further indicating that the Ni nanoparticles are relatively small.

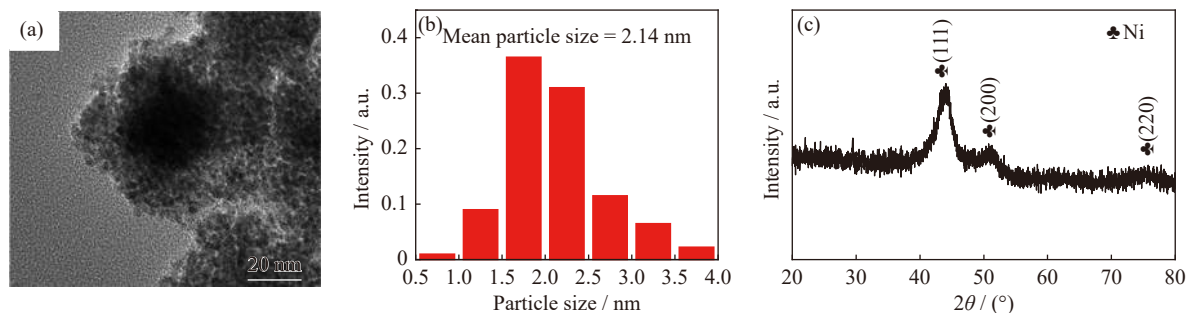


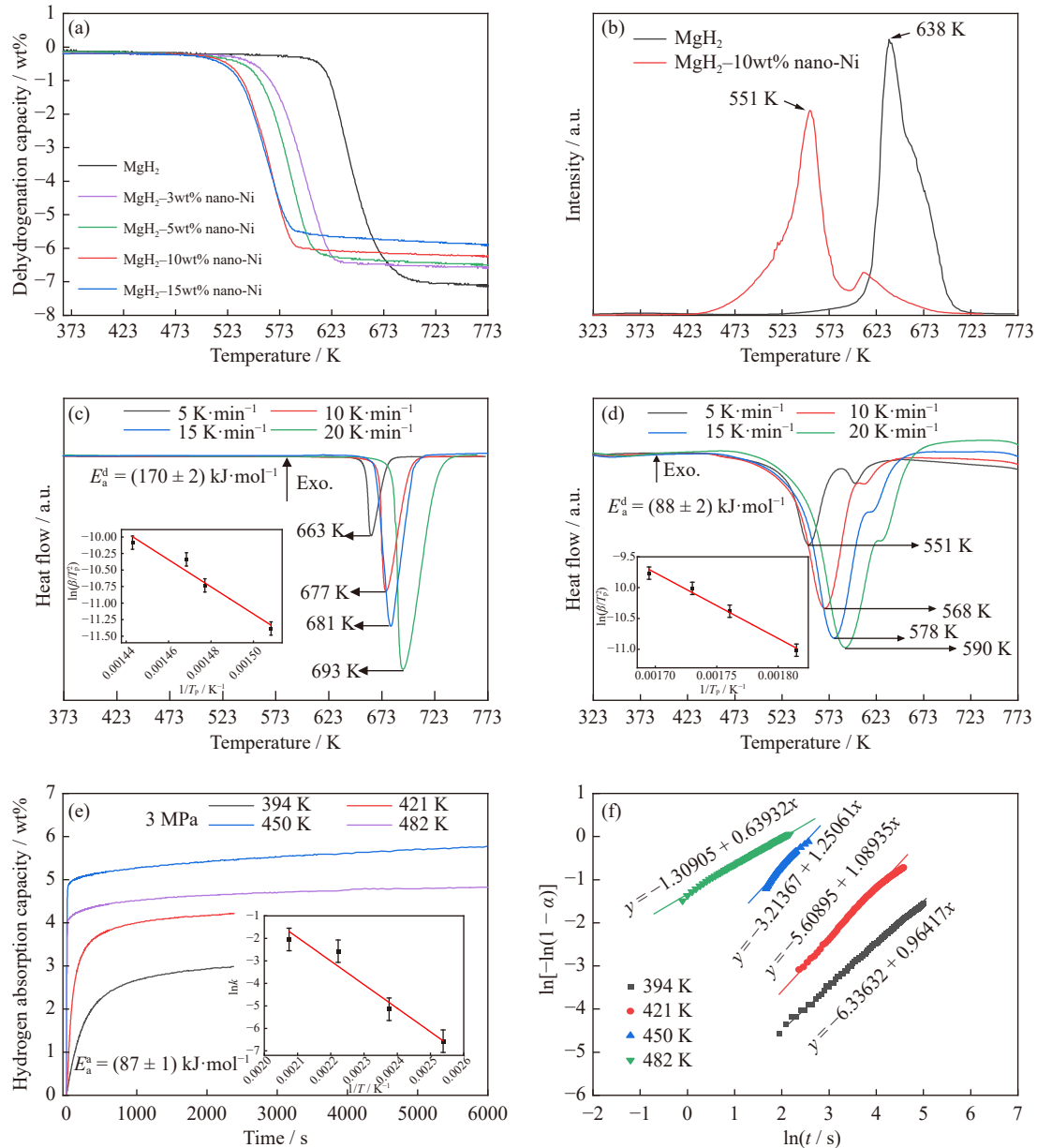
Fig. 2. (a) TEM image of the as-prepared nano-Ni. (b) Particle size distribution of the as-prepared nano-Ni. (c) XRD pattern of the as-prepared nano-Ni.

