



## Research article

# Modification of MgH<sub>2</sub> hydrogen storage performance by nickel-based composite catalyst Ni/NiO

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## ARTICLE INFO

## Keywords:

MgH<sub>2</sub>  
Hydrogen storage performance  
Modification  
Ni/NiO

## ABSTRACT

In this study, the Ni/NiO catalyst was demonstrated to enhance the hydrogen storage performance of MgH<sub>2</sub>. The dehydrogenation of MgH<sub>2</sub>+10 wt% Ni/NiO started at approximately 180 °C, achieving 5.83 wt% of dehydrogenation within 10 min at 300 °C. Completely dehydrogenated, MgH<sub>2</sub> began to rehydrogenate at about 50 °C, absorbing about 4.56 wt% of hydrogen in 10 min at 150 °C. In addition, the activation energies of dehydrogenation and rehydrogenation of MgH<sub>2</sub>+10 wt% Ni/NiO were 87.21 and 34.84 kJ/mol. During the dehydrogenation/rehydrogenation cycle, Mg<sub>2</sub>Ni/Mg<sub>2</sub>NiH<sub>4</sub> could promote hydrogen diffusion, thus enhancing the hydrogen storage performance of Mg/MgH<sub>2</sub>.

## 1. Introduction

Energy is an indispensable part of human life. However, the extensive use of fossil energy sources has resulted in an escalating energy predicament and environmental degradation. Hydrogen is a promising alternative to fossil fuels because of its elevated fuel effectiveness and ecological benevolence (the combustion product is water) [1]. However, hydrogen containment currently poses a pivotal challenge in advancing hydrogen energy. Solid hydrogen storage materials, which offer high safety and heightened hydrogen density while capable of containing hydrogen under low pressure, have attracted much attention [2].

MgH<sub>2</sub>, distinguished by its elevated hydrogen storage capability and favorable reversibility, emerges prominently among numerous solid hydrogen storage substances. Nevertheless, the pragmatic advancement of MgH<sub>2</sub> faces impediments due to its considerable thermodynamic stability and sluggish kinetics in the dehydrogenation/rehydrogenation processes [3]. Many studies have demonstrated that catalyst doping can significantly improve the kinetic properties of Mg/MgH<sub>2</sub>, leading to its rapid dehydrogenation/rehydrogenation at low temperatures.

Currently, various types of transition metals (e.g., Ni [4], Fe [5], Ti [6]) and their constituent metal alloys (e.g., Ni<sub>3</sub>Fe [7], CoFeB [8]), metal compounds (e.g., FeOOH [9], TiO<sub>2</sub> [10]), and metal composites (e.g., the complexes of carbon materials with Ni—Ni@C [11], graphene-supported TiNiFe [12]) have been widely used to improve the hydrogen storage properties of Mg/MgH<sub>2</sub>. In contrast to alternative transition metals, Ni is cost-effective and demonstrates the capacity to enhance the hydrogen storage characteristics of Mg/MgH<sub>2</sub>, drawing considerable interest from researchers.

Rahwanto et al. [4] found that the incorporation of 2 mol% Ni resulted in 5.3 wt% hydrogen uptake by Mg/MgH<sub>2</sub> within 5 min at

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<https://doi.org/10.1016/j.heliyon.2024.e30688>

Received 15 February 2024; Received in revised form 1 May 2024; Accepted 2 May 2024

Available online 4 May 2024

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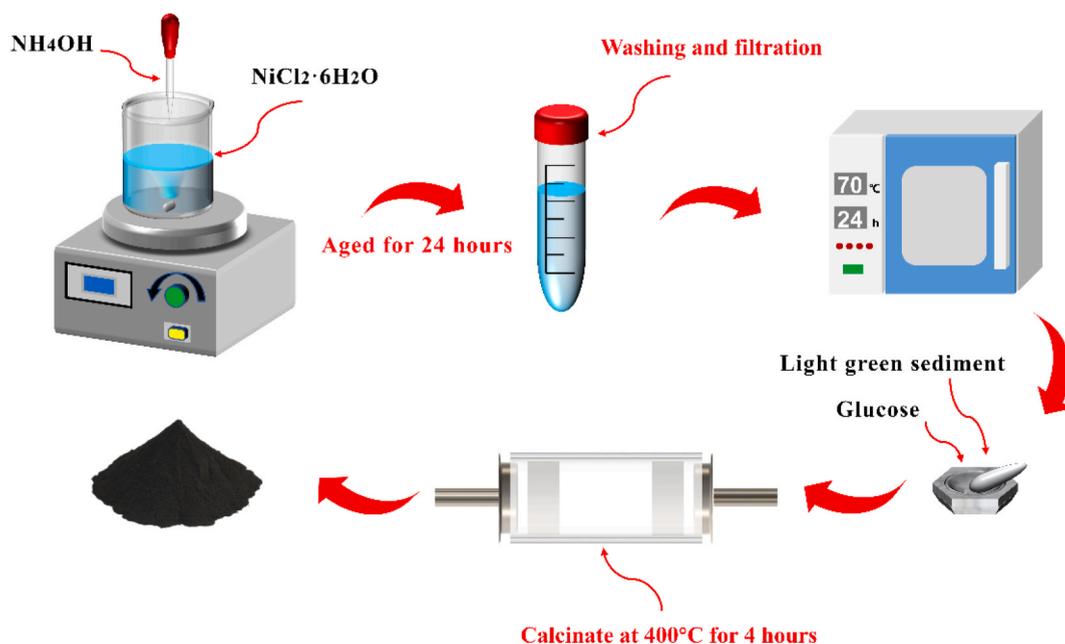


Fig. 1. Schematic diagram of the preparation process of Ni/NiO catalyst.

300 °C and was able to complete dehydrogenation within 4 min at 50 mbar. In addition, Dan et al. [13] discovered that the dehydrogenation/rehydrogenation kinetics of Mg/MgH<sub>2</sub> were significantly enhanced by compositing 2–6 nm nickel nanoparticles with MgH<sub>2</sub>, and MgH<sub>2</sub>-Ni exhibited rapid dehydrogenation, releasing more than 6.5 wt% at 275 °C within 10 min. This enhancement was attributed to Mg<sub>2</sub>NiH<sub>0.3</sub> during dehydrogenation/rehydrogenation cycling.

Not only that, building upon the foundation of nickel, researchers have devised a variety of nickel-based compounds (e.g., NiB [14], NiO [15]) or nickel-based composites (e.g., Ni/Fe<sub>3</sub>O<sub>4</sub>@MIL [16], NiO@KNbO<sub>3</sub> [17]) to enhance the kinetic of the dehydrogenation/rehydrogenation process of Mg/MgH<sub>2</sub>. Liu et al. [14] observed significant improvement in the kinetic properties of MgH<sub>2</sub> by adding 10 wt% NiB, and MgH<sub>2</sub>-10 wt% NiB demonstrated the release of 6.0 wt% hydrogen within 10 min at 300 °C. In addition, Zhang et al. [15] explored compound catalysts, including NiO, Ni<sub>3</sub>C, Ni<sub>3</sub>N, Ni<sub>2</sub>P, etc. The experimental findings indicated that all these catalysts exhibited commendable catalytic effects.

