



# Ni–B-doped NaAlH<sub>4</sub> hydrogen storage materials prepared by a facile two-step synthesis method

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**Abstract** By directly introducing Ni–B into NaAlH<sub>4</sub> system using a facile two-step synthesis method, the effects of Ni–B on NaAlH<sub>4</sub> were systematically investigated. NaAlH<sub>4</sub> can be completely formed after 30 h milling under 1 MPa hydrogen pressure. In addition, the dehydrogenation kinetics of as-prepared NaAlH<sub>4</sub> after different milling times were investigated. As the dehydrogenation temperature rises, both the hydrogen desorption capacity and dehydrogenation rate quickly increase. The apparent activation energy  $E_a$  for Ni–B-doped NaAlH<sub>4</sub> is calculated to be 61.91 kJ·mol<sup>-1</sup> for the first dehydrogenation step. More importantly, the dehydrogenation temperature of as-prepared NaAlH<sub>4</sub> nanocrystalline can be reduced to about 100 °C.

**Keywords** NaAlH<sub>4</sub>; Hydrogen storage; Ni–B catalyst; Dehydrogenation kinetics

## 1 Introduction

Hydrogen is the most ideal fuel in comprehensive clean energy. However, the most critical issues are the practical application of on-board hydrogen storage systems. In recent years, solid light metal complex hydrides [1, 2] drew intensive research interest due to their high hydrogen capacities

and moderate operating conditions. Among various light metal complex hydrides [3–10], sodium aluminum hydride (NaAlH<sub>4</sub>) was widely studied after the pioneering researches of Bogdanović and Schwickardi [11]. Recently, many researches on exploring new kind of catalysts or modifying the microstructure to enhance the synthesis efficiency and dehydrogenation properties of NaAlH<sub>4</sub> were carried out. A lot of kinds of catalysts, such as TiCl<sub>4</sub> [12], TiF<sub>3</sub> [6, 13], Ti powder [14, 15], TiCl<sub>3</sub> [16], etc., are used as possible catalysts to synthesize NaAlH<sub>4</sub>. However, higher hydrogen pressure retards the practical applications of NaAlH<sub>4</sub> system for hydrogen storage. Therefore, it is necessary to explore novel catalysts on the synthesis of NaAlH<sub>4</sub> from NaH and Al.

Ni–B, as an amorphous alloy catalyst, was used for the hydrogenation of benzene, cyclopentadiene, and acrylonitrile [17, 18]. In addition, nickel-based catalysts were also well known for catalytic hydrolysis of metal borohydride owing to its excellent catalytic activity [19, 20]. In our previous work, we successfully prepared NaAlH<sub>4</sub> by ball-milling NaH/Al mixtures with Co–B or TiB<sub>2</sub> [21, 22] catalysts. Based on the above considerations, Ni–B amorphous alloy was synthesized by ball milling and used firstly as catalyst for the synthesis of NaAlH<sub>4</sub>.

Herein, NaAlH<sub>4</sub> can be firstly synthesized by ball-milling the mixture of NaH/Al and Ni–B catalyst under Ar atmosphere for 15 h and then in a low hydrogen pressure. More importantly, as-synthesized nanocrystalline NaAlH<sub>4</sub> can release hydrogen even at 100 °C.

## 2 Experimental

### 2.1 Preparation of Ni–B

Ni–B catalyst was prepared by mechanical ball-milling. Ni powder (99.5 wt%, 48 μm) and B powder (99 wt%) with

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**Table 1** Samples' preparation conditions

Samples	Milling time under Ar/h	Hydrogen pressure/MPa	Milling time under H <sub>2</sub> /h
S0.75 <sup>a</sup> -30 <sup>b</sup>	15	0.75	30
S1-10	15	1.00	10
S1-20	15	1.00	20
S1-30	15	1.00	30
S2-40	15	2.00	40

<sup>a</sup> Hydrogen pressure

<sup>b</sup> Milling time under H<sub>2</sub> (e.g., S0.75<sup>a</sup>-30<sup>b</sup>, the mixture being milled under Ar atmosphere for 15 h, and then milled under 0.75 MPa hydrogen pressure for 30 h at ambient temperature)

molar ratio of 1:1 were placed into a stainless steel container (100 ml) under an Ar atmosphere (purity of 99.99 wt%) in a glove box. The mixture milled for 110 h at 450 r·min<sup>-1</sup> using planetary ball-mill. The ball-to-powder ratio was about 20:1.