### 3.2. Effects of nano-Ni on the $\text{MgH}_2$ system

Fig. 3(a) displays the VR curves at a heating rate of 5  $\text{K}\cdot\text{min}^{-1}$  of  $\text{MgH}_2$ - $x\text{wt}\%$  nano-Ni ( $x = 0, 3, 5, 10, 15$ ) samples. Its initial desorption temperature, final desorption temperature, and desorption capacity can be calculated as summarized in Table 1. Evidently, the system  $\text{MgH}_2$ - $x\text{wt}\%$  nano-Ni ( $x = 3, 5, 10, 15$ ) starts to release hydrogen in the temperature range of 492–518 K, which is remarkably lower than the 580 K for the original  $\text{MgH}_2$  sample.  $\text{MgH}_2$ -3wt% nano-Ni begins to release hydrogen at approximately 518 K, which is 62 K lower than that of undoped  $\text{MgH}_2$ . In addition, the dehydrogenation temperatures of  $\text{MgH}_2$ -5wt% nano-Ni,

$\text{MgH}_2$ -10wt% nano-Ni, and  $\text{MgH}_2$ -15wt% nano-Ni are further lowered to 510, 497, and 492 K, respectively. Furthermore, the three samples are dehydrogenated by the addition of nano-Ni before 672 K, with hydrogen releases of 6.5wt%, 6.2wt%, and 5.9wt%, respectively. The  $\text{MgH}_2$ -15wt% nano-Ni sample delivers an end temperature higher than the  $\text{MgH}_2$ -10wt% nano-Ni sample; thus, the  $\text{MgH}_2$ -10wt% nano-Ni sample seems to be the best choice for this work.

Fig. 3(b) shows the TPD-MS curves of the  $\text{MgH}_2$  and  $\text{MgH}_2$ -10wt% nano-Ni samples at a heating rate of 5  $\text{K}\cdot\text{min}^{-1}$ . For the sample doped by the nano-Ni catalyst, the dehydrogenation peak is apparently shifted to a lower temperature. The peak dehydrogenation temperature of the



**Fig. 3.** (a) Volumetric release curves of as-milled MgH<sub>2</sub>-xwt% nano-Ni (x = 0, 3, 5, 10, 15); (b) TPD-MS curves of the samples of MgH<sub>2</sub>-10wt% nano-Ni and MgH<sub>2</sub>. The temperature ramping rates are all 5 K·min<sup>-1</sup>. DSC curves of the (c) as-milled MgH<sub>2</sub> and (d) MgH<sub>2</sub>-10wt% nano-Ni, respectively; the insertion plots show the activation energies of the samples. (e) Isothermal hydrogenation curves of MgH<sub>2</sub>-10wt% nano-Ni at different temperatures; inset is their Arrhenius plots. (f) The fitted lines reflecting the relationship of ln[-ln(1-α)]-ln t built on the basis of the JMA equation; the slope stands for the activation energy E<sub>a</sub><sup>a</sup>.

**Table 1.** Volumetric release curves of as-milled MgH<sub>2</sub>-xwt% nano-Ni (x = 0, 3, 5, 10, 15)

| Sample                          | Initial desorption temperature / K | End desorption temperature / K | Dehydrogenation capacity / wt% |
|---------------------------------|------------------------------------|--------------------------------|--------------------------------|
| MgH <sub>2</sub>                | 580                                | 672                            | 7.2                            |
| MgH <sub>2</sub> -3wt% nano-Ni  | 518                                | 621                            | 6.6                            |
| MgH <sub>2</sub> -5wt% nano-Ni  | 510                                | 605                            | 6.5                            |
| MgH <sub>2</sub> -10wt% nano-Ni | 497                                | 583                            | 6.2                            |
| MgH <sub>2</sub> -15wt% nano-Ni | 492                                | 585                            | 5.9                            |

MgH<sub>2</sub>-10wt% nano-Ni sample is significantly reduced by 87 K compared with that of pure MgH<sub>2</sub>. In addition, a minor dehydrogenation peak occurs at 673 K after ball milling of pure MgH<sub>2</sub>, which is probably caused by the heterogeneous distri-

bution of magnesium hydride particle size according to Ref. [51].

To further investigate the desorption kinetics, DSC measurements of MgH<sub>2</sub> and MgH<sub>2</sub>-10wt% nano-Ni samples were

performed, as displayed in Fig. 3(c) and (d). The dehydrogenation temperature of MgH<sub>2</sub> is significantly lowered by nano-Ni. The endothermic peak of MgH<sub>2</sub>-10wt% nano-Ni is 112 K lower than that of the original MgH<sub>2</sub>. According to the different heating rates of DSC curves, the activation energy for desorption was calculated by Kissinger's equation [52], as shown in Eq. (1),

$$\frac{d \left[ \ln \left( \frac{\beta}{T_p^2} \right) \right]}{d \left( \frac{1}{T_p} \right)} = - \frac{E_a^d}{R} \quad (1)$$

where  $\beta$  represents the heating rate,  $E_a^d$  denotes the activation energy for desorption,  $T_p$  stands for the endothermic peak temperature, and  $R$  is the gas constant. The activation energy of the MgH<sub>2</sub>-10wt% nano-Ni system decreased to  $(88 \pm 2)$  kJ·mol<sup>-1</sup>, indicating that the nano-Ni additive could alleviate the kinetic barrier of MgH<sub>2</sub> dehydrogenation and greatly improve the MgH<sub>2</sub> dehydrogenation kinetics.