Based on the element nickel, various nickel-based composites developed by scholars have likewise exhibited good catalytic properties [16–21]. For example, Ren et al. [16] prepared Ni/Fe<sub>3</sub>O<sub>4</sub>@MIL based on nickel and found that at 598 K, MgH<sub>2</sub>-Ni/Fe<sub>3</sub>O<sub>4</sub>@MIL could dehydrogenate about 3.3 wt% in 10 min. In addition, Hou et al. [20] found that MgH<sub>2</sub>+10 wt% Ni/BC-3 commenced hydrogen liberation at 187.8 °C. At 300 °C, MgH<sub>2</sub>+10 wt% Ni/BC-3 can dehydrogenate about 6.3 wt% in 5 min. It is worth mentioning that Hou's team developed Ni/BC-3 based on Ni and NiO/C based on NiO. It was demonstrated that the incorporation of 9 wt% NiO/C resulted in a 155 °C decrease in the initial dehydrogenation temperature of MgH<sub>2</sub>. Moreover, MgH<sub>2</sub>+9 wt% NiO/C could dehydrogenate 6.21 wt% at 300 °C for 10 min [21]. Wu et al. [17] observed a reduction of 111 °C in the initial dehydrogenation temperature of MgH<sub>2</sub>, decreasing from the original 286 °C–175 °C, adding 5 wt% NiO@KNbO<sub>3</sub>. Additionally, at 300 °C, MgH<sub>2</sub>-5wt% NiO@KNbO<sub>3</sub> demonstrated the release of 3.92 wt% within 10 min. These studies show that Ni or NiO with good catalytic properties can be combined with more active catalytic substances to form high-quality, high-performance catalysts to boost the hydrogen storage capabilities of Mg/MgH<sub>2</sub>.

Considering the excellent modification ability of Ni and NiO and their composites to Mg/MgH<sub>2</sub>, there is no research on catalysts combining Ni and NiO. It was decided to prepare a catalyst combining Ni and NiO's advantages to enhance the hydrogen storage capabilities of Mg/MgH<sub>2</sub>. In this study, Ni/NiO was synthesized using the co-precipitation method, and its impact on the hydrogen storage capabilities of Mg/MgH<sub>2</sub> was investigated.

## 2. Experimental

### 2.1. Synthesis of Ni/NiO

The synthesis process of the Ni/NiO catalyst is based on the relevant literature that has been reported [22]. First, NH<sub>4</sub>OH was added dropwise to a 10% mass fraction of NiCl<sub>2</sub>·6H<sub>2</sub>O solution, stirred constantly until the pH of the solution reached 11, and the mixture was aged for 24 h. Then, the light green sediment produced by the mixture was washed with deionized water and anhydrous ethanol, respectively, and filtered, and the sediment was dried at 70 °C. Finally, the dried sediment was mixed and ground with glucose in a mortar at a mass ratio of 1:2, and then the mixture was calcined in a covered crucible at 400 °C for 4 h to obtain a Ni/NiO catalyst. The

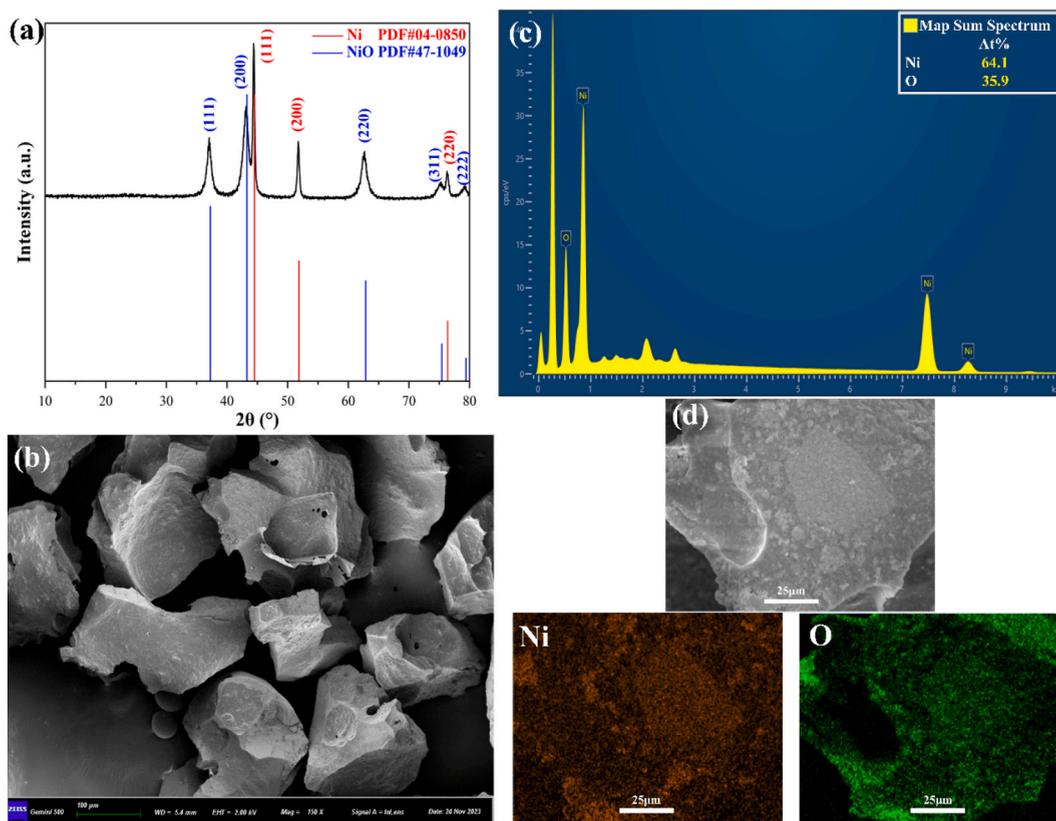


Fig. 2. XRD image (a), SEM image (b), EDS images (c, d) of Ni/NiO catalyst.

prepared catalyst was placed in a glove box before use. Fig. 1 briefly shows the preparation steps of the Ni/NiO catalyst.

## 2.2. Preparation of $MgH_2+Ni/NiO$

First, the Mg powder was hydrogenated at a hydrogen pressure of 70 bar and 380 °C for 2 h. Subsequently, the  $MgH_2$  powder was placed into a ball mill jar and ball-milled at a rotational speed of 450 r/min for 5 h in a planetary ball mill. After the ball milling, the sample was hydrogenated again under the same conditions as the first time. Next, the sample was ball-milled at 450 r/min for 5 h and pounded every 1 h. Finally, the sample was subjected to the last hydrogenation under hydrogenation conditions consistent with the first time. After these operations, the  $MgH_2$  powder was successfully prepared.

$MgH_2$  and Ni/NiO were mixed into ball mills in an argon atmosphere according to mass ratios of 95:5, 90:10, and 85:15 and mixed at a rotational speed of 450 r/min for 2 h. After ball milling, the samples were pounded and collected, recorded as  $MgH_2+5$  wt% Ni/NiO,  $MgH_2+10$  wt% Ni/NiO, and  $MgH_2+15$  wt% Ni/NiO, respectively. All samples were processed in a glove box with water and oxygen concentrations below 0.1 ppm.

## 3. Results and discussions

### 3.1. Characterization of Ni/NiO

The XRD of the Ni/NiO catalyst is shown in Fig. 2(a), where two different colors of diffraction peaks can be found. The red diffraction peaks are typical of Ni (PDF#04-0850), and it can be seen that there are robust diffraction features at  $2\theta = 44.507^\circ$ ,  $51.846^\circ$ , and  $76.370^\circ$ , aligning with the (111), (200) and (220) lattice planes, respectively. In addition, the blue diffraction peaks are typical of NiO (PDF#47-1049), and the diffraction peaks mainly appear at  $2\theta = 37.248^\circ$ ,  $43.275^\circ$ , and  $62.878^\circ$ , corresponding to the (111), (200), and (220) lattice planes, respectively. Fig. 2(b) shows that the Ni/NiO catalyst exhibits a large-scale, micron-scale irregular structure. Fig. 2(c, d) shows the elemental composition of the catalyst as Ni and O, and their relative elemental contents are 64.1% and 35.9%, respectively.