## 2.2 Preparation of NaAlH<sub>4</sub>

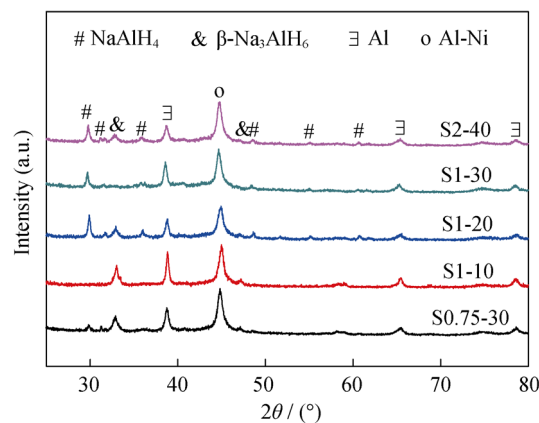
About 2.5 g mixture of NaH (97 %, Alfa Aesar)/Al (99.5 %, Alfa Aesar) powders (molar ratio 1:1) and 10 mol% Ni-B was introduced into a stainless-steel vessel with stainless-steel balls and milled in a planetary ball-mill. The ball-to-powder ratio was about 40:1, and the mixture was milled at 450 r·min<sup>-1</sup> under Ar atmosphere for 15 h in advance, then milled under 0.75–2.00 MPa hydrogen pressure for different time. All the operations were carried out in the glove box (Super 1220/750/900) under high-purified argon atmosphere (H<sub>2</sub>O: <10 × 10<sup>6</sup>; O<sub>2</sub>: <10 × 10<sup>6</sup>). For convenience, detailed preparation conditions for those samples are given in Table 1.

## 2.3 Sample measurements

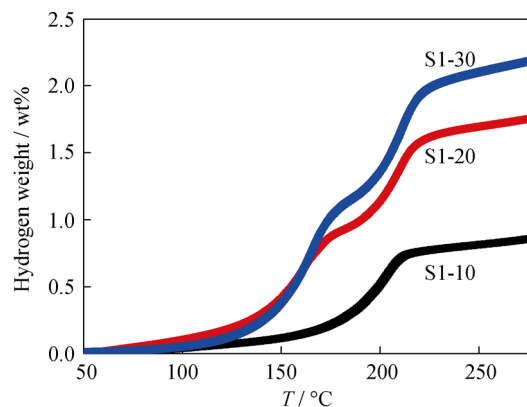
Structural characteristics of the samples were studied by X-ray diffraction (XRD, Rigaku D/Max PC2500, Cu K $\alpha$  radiation). Temperature programmed desorption (TPD) of H<sub>2</sub> was performed using in a home-made apparatus. About 70 mg sample was loaded into the reactor and heated in a 35 ml·min<sup>-1</sup> Ar flow at a ramping rate of 2 °C·min<sup>-1</sup>, while heating from 50 to 300 °C. Hydrogen desorption was measured by isothermal dehydrogenation apparatus using a volumetric method. In the dehydrogenation experiment, the sample was quickly heated to and kept at a given temperature. The weight loss percentage of the samples was calculated according to the weight of NaAlH<sub>4</sub> and Ni-B.

## 3 Results and discussion

Figure 1 shows the XRD patterns of Samples S0.75-30, S1-10, S1-20, S1-30, and S2-40. Detailed preparation



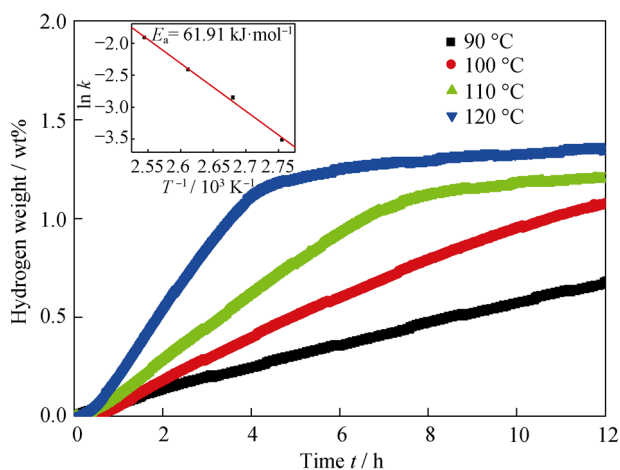
**Fig. 1** XRD patterns of Samples S0.75-30, S1-10, S1-20, S1-30, and S2-40



**Fig. 2** Temperature programmed desorption profiles of H<sub>2</sub> for Samples S1-10, S1-20, and S1-30 with heating rate of 2 °C·min<sup>-1</sup>

conditions for those samples are given in Table 1. It demonstrates that Na<sub>3</sub>AlH<sub>6</sub> is the main phase and NaAlH<sub>4</sub> peaks can be detected in S0.75-30. When the hydrogen pressure increases to 1 MPa, Na<sub>3</sub>AlH<sub>6</sub> diffraction peaks are also detected in S1-10, and Al peaks are broad and weak. The intensity of Na<sub>3</sub>AlH<sub>6</sub> gradually decreases and NaAlH<sub>4</sub> gradually increases with increasing the milling time to 20 h (S1-20). As the milling time increases to 30 h (S1-30), Na<sub>3</sub>AlH<sub>6</sub> diffraction peaks completely disappear, suggesting that Na<sub>3</sub>AlH<sub>6</sub> is completely hydrogenated to become NaAlH<sub>4</sub>. Therefore, a higher hydrogen pressure is helpful for the conversion from Na<sub>3</sub>AlH<sub>6</sub> to NaAlH<sub>4</sub>. However, when the milling time increases to 40 h under 2 MPa hydrogen pressure (S2-40), Na<sub>3</sub>AlH<sub>6</sub> peaks appear, indicating that NaAlH<sub>4</sub> can decompose into Na<sub>3</sub>AlH<sub>6</sub> under higher hydrogen pressure and longer milling time.