Aside from the remarkable improvement in the dehydrogenation properties, the hydrogen adsorption kinetics of the MgH<sub>2</sub>-10wt% nano-Ni sample were also investigated. Isothermal hydrogen absorption measurements are shown in Fig. 3(e) and (f). An Arrhenius equation [53] could be established according to the following equation (Eq. (2)):

$$\ln k = - \frac{E_a^a}{RT} + \ln A \quad (2)$$

$$\alpha = 1 - e^{-(kt)^n} \quad (3)$$

where  $k$  is the reaction rate constant,  $E_a^a$  denotes the activation energy of hydrogen absorption,  $T$  is the temperature,  $R$  stands for the gas constant, and  $A$  is the pre-exponential factor. In Eq. (3),  $\alpha$  is the hydrogen absorption rate, which represents the ratio of the sample hydrogen absorption capacity to the saturation hydrogen absorption capacity at a certain time,  $n$  is Avrami index, and  $t$  is the reaction time. The activation energy ( $E_a^a$ ) was calculated as  $(87 \pm 1)$  kJ·mol<sup>-1</sup> by using the Arrhenius formula and the John-Mehl-Avrami (JMA) formula (Eq. (3)) [54]. As shown in Fig. 3(e), as the hydrogen absorption temperature of MgH<sub>2</sub>-10wt% nano-Ni increases, the saturated hydrogenation capacity gradually increases. In particular, the sample could rapidly absorb

5.3wt% H<sub>2</sub> within 1000 s at 482 K and under 3 MPa hydrogen pressure. In addition, the sample could absorb a total of 3wt% H<sub>2</sub> at 394 K. However, Fig. 4 shows that under the same conditions (482 K, 3 MPa H<sub>2</sub>), reabsorbing hydrogen is difficult for MgH<sub>2</sub> after dehydrogenation, which indicates that the hydrogen absorption performance of MgH<sub>2</sub> can be significantly improved by the addition of nano-Ni.

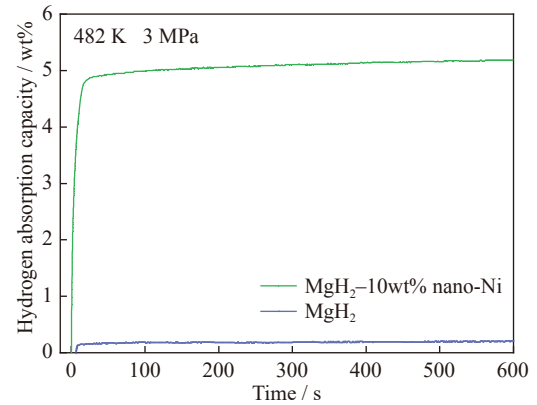


Fig. 4. Isothermal rehydrogenation curves of as-milled MgH<sub>2</sub> and MgH<sub>2</sub>-10wt% nano-Ni composite at a temperature of 482 K under 3 MPa H<sub>2</sub>.

The PCI curves of MgH<sub>2</sub> were measured at 647, 676, 681, and 698 K, and the MgH<sub>2</sub>-10wt% nano-Ni sample was measured at 565, 587, 591, and 604 K, as shown in Fig. 5(a) and (b). Their Van 't-Hoff plots are shown in the insets of Fig. 5(a) and (b). The dehydrogenation enthalpy of MgH<sub>2</sub>-10wt% nano-Ni and original MgH<sub>2</sub> were calculated by using the Van 't Hoff equation (Eq. (4)) [55].

$$\ln \left( \frac{P}{P_0} \right) = \frac{1}{T} \left( \frac{-\Delta H}{R} \right) + C \quad (4)$$

where  $P$  and  $P_0$  represent the equilibrium atmosphere and the normal atmosphere (100 kPa), respectively;  $T$  is the temperature;  $\Delta H$  means the enthalpy of desorption;  $R$  is the gas constant;  $C$  represents a constant whose value is equal to  $\Delta S/R$ , where  $\Delta S$  is the entropy change (the value of the metal hydride is usually 130 J·mol<sup>-1</sup>·K<sup>-1</sup>). The dehydrogenation enthalpy value shifts slightly from  $(77.7 \pm 0.5)$  kJ per mol H<sub>2</sub> for the original MgH<sub>2</sub> to  $(72.2 \pm 0.5)$  kJ per mol H<sub>2</sub> for the