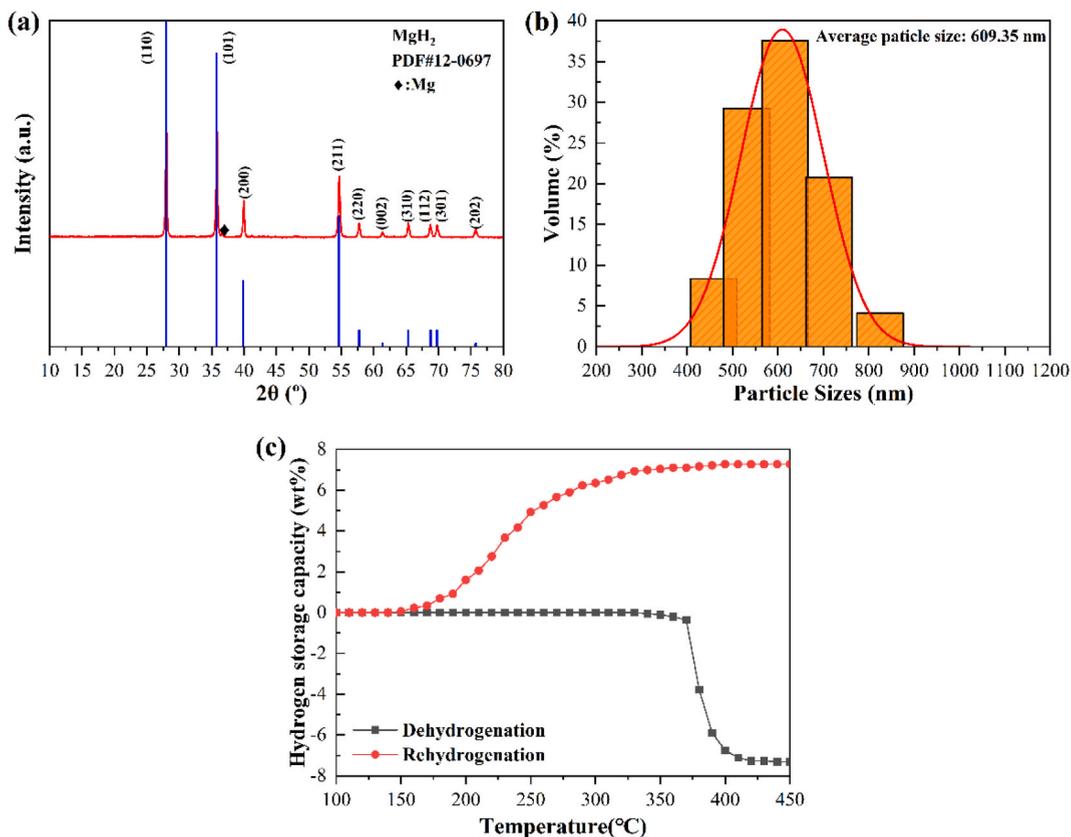


Fig. 3. XRD (a), PSDA (b), and hydrogen storage performance test chart (c) of MgH<sub>2</sub>.

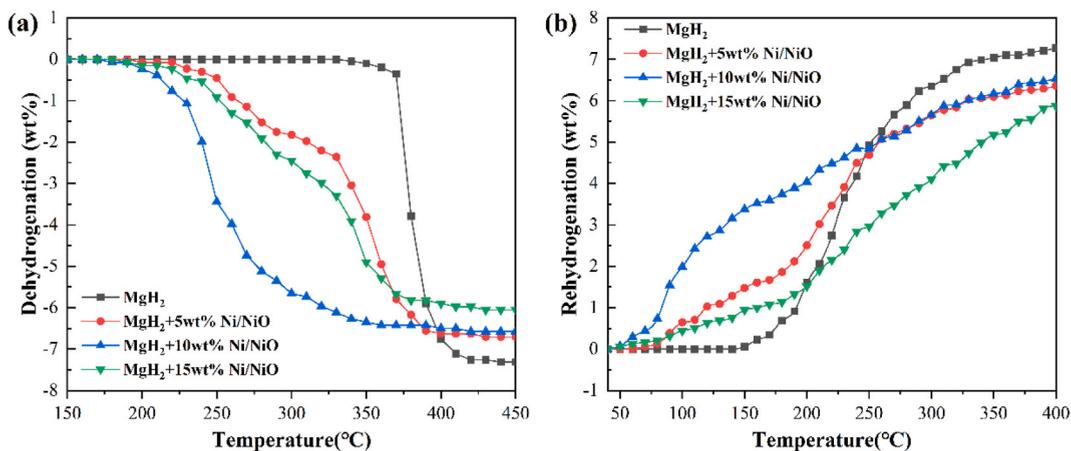
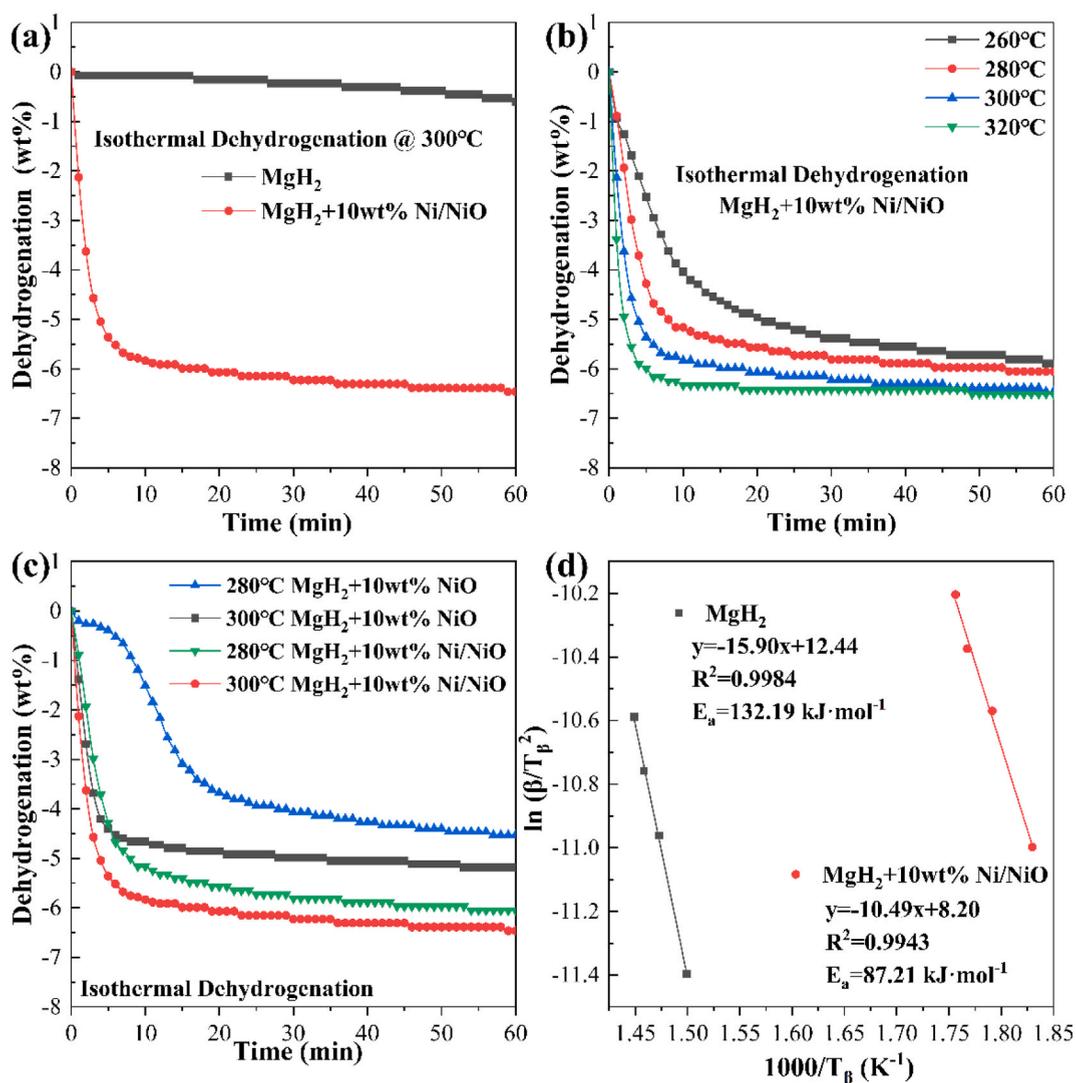