Figure 2 displays thermal decomposition characteristics of S1-10, S1-20, and S1-30 samples. It shows that there are two plateau regions for the decomposition reactions, which are attributed to the dehydrogenation of the NaAlH<sub>4</sub> and Na<sub>3</sub>AlH<sub>6</sub>, respectively. It also can be seen that the onset



**Fig. 3** Dehydrogenation kinetic curves of Sample S1-30 at different temperatures. *Inset* being Arrhenius plot for dehydrogenating kinetics of Sample S1-30

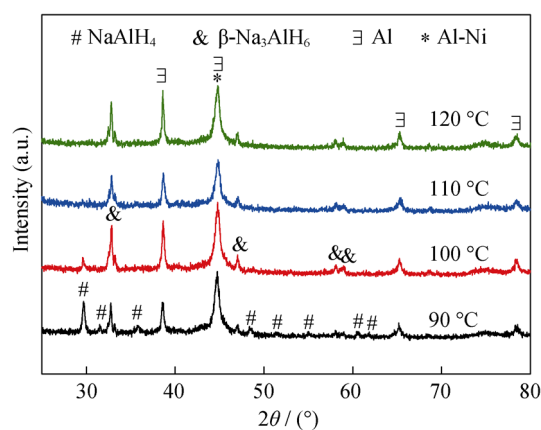
dehydrogenation temperatures are lowered to about 100 and 165 °C, respectively. When the milling time is 10 h, a weight loss of about 0.82 wt% is observed, which is attributed to the dehydrogenation of synthesized Na<sub>3</sub>AlH<sub>6</sub>. The dehydrogenation capacity obviously increases to about 1.76 wt% in S1-20. For S1-30, the dehydrogenation capacities for the two dehydrogenation steps reach to about 1.20 wt% and 1.02 wt%, respectively. The results indicate that synthetic efficiency of NaAlH<sub>4</sub> can be enhanced by increasing the milling time.

Figure 3 shows the dehydrogenation rate of S1-30 at different temperatures. More interestingly, it is clearly observed from Fig. 3 that as-synthesized NaAlH<sub>4</sub> sample can release hydrogen even at a temperature as low as 100 °C. As dehydrogenation temperature increases from 90 to 120 °C, the dehydrogenation rate obviously increases due to the improvement in thermodynamic reactivity. The Arrhenius plot (*inset* in Fig. 3) of the dehydrogenation kinetic gives an activation energy value of about 61.91 kJ·mol<sup>-1</sup>, which is lower than that of the Ti-doped NaAlH<sub>4</sub> reported before [23, 24]. The Arrhenius equation is as follows:

$$\ln k = \ln A - \frac{E_a}{RT}, \quad (1)$$

where  $k$  is the maximum hydrogen generation rates,  $A$  is a temperature-independent coefficient,  $E_a$  is apparent activation energy for the decomposition of NaAlH<sub>4</sub>,  $R$  is gas constant, and  $T$  is absolute temperature.

Figure 4 reveals that XRD patterns of S1-30 after dehydrogenation at different temperatures. The intensity of NaAlH<sub>4</sub> in Fig. 4 is intense, indicating that most of NaAlH<sub>4</sub> cannot decompose at 90 °C. We can also find that most of NaAlH<sub>4</sub> decomposes into Na<sub>3</sub>AlH<sub>6</sub> at 100 °C,



**Fig. 4** XRD patterns of Sample S1-30 after dehydrogenation at different temperatures

suggesting that only the first decomposition step of NaAlH<sub>4</sub> occurs at 100 °C. With the temperature elevation up to 120 °C, the sample fully decomposes (the first dehydrogenation step), reaching a dehydrogenation capacity of 1.36 wt%. It is also observed that Al–Ni diffraction peaks appear in Fig. 4. Results demonstrate that Ni–B is a promising catalyst for enhancing dehydrogenation properties of light-metal complex hydrides. Further investigations about the function of Ni–B in the synthesis and dehydrogenation of sodium alanate hydride are on the way.

#### 4 Conclusion

Nanocrystalline NaAlH<sub>4</sub> was successfully synthesized with Ni–B catalyst under a low hydrogen pressure by a facile two-step synthesis method. The synthetic efficiency of NaAlH<sub>4</sub> can be enhanced by increasing the milling time and hydrogen pressure. The activation energy value for the first dehydrogenation step is 61.91 kJ·mol<sup>-1</sup>. TPD measurements show that Ni–B catalyst markedly lowers the dehydrogenation temperature of NaAlH<sub>4</sub>. More importantly, as-synthesized NaAlH<sub>4</sub> can release hydrogen even at 100 °C. Results demonstrate that synthesized Ni–B by ball-milling is a promising catalyst for enhancing the dehydrogenation performances of light-metal complex hydrides.

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