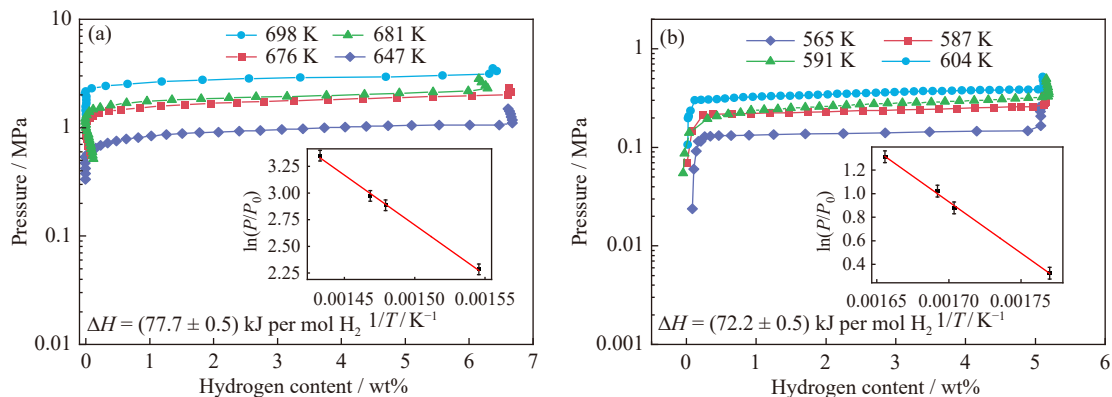


Fig. 5. PCI curves of (a) as-milled MgH<sub>2</sub> and (b) MgH<sub>2</sub>-10wt% nano-Ni sample; the inserted Van 't Hoff plots show the dehydrogenation enthalpy values of the samples.

MgH<sub>2</sub>-10wt% nano-Ni sample, as shown in Fig. 5(a). Hence, additional nano-Ni should be the main cause of the lower initial dehydrogenation temperature of the dehydrogenation. Therefore, we can conclude that nano-Ni might play a role in destabilizing MgH<sub>2</sub> during dehydrogenation.

### 3.3. Reaction mechanism

The diffraction peaks of the metallic Mg phase appear at 503 K, indicating that the MgH<sub>2</sub>-10wt% nano-Ni sample begins to decompose and release hydrogen at this temperature, as shown in Fig. 6. The diffraction peaks of the Mg phase (PDF: 017-0902) gradually become noticeable with increasing temperature. Meanwhile, the MgH<sub>2</sub> phase (PDF: 002-6624) gradually weakens and finally disappears at 673 K, suggesting that the dehydrogenation is completed. Small traces of MgO and Mg(OH)<sub>2</sub> are also detected in the XRD patterns, which could be attributed to the sample's brief exposure to air while transferred from the glove box to the holder.

The SAED patterns from TEM image and inverse Fourier transform are shown in Fig. 7(a) and (b). The plane with a spacing of 0.225 nm can be considered as lattice fringes of the MgH<sub>2</sub> (110) planes (Fig. 7(c)). Crystal planes with spacing up to 0.205 and 0.178 nm correspond to the (111) and (200) planes of Ni, respectively. Such results confirm that no intermediate phase is formed during the ball milling and the ball milling products are Ni and MgH<sub>2</sub>. On account of the high surface free energy of small particles, the sample after ball milling presents an aggregation distribution of small particles, as shown in Fig. 7(d). The TEM and Fourier transform images of the MgH<sub>2</sub>-10wt% nano-Ni composite after dehydrogenation are shown in Fig. 7(e) and (f). They confirm the presence of Mg (101), Mg (103), Ni (220), and Mg<sub>2</sub>Ni (114) planes in the dehydrogenated products, as shown by the *in-situ* XRD in Fig. 6. We can speculate that nano-Ni is involved in the MgH<sub>2</sub> dehydrogenation.

Furthermore, as shown in Fig. 7(g) and (h), the (002) plane of MgH<sub>2</sub>, the (111) plane of Ni, and the (220) and (400)

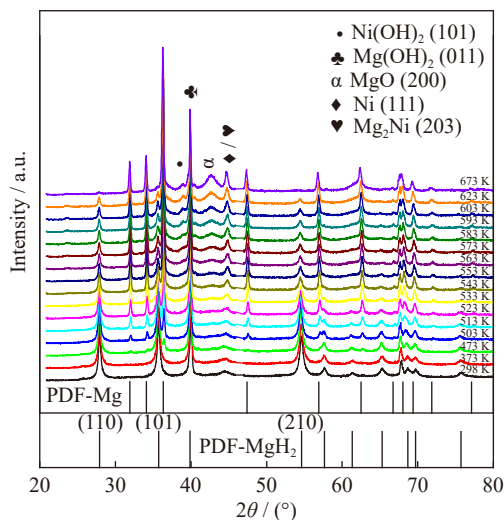
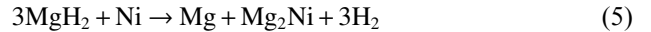


Fig. 6. *In-situ* XRD patterns of MgH<sub>2</sub>-10wt% nano-Ni from room temperature to 673 K.

planes of Mg<sub>2</sub>NiH<sub>4</sub> can be recognized in the SAED patterns of the rehydrogenated sample. The appearance of the Mg<sub>2</sub>NiH<sub>4</sub> phase indicates that the product Mg<sub>2</sub>Ni, as an intermediate phase in the absorption/desorption process, could promote the reversible absorption and desorption of the system. This result is consistent with the PCI measurement results, where the system is slightly destabilized during dehydrogenation. For MgH<sub>2</sub>-Ni, the dehydrogenation is as follows:



The rehydrogenation could be expressed as follows:



For this system, the dehydrogenation for the second time is described as follows:



In addition, the Ni phase is identified during the dehydrogenation and rehydrogenation processes, indicating that some nano-Ni still plays a catalytic role in the system.