Fig. 4. Heating dehydrogenation plots (a) and heating rehydrogenation plots (b) of pure MgH<sub>2</sub>, MgH<sub>2</sub>+5 wt% Ni/NiO, MgH<sub>2</sub>+10 wt% Ni/NiO and MgH<sub>2</sub>+15 wt% Ni/NiO.

### 3.2. Characterization and testing of MgH<sub>2</sub>

To verify the authenticity and validity of the homemade MgH<sub>2</sub>, XRD and PSDA characterization were performed, as illustrated in Fig. 3(a) and (b). The diffraction features of XRD are in complete agreement with the standard card for MgH<sub>2</sub> (PDF#12-0697), which indicates that the preparation of MgH<sub>2</sub> was successful. Fig. 3(b) shows that the particle dimensions of MgH<sub>2</sub> vary between 400 and 900 nm, with a mean particle size of 609.35 nm. Fig. 3(c) shows the dehydrogenated and rehydrogenated properties of pure MgH<sub>2</sub>. MgH<sub>2</sub> exhibited a dehydrogenation onset temperature of approximately 340  $^\circ$ C, and the hydrogen absorption temperature was about 150  $^\circ$ C.



**Fig. 5.** Isothermal dehydrogenation profiles of pure MgH<sub>2</sub> and MgH<sub>2</sub>+10 wt% Ni/NiO at 300 °C (a), isothermal dehydrogenation profiles of MgH<sub>2</sub>+10 wt% Ni/NiO at different temperatures (b), isothermal dehydrogenation profiles of MgH<sub>2</sub>+10 wt% NiO and MgH<sub>2</sub>+10 wt% Ni/NiO at 280 °C and 300 °C (c) and dehydrogenated activation energy of pure MgH<sub>2</sub> and MgH<sub>2</sub>+10 wt% Ni/NiO (d).

The final dehydrogenation and rehydrogenation could reach about 7.31 wt% and 7.27 wt%, respectively, reaching 96.2% and 95.7% of the theoretical value (7.6 wt%).

### 3.3. Preliminary exploration of the dehydrogenation/rehydrogenation performance of MgH<sub>2</sub>+Ni/NiO

Fig. 4(a) shows the influence of various ratios of Ni/NiO catalysts on the dehydrogenation efficacy of MgH<sub>2</sub>. The dehydrogenation temperature after Ni/NiO doping was significantly reduced compared with pure MgH<sub>2</sub>. The effect of 10 wt% Ni/NiO was the most significant, and its introduction reduced the initiation temperature of MgH<sub>2</sub> dehydrogenation from around 340 °C–180 °C. The doping of 5 wt% Ni/NiO and 15 wt% Ni/NiO resulted in the dehydrogenation of MgH<sub>2</sub> at 200 °C and 190 °C, with final dehydrogenation amounts of 6.71 wt% and 6.05 wt%, respectively. It is worth mentioning that the dehydrogenation rate of MgH<sub>2</sub>+10 wt% Ni/NiO was very rapid, with 6.42 wt% dehydrogenation at 360 °C, reaching 97.7% of the total dehydrogenation (6.57 wt%). Fig. 4(b) shows the rehydrogenation performance of the MgH<sub>2</sub>+Ni/NiO. The introduction of Ni/NiO significantly reduced the reabsorption temperature of MgH<sub>2</sub>. The temperature for reabsorption of hydrogen by MgH<sub>2</sub> was approximately 150 °C, and the composite could start reabsorption at 50 °C after adding the Ni/NiO catalyst. After hydrogen reabsorption, the hydrogen reabsorption of MgH<sub>2</sub>+10 wt% Ni/NiO could reach 6.54 wt%, while the reabsorption of MgH<sub>2</sub>+15 wt% Ni/NiO could reach 5.87 wt%. From the view of total hydrogen storage, the hydrogen storage capacities of MgH<sub>2</sub>+5 wt% Ni/NiO and MgH<sub>2</sub>+10 wt% Ni/NiO were highly similar. However, the dehydrogenation/rehydrogenation rate of MgH<sub>2</sub>+10 wt% Ni/NiO was more significant. Considering the dehydrogenation/rehydrogenation

**Table 1**  
The dehydrogenation activation energy of Mg/MgH<sub>2</sub> hydrogen storage systems doped with different nickel-based catalysts.

Hydrogen storage systems	E <sub>a</sub> (kJ/mol)	Ref.
MgH <sub>2</sub> +10 wt% Ni/NiO	87.21	This work
MgH <sub>2</sub> +10 wt% Ni@C	93.08	[11]
MgH <sub>2</sub> +5 wt% Ni <sub>3</sub> C	97.8	[15]
MgH <sub>2</sub> +10 wt% ZrNi <sub>5</sub>	110.06	[27]
MgH <sub>2</sub> +10 wt% NiMoO <sub>4</sub>	119.47	[28]
MgH <sub>2</sub> +Ni <sub>3</sub> S <sub>2</sub> @C-4	115.2	[29]
MgH <sub>2</sub> +10 wt% CrFeCoNi	133.06	[30]
MgH <sub>2</sub> +10 wt% TiMgVNi <sub>3</sub>	94.42	[31]

characteristics of MgH<sub>2</sub>+Ni/NiO, MgH<sub>2</sub>+10 wt% Ni/NiO was used for further research.

### 3.4. Further exploration of the dehydrogenation/rehydrogenation performance of MgH<sub>2</sub>+10 wt% Ni/NiO

In Fig. 5(a), the dehydrogenation rate of MgH<sub>2</sub> at 300 °C was prolonged, with only 0.60 wt% dehydrogenation in 60 min. However, under the same condition, the dehydrogenation rate of MgH<sub>2</sub>+10 wt% Ni/NiO was very significant, with about 5.83 wt% dehydrogenation in 10 min and a total dehydrogenation of 6.46 wt%. Compared with previous reports, MgH<sub>2</sub>-NiO could dehydrogenate 4.1 wt% in 20 min at 300 °C [15]. The dehydrogenation of MgH<sub>2</sub>+9 wt% Ni could reach 6.3 wt% in 2.5min at 300 °C [23]. Furthermore, MgH<sub>2</sub> doped with catalyst MgCCo<sub>1.5</sub>Ni<sub>1.5</sub> released about 5 wt% hydrogen within 10 min at 325 °C [24]. MgH<sub>2</sub> doped with Ni-50%Cu released about 5.14 wt% hydrogen in 15 min at 300 °C [25]. MgH<sub>2</sub> doped with 10 wt% Ni@C released about 4.8 wt% within 10 min at 300 °C [11]. Fig. 5(b) shows that the total amount and rate of dehydrogenation of MgH<sub>2</sub>+10 wt% Ni/NiO increased effectively with the increase in temperature. Under the condition of 260 °C, the dehydrogenation of MgH<sub>2</sub>+10 wt% Ni/NiO could reach 5.38 wt% within 30min.

In this paper, the excellent performance of the Ni/NiO catalyst was further verified by the comparative experiments in Fig. 5(c). With the increase in temperature, although the dehydrogenation rate of MgH<sub>2</sub>+10 wt% NiO was improved, it still needed to be improved compared to that of MgH<sub>2</sub>+10 wt% Ni/NiO. It is worth mentioning that the dehydrogenation of MgH<sub>2</sub>+10 wt% NiO was only 5.18 wt% in 60 min at 300 °C, which was not as good as the dehydrogenation (5.24 wt%) of MgH<sub>2</sub>+10 wt% Ni/NiO in 12 min at 280 °C. It can be seen that the Ni/NiO catalyst formed by combining Ni and NiO has a better catalytic performance than NiO, and the introduction of Ni may help improve NiO's catalytic effect, which is a crucial point to be explored in future research.

The activation energy for dehydrogenation in pure MgH<sub>2</sub> and MgH<sub>2</sub>+10 wt% Ni/NiO calculated by combining the Kissinger formula [26] is depicted in Fig. 5(d). The activation energy of pure MgH<sub>2</sub> was recorded at 132.19 kJ/mol, which decreased to 87.21 kJ/mol following the incorporation of 10 wt% Ni/NiO. Therefore, adding 10 wt% Ni/NiO enhanced the dehydrogenation reaction of MgH<sub>2</sub>, decreased its dehydrogenation temperature and activation energy and enhanced its dehydrogenation rate. Table 1 shows the dehydrogenation activation energy of Mg/MgH<sub>2</sub> hydrogen storage systems doped with nickel-based materials.

For MgH<sub>2</sub>+10 wt% Ni/NiO, the constant temperature rehydrogenation performance test is also critical. Fig. 6(b) shows the continuous temperature rehydrogenation performance of fully dehydrogenated MgH<sub>2</sub>+10 wt% Ni/NiO within 60 min. The fully dehydrogenated MgH<sub>2</sub>+10 wt% Ni/NiO had a reasonable hydrogen uptake rate at 150 °C, with reabsorption up to 5.35 wt% in 60 min. Even when the temperature was reduced to 100 °C, the fully dehydrogenated MgH<sub>2</sub>+10 wt% Ni/NiO could still absorb 4.29 wt% of hydrogen. As a comparison, the completely dehydrogenated MgH<sub>2</sub> was tested for constant temperature reabsorption at various temperatures, and the outcomes are presented in Fig. 6(a). When the temperature exceeded 210 °C, the reabsorption of hydrogen by MgH<sub>2</sub> was comparable to that of MgH<sub>2</sub>+10 wt% Ni/NiO. Incorporating Ni/NiO catalyst enhanced the hydrogen reuptake kinetics of MgH<sub>2</sub>. The activation energy for hydrogen absorption is a crucial parameter characterizing the kinetic of hydrogen reuptake. Data from constant temperature hydrogen reabsorption was utilized as the foundational parameter, and the curves were fitted with the help of the JMAK equation [26], as depicted in Fig. 6(c) and (d). The curves at different temperatures have a good fit. The Arrhenius equation [30] was used to calculate the activation energy of the hydrogen uptake. Fig. 6(e) illustrates that the two curves exhibited strong fits, one at 0.999 and the other at 0.994. The activation energies of pure MgH<sub>2</sub> and MgH<sub>2</sub>+10 wt% Ni/NiO were 68.36 and 34.84 kJ/mol. Introducing Ni/NiO reduced the reabsorption temperature of fully dehydrogenated MgH<sub>2</sub>, greatly reduced its reaction energy barrier, and significantly improved its rehydrogenation kinetic. Table 2 shows the hydrogen absorption activation energy of the Mg/MgH<sub>2</sub> hydrogen storage systems doped with nickel-based materials.

### 3.5. Study on the stability of the dehydrogenation/rehydrogenation cycle of MgH<sub>2</sub>+10 wt% Ni/NiO

To explore the cycling stability of MgH<sub>2</sub>+10 wt% Ni/NiO, 10 dehydrogenation/rehydrogenation cycles were tested under hydrogen at 3 MPa and 320 °C, as depicted in Fig. 7. The extent of hydrogen release and rehydrogenation during the initial cycle was 6.34 wt% and 6.01 wt%. At the end of the third cycle, the dehydrogenation value of the composite decayed from 6.34 wt% to 5.90 wt%, a decrease of 0.44 wt%. Within the subsequent seven cycles, the dehydrogenation value of the composite decayed from 5.90 wt% to 5.72 wt%, a decrease of only 0.18 wt%. This suggests that the dehydrogenation of the composite stabilized at the end of the third cycle. In addition, in the first cycle, the rehydrogenation value of the composite was 0.33 wt% less than the dehydrogenation value. However,