Previous work by Chen *et al.* [50] indicated that the onset dehydrogenation temperature of MgH<sub>2</sub> doped with 20–30 nm Ni particles is 490 K, and the final temperature is about 643

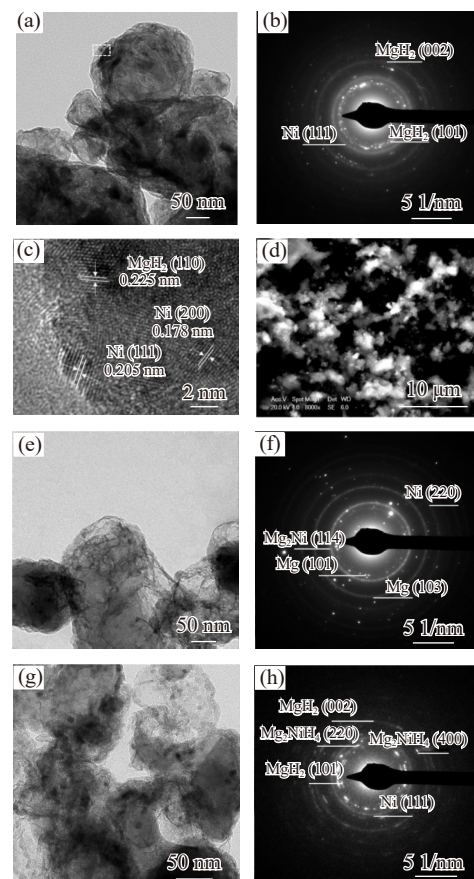


Fig. 7. (a) TEM, (b) SAED patterns, (c) HRTEM, and (d) SEM images of MgH<sub>2</sub>-10wt% nano-Ni after preparation. (e) TEM image and (f) SAED patterns of the sample after dehydrogenation; those clusters are identified as Mg, Mg<sub>2</sub>Ni, and Ni according to their SAED image. (g) TEM image and (h) SAED patterns of the sample after rehydrogenation remaining MgH<sub>2</sub>, Mg<sub>2</sub>NiH<sub>4</sub>, and Ni phases.

K. As shown in Table 2, compared with their study, the final temperature in this work is decreased by 60 K, although the onset dehydrogenation temperature of MgH<sub>2</sub> catalyzed by nano-Ni with an average particle size of 2.14 nm is 497 K. This finding suggests that the Ni nanoparticles tend to agglomerate in the reaction and weaken the catalytic effect because of the loss of great active surfaces.

From the results obtained by Chen *et al.* [50], the dehydrogenation

enthalpy of the MgH<sub>2</sub>-Ni/CMK-3 system is decreased by 3 kJ per mol H<sub>2</sub>, which is still 2.5 kJ per mol H<sub>2</sub> higher than that of the MgH<sub>2</sub>-nano-Ni system. This result means that after ball milling, the small Ni nanoparticles should have a larger interface and be in closer contact with MgH<sub>2</sub>, thus more actively participating in the reaction with MgH<sub>2</sub> and more effectively destabilizing the MgH<sub>2</sub> system than the large Ni nanoparticles can.

**Table 2.** Initial desorption temperature, end desorption temperature, and  $E_a^d$  of MgH<sub>2</sub>-10wt% nano-Ni, MgH<sub>2</sub>-10wt% Ni, and MgH<sub>2</sub>

| Sample                                      | Initial desorption temperature / K | End desorption temperature / K | $E_a^d$ / (kJ·mol <sup>-1</sup> ) | $\Delta H$ / (kJ per mol H <sub>2</sub> ) |
|---|------------------------------------|--------------------------------|-----------------------------------|---|
| MgH <sub>2</sub> (This work)                | 580                                | 672                            | 170                               | 77.7                                      |
| MgH <sub>2</sub> -10wt% nano-Ni (This work) | 497                                | 583                            | 88                                | 72.2                                      |
| MgH <sub>2</sub> -10wt% Ni [50]             | 490                                | 643                            | 121.8                             | —   |
| MgH <sub>2</sub> -10wt% Ni/CMK-3 [50]       | 433                                | 568                            | 43.4                              | 74.7                                      |

## 4. Conclusion

Nano-Ni with an average particle size of 2.14 nm has been synthesized via the reduction method. The optimal MgH<sub>2</sub>-10wt% nano-Ni starts to release hydrogen at 497 K and offers a dehydrogenation capacity of 6.2wt% below 583 K. The dehydrogenated MgH<sub>2</sub>-10wt% nano-Ni system can absorb 5.3wt% H<sub>2</sub> in 1000 s at 482 K under 3 MPa hydrogen pressure. More remarkably, even at 394 K and 3 MPa hydrogen pressure, MgH<sub>2</sub>-10wt% nano-Ni can uptake 3wt% hydrogen. In summary, the synthesized nano-Ni mainly exhibits excellent performance in reducing the enthalpy of dehydrogenation of MgH<sub>2</sub> and its decomposition. However, the catalytic activity is degraded as a result of the easy agglomeration of particles. Supporting materials such as CMK-3, reduced graphene oxide (rGO), and other carbon materials can be added to the support to disperse the catalysts and produce steady catalytic activity. Further work to avoid particle agglomeration is underway.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 52071177), the Natural Science Foundation of Guangxi, China (No. 2020GXNSFAA297074), the Jiangsu Key Laboratory for Advanced Metallic Materials (No. BM2007204), and the Guangxi Key Laboratory of Information Materials (No. 211021-K).

## Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## References

[1] X.L. Yang, J.Q. Zhang, Q.H. Hou, X.T. Guo, and G.Z. Xu, Im-

- provement of Mg-based hydrogen storage materials by metal catalysts: Review and summary, *ChemistrySelect*, 6(2021), No. 33, p. 8809.
- [2] T. He, H.J. Cao, and P. Chen, Complex hydrides for energy storage, conversion, and utilization, *Adv. Mater.*, 31(2019), No. 50, art. No. 1902757.
- [3] Y.R. Wang, X.W. Chen, H.Y. Zhang, G.L. Xia, D.L. Sun, and X.B. Yu, Heterostructures built in metal hydrides for advanced hydrogen storage reversibility, *Adv. Mater.*, 32(2020), No. 31, art. No. 2002647.
- [4] X. Zhao, S.M. Han, Y. Li, X.C. Chen, and D.D. Ke, Effect of CeH<sub>2.29</sub> on the microstructures and hydrogen properties of LiBH<sub>4</sub>-Mg<sub>2</sub>NiH<sub>4</sub> composites, *Int. J. Miner. Metall. Mater.*, 22(2015), No. 4, p. 423.
- [5] Q. Li, X. Lin, Q. Luo, *et al.*, Kinetics of the hydrogen absorption and desorption processes of hydrogen storage alloys: A review, *Int. J. Miner. Metall. Mater.*, 29(2022), No. 1, p. 32.
- [6] X.B. Yu, Z.W. Tang, D.L. Sun, L.Z. Ouyang, and M. Zhu, Recent advances and remaining challenges of nanostructured materials for hydrogen storage applications, *Prog. Mater. Sci.*, 88(2017), p. 1.
- [7] M.D. Allendorf, Z. Hulvey, T. Gennett, *et al.*, An assessment of strategies for the development of solid-state adsorbents for vehicular hydrogen storage, *Energy Environ. Sci.*, 11(2018), No. 10, p. 2784.
- [8] B. Sakintuna, F. Lamari-Darkrim, and M. Hirscher, Metal hydride materials for solid hydrogen storage: A review, *Int. J. Hydrogen Energy*, 32(2007), No. 9, p. 1121.
- [9] I. Sreedhar, K.M. Kamani, B.M. Kamani, B.M. Reddy, and A. Venugopal, A Bird's Eye view on process and engineering aspects of hydrogen storage, *Renewable Sustainable Energy Rev.*, 91(2018), p. 838.
- [10] J.Z. Song, Z.Y. Zhao, X. Zhao, R.D. Fu, and S.M. Han, Hydrogen storage properties of MgH<sub>2</sub> co-catalyzed by LaH<sub>3</sub> and NbH<sub>5</sub>, *Int. J. Miner. Metall. Mater.*, 24(2017), No. 10, p. 1183.
- [11] M. Hirscher, V.A. Yartys, M. Baricco, *et al.*, Materials for hydrogen-based energy storage—Past, recent progress and future outlook, *J. Alloys Compd.*, 827(2020), art. No. 153548.
- [12] L.Z. Ouyang, X.S. Yang, M. Zhu, *et al.*, Enhanced hydrogen storage kinetics and stability by synergistic effects of *in situ* formed CeH<sub>2.73</sub> and Ni in CeH<sub>2.73</sub>-MgH<sub>2</sub>-Ni nanocomposites, *J. Phys. Chem. C*, 118(2014), No. 15, p. 7808.
- [13] J.O. Abe, A.P.I. Popoola, E. Ajenifuja, and O.M. Popoola, Hydrogen energy, economy and storage: Review and recommendation, *Int. J. Hydrogen Energy*, 44(2019), No. 29, p. 15072.
- [14] I.P. Jain, C. Lal, and A. Jain, Hydrogen storage in Mg: A most



- promising material, *Int. J. Hydrogen Energy*, 35(2010), No. 10, p. 5133.
- [15] J.F. Zhang, Z.N. Li, Y.F. Wu, et al., Recent advances on the thermal destabilization of Mg-based hydrogen storage materials, *RSC Adv.*, 9(2019), No. 1, p. 408.
- [16] F. Dawood, M. Anda, and G.M. Shafiullah, Hydrogen production for energy: An overview, *Int. J. Hydrogen Energy*, 45(2020), No. 7, p. 3847.
- [17] Q. Luo, J.D. Li, B. Li, B. Liu, H.Y. Shao, and Q. Li, Kinetics in Mg-based hydrogen storage materials: Enhancement and mechanism, *J. Magnes. Alloys*, 7(2019), No. 1, p. 58.
- [18] X.B. Xie, C.X. Hou, C.G. Chen, et al., First-principles studies in Mg-based hydrogen storage materials: A review, *Energy*, 211(2020), art. No. 118959.
- [19] C.S. Zhou, Z.Z. Fang, and P. Sun, An experimental survey of additives for improving dehydrogenation properties of magnesium hydride, *J. Power Sources*, 278(2015), p. 38.
- [20] Z. Abdin, A. Zafaranloo, A. Rafiee, W. Mérida, W. Lipiński, and K.R. Khalilpour, Hydrogen as an energy vector, *Renewable Sustainable Energy Rev.*, 120(2020), art. No. 109620.
- [21] L.Z. Ouyang, K. Chen, J. Jiang, X.S. Yang, and M. Zhu, Hydrogen storage in light-metal based systems: A review, *J. Alloys Compd.*, 829(2020), art. No. 154597.
- [22] F. Li, X. Jiang, J.J. Zhao, and S.B. Zhang, Graphene oxide: A promising nanomaterial for energy and environmental applications, *Nano Energy*, 16(2015), p. 488.
- [23] P. Rizo-Acosta, F. Cuevas, and M. Lacroche, Hydrides of early transition metals as catalysts and grain growth inhibitors for enhanced reversible hydrogen storage in nanostructured magnesium, *J. Mater. Chem. A*, 7(2019), No. 40, p. 23064.
- [24] L.Z. Ouyang, F. Liu, H. Wang, et al., Magnesium-based hydrogen storage compounds: A review, *J. Alloys Compd.*, 832(2020), art. No. 154865.
- [25] E. Boateng and A.C. Chen, Recent advances in nanomaterial-based solid-state hydrogen storage, *Mater. Today Adv.*, 6(2020), art. No. 100022.
- [26] X. Zhang, Y.F. Liu, Z.H. Ren, et al., Realizing 6.7 wt.% reversible storage of hydrogen at ambient temperature with non-confined ultrafine magnesium hydrides, *Energy Environ. Sci.*, 14(2021), No. 4, p. 2302.
- [27] J.C. Crivello, B. Dam, R.V. Denys, et al., Review of magnesium hydride-based materials: Development and optimisation, *Appl. Phys. A*, 122(2016), No. 2, art. No. 97.
- [28] H. Wang, H.J. Lin, W.T. Cai, L.Z. Ouyang, and M. Zhu, Tuning kinetics and thermodynamics of hydrogen storage in light metal element based systems – A review of recent progress, *J. Alloys Compd.*, 658(2016), p. 280.
- [29] H.Y. Shao, L.Q. He, H.J. Lin, and H.W. Li, Progress and trends in magnesium-based materials for energy-storage research: A review, *Energy Technol.*, 6(2018), No. 3, p. 445.
- [30] Y. Wang and Y.J. Wang, Recent advances in additive-enhanced magnesium hydride for hydrogen storage, *Prog. Nat. Sci. Mater. Int.*, 27(2017), No. 1, p. 41.
- [31] M.E. Khatibi, M. Bhihi, S. Najji, et al., Study of doping effects with 3d and 4d-transition metals on the hydrogen storage properties of MgH<sub>2</sub>, *Int. J. Hydrogen Energy*, 41(2016), No. 8, p. 4712.
- [32] S. Chakrabarti and K. Biswas, Effect on de-hydrogenation efficiency on doping of rare earth elements (Pr, Nd, Gd, Dy) in MgH<sub>2</sub> – A density functional theory study, *Int. J. Hydrogen Energy*, 42(2017), No. 2, p. 1012.
- [33] X.L. Zhang, Y.F. Liu, X. Zhang, J.J. Hu, M.X. Gao, and H.G. Pan, Empowering hydrogen storage performance of MgH<sub>2</sub> by nanoengineering and nanocatalysis, *Mater. Today Nano*, 9(2020), art. No. 100064.
- [34] V.A. Yartys, M.V. Lototsky, E. Akiba, et al., Magnesium based materials for hydrogen based energy storage: Past, present and future, *Int. J. Hydrogen Energy*, 44(2019), No. 15, p. 7809.
- [35] Z. Sun, X. Lu, F.M. Nyahuma, et al., Enhancing hydrogen storage properties of MgH<sub>2</sub> by transition metals and carbon materials: A brief review, *Front. Chem.*, 8(2020), art. No. 552.
- [36] N. Hanada, T. Ichikawa, and H. Fujii, Catalytic effect of nanoparticle 3d-transition metals on hydrogen storage properties in magnesium hydride MgH<sub>2</sub> prepared by mechanical milling, *J. Phys. Chem. B*, 109(2005), No. 15, p. 7188.
- [37] M. Lakhali, M. Bhihi, A. Benyoussef, A.E. KENZ, M. Loulidi, and S. Najji, The hydrogen ab/desorption kinetic properties of doped magnesium hydride MgH<sub>2</sub> systems by first principles calculations and kinetic Monte Carlo simulations, *Int. J. Hydrogen Energy*, 40(2015), No. 18, p. 6137.
- [38] H. Yu, S. Bennici, and A. Auroux, Hydrogen storage and release: Kinetic and thermodynamic studies of MgH<sub>2</sub> activated by transition metal nanoparticles, *Int. J. Hydrogen Energy*, 39(2014), No. 22, p. 11633.
- [39] L.S. Xie, J.S. Li, T.B. Zhang, and H.C. Kou, Understanding the dehydrogenation process of MgH<sub>2</sub> from the recombination of hydrogen atoms, *Int. J. Hydrogen Energy*, 41(2016), No. 13, p. 5716.
- [40] M. Chen, X.Z. Xiao, M. Zhang, et al., Excellent synergistic catalytic mechanism of *in-situ* formed nanosized Mg<sub>2</sub>Ni and multiple valence titanium for improved hydrogen desorption properties of magnesium hydride, *Int. J. Hydrogen Energy*, 44(2019), No. 3, p. 1750.
- [41] H.X. Shao, Y.K. Huang, H.N. Guo, Y.F. Liu, Y.S. Guo, and Y.J. Wang, Thermally stable Ni MOF catalyzed MgH<sub>2</sub> for hydrogen storage, *Int. J. Hydrogen Energy*, 46(2021), No. 76, p. 37977.
- [42] Y.K. Huang, C.H. An, Q.Y. Zhang, et al., Cost-effective mechanochemical synthesis of highly dispersed supported transition metal catalysts for hydrogen storage, *Nano Energy*, 80(2021), art. No. 105535.
- [43] Q.Y. Zhang, L. Zang, Y.K. Huang, et al., Improved hydrogen storage properties of MgH<sub>2</sub> with Ni-based compounds, *Int. J. Hydrogen Energy*, 42(2017), No. 38, p. 24247.
- [44] M.S. El-Eskandarany, E. Shaban, N. Ali, F. Aldakheel, and A. Alkandary, *In-situ* catalyzed approach for enhancing the hydrogenation/dehydrogenation kinetics of MgH<sub>2</sub> powders with Ni particles, *Sci. Rep.*, 6(2016), art. No. 37335.
- [45] T.Z. Si, X.Y. Zhang, J.J. Feng, X.L. Ding, and Y.T. Li, Enhancing hydrogen sorption in MgH<sub>2</sub> by controlling particle size and contact of Ni catalysts, *Rare Met.*, 40(2021), No. 4, p. 995.
- [46] H.G. Gao, R. Shi, J.L. Zhu, et al., Interface effect in sandwich like Ni/Ti<sub>3</sub>C<sub>2</sub> catalysts on hydrogen storage performance of MgH<sub>2</sub>, *Appl. Surf. Sci.*, 564(2021), art. No. 150302.
- [47] J. Chen, G.L. Xia, Z.P. Guo, Z.G. Huang, H.K. Liu, and X.B. Yu, Porous Ni nanofibers with enhanced catalytic effect on the hydrogen storage performance of MgH<sub>2</sub>, *J. Mater. Chem. A*, 3(2015), No. 31, p. 15843.
- [48] W. Zhu, S. Panda, C. Lu, et al., Using a self-assembled two-dimensional MXene-based catalyst (2D-Ni@Ti<sub>3</sub>C<sub>2</sub>) to enhance hydrogen storage properties of MgH<sub>2</sub>, *ACS Appl. Mater. Interfaces*, 12(2020), No. 45, p. 50333.
- [49] D. Rahmalina, R.A. Rahman, A. Suwandi, and Ismail, The recent development on MgH<sub>2</sub> system by 16 wt.% nickel addition and particle size reduction through ball milling: A noticeable hydrogen capacity up to 5 wt.% at low temperature and pressure, *Int. J. Hydrogen Energy*, 45(2020), No. 53, p. 29046.
- [50] G. Chen, Y. Zhang, J. Chen, X.L. Guo, Y.F. Zhu, and L.Q. Li, Enhancing hydrogen storage performances of MgH<sub>2</sub> by Ni nano-particles over mesoporous carbon CMK-3, *Nanotechnology*, 29(2018), No. 26, art. No. 265705.
- [51] H.H. Cheng, G. Chen, Y. Zhang, Y.F. Zhu, and L.Q. Li, Boosting low-temperature de/re-hydrogenation performances of