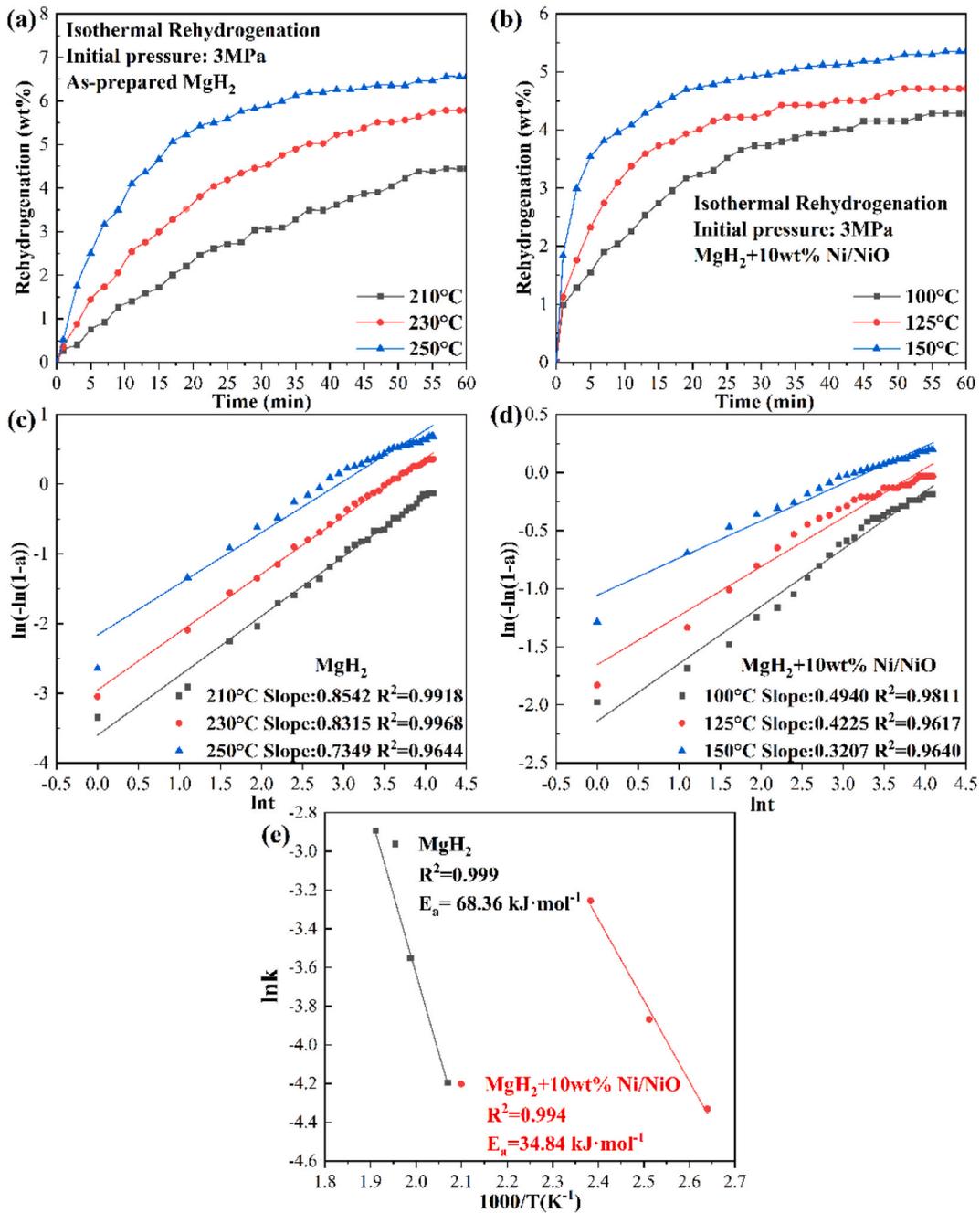


Fig. 6. Isothermal reabsorption curves of fully dehydrogenated pure MgH<sub>2</sub>(a) and MgH<sub>2</sub>+10 wt% Ni/NiO(b) under various temperature conditions, JMAK plots of pure MgH<sub>2</sub>(c) and MgH<sub>2</sub>+10 wt% Ni/NiO(d), absorption activation energy of pure MgH<sub>2</sub> and MgH<sub>2</sub>+10 wt% Ni/NiO (e).

after ten cycles, the rehydrogenation value of the composite only decayed by 0.29 wt%, which indicated that the rehydrogenation performance of the composite stabilized within ten cycles. Although the quantity of hydrogen assimilated and released decreased, the final dehydrogenation and reabsorption remained at 90.22% and 95.17%. In general, MgH<sub>2</sub>+10 wt% Ni/NiO has both rapid dehydrogenation/rehydrogenation kinetic and relatively stable cycling performance.

### 3.6. Catalytic mechanism of Ni/NiO on the hydrogen storage performance of MgH<sub>2</sub>

To reveal the catalytic mechanism of Ni/NiO, transmission electron microscopy and XRD were used to study the structural changes in the composite during the dehydrogenation/rehydrogenation process.

**Table 2**

Absorption activation energy of Mg/MgH<sub>2</sub> hydrogen storage systems doped with different nickel-based catalysts.

Hydrogen storage systems	E <sub>a</sub> (kJ/mol)	Refs.
MgH <sub>2</sub> +10 wt% Ni/NiO	34.84	This work
MgH <sub>2</sub> +Ni <sub>3</sub> S <sub>2</sub> @C-4	39.6	[29]
MgH <sub>2</sub> +10 wt% CrFeCoNi	55.73	[30]
MgH <sub>2</sub> +10 wt% Ni <sub>np</sub> s	87.0	[32]
MgH <sub>2</sub> +Ni@rGO	51.2	[33]
MgH <sub>2</sub> +Pd <sub>30</sub> Ni <sub>70</sub> /CMK-3	78.5	[34]
Mg-Ni-V	52.8	[35]
Mg-5wt% NiS	45.45	[36]

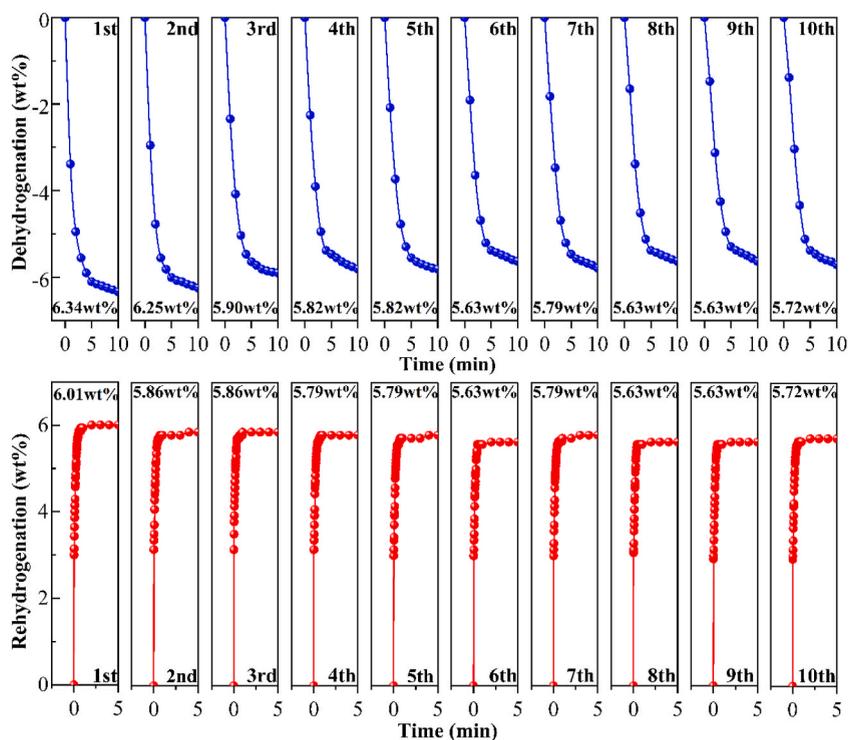


Fig. 7. Dehydrogenation/reabsorption cycle plots of MgH<sub>2</sub>+10 wt% Ni/NiO at 320 °C.

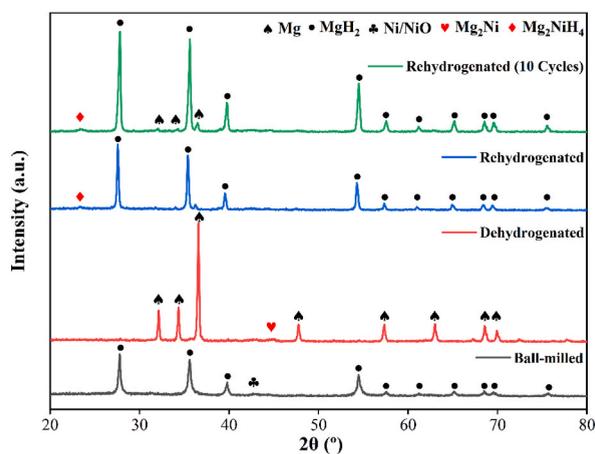
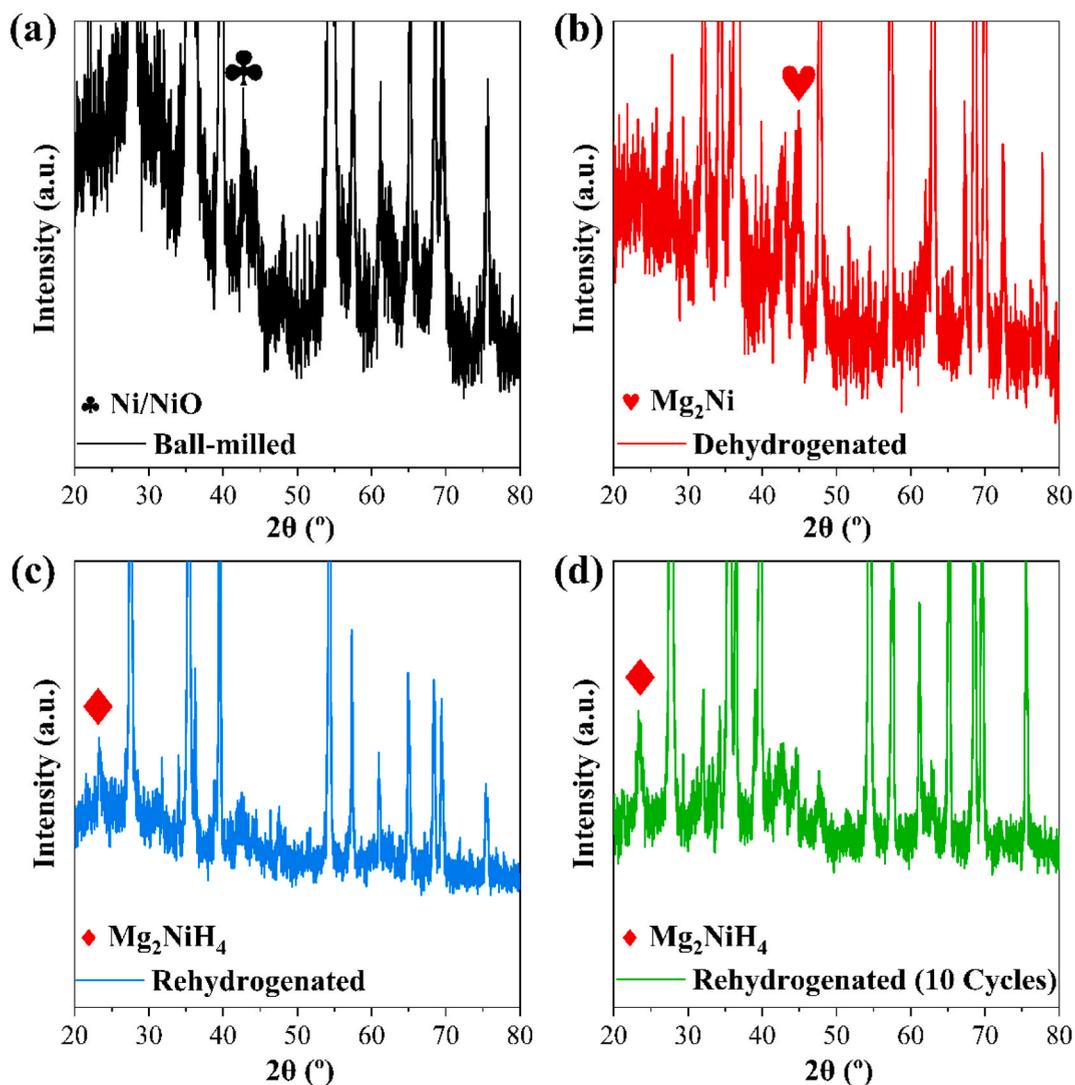