- MgH<sub>2</sub> with Pd–Ni bimetallic nanoparticles supported by mesoporous carbon, *Int. J. Hydrogen Energy*, 44(2019), No. 21, p. 10777.
- [52] P. Plerdsranoy, S. Thiangviriyaya, P. Dansirima, *et al.*, Synergistic effects of transition metal halides and activated carbon nanofibers on kinetics and reversibility of MgH<sub>2</sub>, *J. Phys. Chem. Solids*, 124(2019), p. 81.
- [53] T.P. Huang, J.X. Zou, H.B. Liu, and W.J. Ding, Effect of different transition metal fluorides TMF<sub>x</sub> (TM=Nb, Co, Ti) on hydrogen storage properties of the 3NaBH<sub>4</sub>–GdF<sub>3</sub> system, *J. Alloys Compd.*, 823(2020), art. No. 153716.
- [54] F.H. Wang, Y.F. Liu, M.X. Gao, K. Luo, H.G. Pan, and Q.D. Wang, Formation reactions and the thermodynamics and kinetics of dehydrogenation reaction of mixed alanate Na<sub>2</sub>LiAlH<sub>6</sub>, *J. Phys. Chem. C*, 113(2009), No. 18, p. 7978.
- [55] N. Patelli, M. Calizzi, A. Migliori, V. Morandi, and L. Pasquini, Hydrogen desorption below 150°C in MgH<sub>2</sub>–TiH<sub>2</sub> composite nanoparticles: Equilibrium and kinetic properties, *J. Phys. Chem. C*, 121(2017), No. 21, p. 11166.