Fig. 8. XRD of MgH<sub>2</sub>+10 wt% Ni/NiO after ball milling, dehydrogenation, hydrogen resorption, and 10 cycles.



**Fig. 9.** XRD of Ni/NiO and its derivatives after ball milling (a), dehydrogenation (b), hydrogen resorption (c), and 10 cycles (d).

**Fig. 8** shows the XRD plot of  $\text{MgH}_2+10$  wt% Ni/NiO after ball milling, dehydrogenation, reabsorption, and 10 cycles. In addition, **Fig. 9(a–d)** shows the details of the catalyst and its derivatives in the XRD plots. The  $\text{MgH}_2$  and Mg phases dominated the XRD curves. Following ball milling, the peak of Ni/NiO appeared in the  $\text{MgH}_2+10$  wt% Ni/NiO sample, and no new phase was found, which was because there was no chemical reaction between  $\text{MgH}_2$  and Ni/NiO, and no new species were produced. After the initial dehydrogenation, the Mg phase was dominant, and a diffraction peak of  $\text{Mg}_2\text{Ni}$  appeared. This was due to the chemical reaction between  $\text{MgH}_2$  and Ni/NiO during the high-temperature hydrogen release process, where Ni/NiO promoted the decomposition of  $\text{MgH}_2$  to produce hydrogen and in-situ generation of the active factor  $\text{Mg}_2\text{Ni}$ . After the initial reuptake of the sample, the diffraction peak of  $\text{MgH}_2$  regained its dominance. It is worth mentioning that  $\text{Mg}_2\text{Ni}$  disappeared, and  $\text{Mg}_2\text{NiH}_4$  appeared. This was because  $\text{Mg}_2\text{Ni}$  induced Mg to absorb hydrogen at high temperatures to form  $\text{MgH}_2$ , while  $\text{Mg}_2\text{Ni}$  formed  $\text{Mg}_2\text{NiH}_4$ .  $\text{Mg}_2\text{Ni}/\text{Mg}_2\text{NiH}_4$  aided hydrogen diffusion and thus enhanced the rate of dehydrogenation and hydrogen absorption [21,29]. After 10 cycles, the  $\text{MgH}_2$  phase was dominant, and  $\text{Mg}_2\text{NiH}_4$  still existed because the last cycle caused  $\text{Mg}_2\text{Ni}$  to form  $\text{Mg}_2\text{NiH}_4$  again in situ. It can be seen that  $\text{Mg}_2\text{Ni}$  and  $\text{Mg}_2\text{NiH}_4$  are the factors for Ni/NiO to enhance the hydrogen storage capabilities of  $\text{MgH}_2$ .  $\text{Mg}_2\text{Ni}/\text{Mg}_2\text{NiH}_4$  repeatedly switches during the dehydrogenation/rehydrogenation of composite, promoting the diffusion of hydrogen and increasing the dehydrogenation/rehydrogenation rate, which has been confirmed in many reports [21,28,29].

**Fig. 10(b)** shows the interplanar spacing at  $\text{MgH}_2(101)$ , Ni(200), and NiO(200), recorded at distances of 0.251, 0.176, and 0.209 nm, respectively. In addition, the diffraction patterns related to  $\text{MgH}_2(101)$ , Ni(200), and NiO(200) are observable in **Fig. 10(c)**. The authenticity of the composite is further demonstrated in **Fig. 10(d)**, where the sample's elemental composition includes Mg, Ni, and O.

To further illustrate the evolution of the Ni/NiO catalyst, Ni 2p XPS tests were performed on the  $\text{MgH}_2+10$  wt% Ni/NiO samples after ball-milling and hydrogen release as shown in **Fig. 11**. The peak shapes of  $\text{Ni}^0$  and  $\text{Ni}^{2+}$  valence states can be seen from the xps

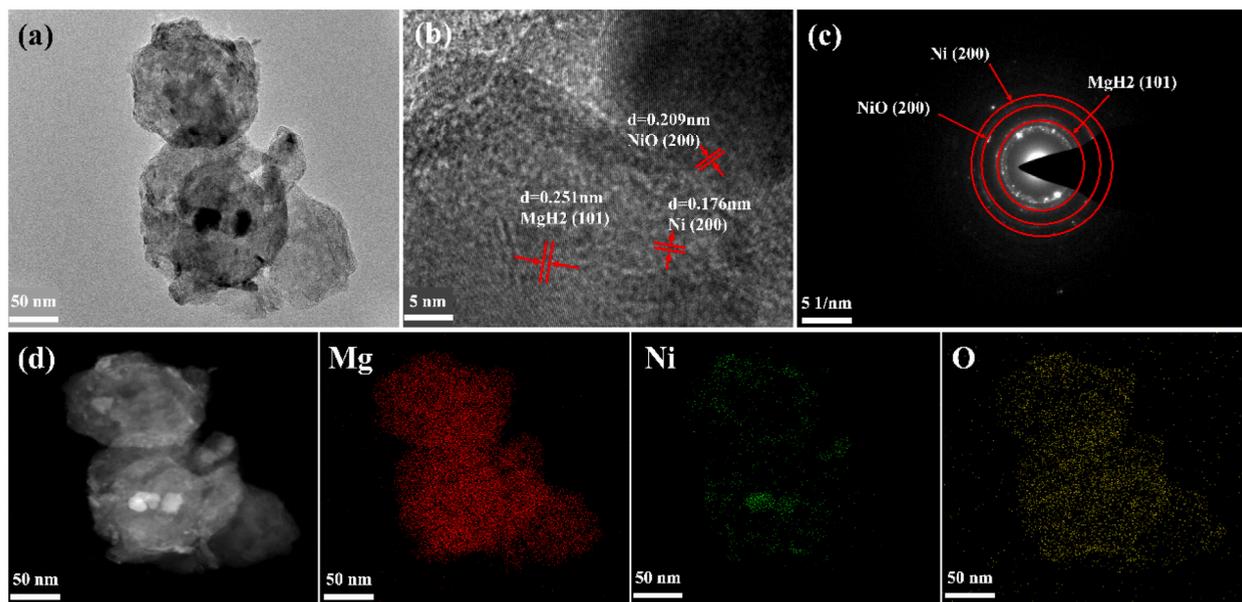


Fig. 10. TEM image (a), HRTEM image (b), SAED image (c), and EDS images (d) of  $\text{MgH}_2+10 \text{ wt}\% \text{Ni/NiO}$ .

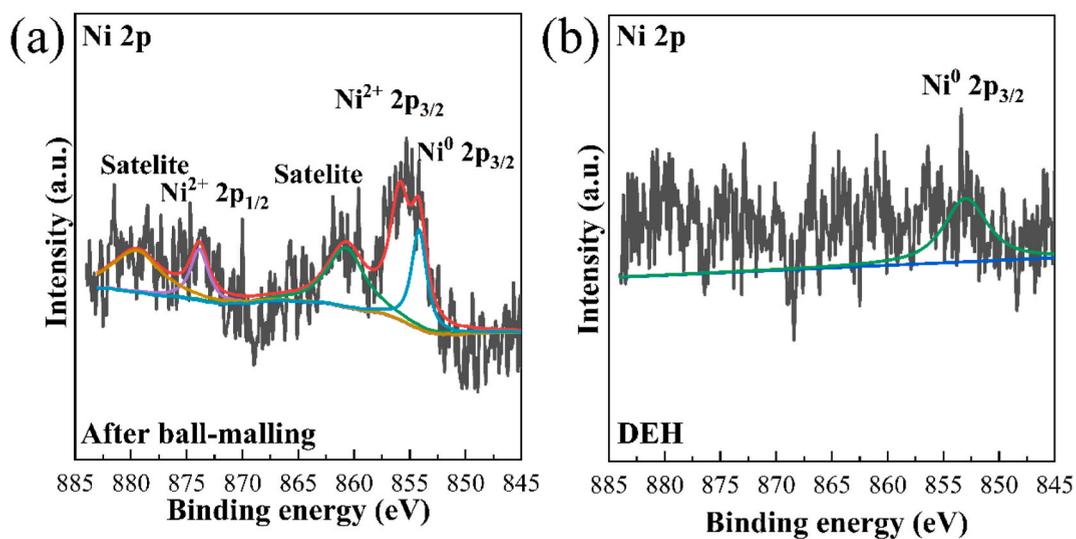


Fig. 11. Ni 2p XPS spectra of  $\text{MgH}_2+10 \text{ wt}\% \text{Ni/NiO}$  after ball-milling (a) and dehydrogenation (b).

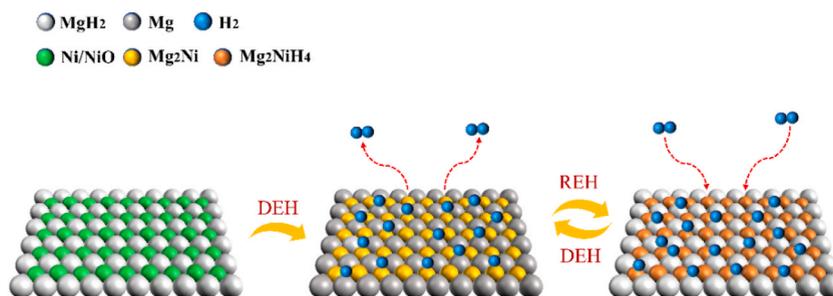


Fig. 12. Catalytic mechanism diagram of Ni/NiO catalyst.

plot of Fig. 11(a), indicating the presence of Ni and NiO in the ball-milled sample, respectively. The Ni<sup>0</sup> peak has a binding energy of 853 eV, and the peaks with binding energies of 855 eV and 873 eV are attributed to Ni<sup>2+</sup>. After the dehydrogenation of MgH<sub>2</sub>+10 wt% Ni/NiO, only the peak of Ni<sup>0</sup> is retained in the XPS plot, which is derived from the Mg<sub>2</sub>Ni produced by the reaction of MgH<sub>2</sub> and Ni/NiO, which is a further confirmation of the presence of Mg<sub>2</sub>Ni.

Combined with XRD, TEM, EDS, and other characterization images, the catalytic mechanism of Ni/NiO for MgH<sub>2</sub> was analyzed, as shown in Fig. 12. After ball milling, Ni/NiO was dispersed on the surface of MgH<sub>2</sub>. Subsequently, during the initial dehydrogenation process of the composite, Ni/NiO not only assisted in the conversion of MgH<sub>2</sub> into Mg but also increased the hydrogen release rate and transformed it into the catalytic factor Mg<sub>2</sub>Ni. Then, during the first rehydrogenation process, Mg<sub>2</sub>Ni assisted in converting Mg into MgH<sub>2</sub>, increased the reabsorption rate, and converted itself into Mg<sub>2</sub>NiH<sub>4</sub>. In the dehydrogenation/rehydrogenation cycles, Mg<sub>2</sub>Ni/Mg<sub>2</sub>NiH<sub>4</sub> promoted hydrogen migration across the interface of Mg/MgH<sub>2</sub>, thereby improving the dehydrogenation/rehydrogenation kinetic of Mg/MgH<sub>2</sub>.

#### 4. Conclusion

Ni/NiO was synthesized by co-precipitation and introduced into MgH<sub>2</sub>. At the same time, the excellent modification effect of the Ni/NiO on the hydrogen storage performance of MgH<sub>2</sub> was proved.

The dehydrogenation temperature of MgH<sub>2</sub>+10 wt% Ni/NiO was approximately 180 °C. Moreover, the composite dehydrated 5.83 wt% within 10 min at 300 °C. The activation energies of dehydrogenation and rehydrogenation of MgH<sub>2</sub>+10 wt% Ni/NiO were 87.21 and 34.84 kJ/mol. In the stability test of 10 cycles, the final dehydrogenation and reabsorption of MgH<sub>2</sub>+10 wt% Ni/NiO were maintained at 90.22% and 95.17%, respectively. During the cycles of the composite system, Mg<sub>2</sub>Ni and Mg<sub>2</sub>NiH<sub>4</sub> were interconverted to promote hydrogen migration across the interface of Mg/MgH<sub>2</sub>.

#### Data availability

Sharing research data helps other researchers evaluate your findings, build on your work and to increase trust in your article. We encourage all our authors to make as much of their data publicly available as reasonably possible. Please note that your response to the following questions regarding the public data availability and the reasons for potentially not making data available will be available alongside your article upon publication.

Has data associated with your study been deposited into a publicly available repository?

No.

#### CRediT authorship contribution statement

**Wenxuan Li:** Writing – review & editing, Writing – original draft. **Xinglin Yang:** Writing – review & editing. **Quanhui Hou:** Writing – review & editing. **Xiaohui Lu:** Writing – review & editing. **Jie Kong:** Writing – review & editing. **Jianye Su:** Writing – review & editing.

#### Declaration of competing 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.

#### Acknowledgements

This research was funded by the Postgraduate Research & Practice Innovation Program of Jiangsu Province (Grant No. SJCX23\_2217).

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