Synthesis of NaBH₄ based on a solid-state reaction under Ar atmosphere

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ABSTRACT

Sodium borohydride, NaBH₄, was successfully synthesized via solid-state reaction under Ar instead of H₂ atmosphere. A 4NaH–NaBO₂–2SiO₂ ternary mixture was first ball-milled and pressed into pellet, and then calcined under Ar atmosphere at 480 °C for 5 h. NaBH₄ was obtained in 32% yield when the pressing pressure was up to 30 MPa. The influence of the pressing pressure on the solid-state reaction was studied; a plausible reaction pathway and the role of the added SiO₂ were discussed.

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1. Introduction

Sodium borohydride (NaBH₄) has been used as a reducing agent since Schlesinger et al. [1] proposed a solid–liquid-state synthesis method using NaH and methyl borate as the reactants. Recently, it has been considered as one of the hydrogen sources for fuel cells in automotive applications [2–6]. As indicated in reaction (1), NaBH₄ releases more hydrogen (10.8 wt.% in theory) than it contains (10.6 wt.%) via hydrolysis reaction:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \qquad (1)$$

This hydrolysis process can be easily manipulated since NaBH₄ is stable in an alkaline solution until it is destabilized by catalysts [7–10]. However, the high cost eliminates it from any large-scale utilization, thus exploring practical and affordable synthesis method becomes highly desirable [11]. In order to achieve this goal, various boron [12–16] and protide (H⁻: hydride ion) suppliers [17–19] have been investigated. One of the most interesting efforts is to develop a method capable of recycling NaBO₂ (the product of reaction (1)) back to NaBH₄ [20,21]. But NaBO₂ is inactive even at temperatures up to 400 °C [22], thus, high temperature and high hydrogen pressure are necessary for NaBH₄ synthesis based on a solid-H₂ reaction. For instance, H₂ gas with a pressure of 2–10 MPa is normally required to generate activated protides [21–23]. Although the temperature for the synthesis can be reduced by applying a ball-milling process [24–26], the preparation of

NaBH₄ through the solid-H₂ reaction suffers from the employment of high-pressure hydrogen and the poor dispersion of light metals arising from their sticky problem.

Some metal hydrides such as NaH and LiH may be used as alternatives to high-pressure H₂ gas since they can supply protides, as well as their advantages of good availability, low cost, and easy handling [27,28]. Following this idea, we propose a solid-state reaction for the preparation of NaBH₄ by calcining a pressed mixture of NaH and NaBO₂ under Ar atmosphere. In order to facilitate the reaction, SiO₂ is used as the additive [29]. The procedure is illustrated in Scheme 1. Notably, the calcination process is carried out in Ar atmosphere, rather than hydrogen atmosphere as used in previous work. To understand how the reaction occurs, the reactant pellets are subject to pre-treatments under various external pressures, prior to calcination. It is found that the reaction pathway alters with the pressure, and the additive SiO₂ enhances the formation of NaBH₄.

2. Experimental

The powders of 0.4 mol NaH and 0.1 mol NaBO₂ were mixed by ball-miller for 4 h at a rate of 400 rpm; 0.2 mol SiO₂ was then added into the mixture, and ball-milling was continued for 2 h to form the 4NaH–NaBO₂–2SiO₂ ternary mixture. Afterwards, the as-received mixture was respectively pressed into pellets under static pressures of 10 MPa, 20 MPa and 30 MPa in an Ar-filled glove box, followed by calcination at 480 °C for 5 h under 0.1 MPa Ar atmosphere.

The product was extracted by anhydrous isopropyl amine in a modified Soxhlet apparatus for 3 h. Hardened filter paper was used to separate the solution and the reactants. NaBH₄ was obtained by evaporating the extraction solution at 50 °C. Thermogravimetry (TG) and differential scanning calorimetry (DSC) measurements on the prepared samples were simultaneously carried out under an Ar gas flow (50 mL min⁻¹) at a heating rate of 10 °C min⁻¹ on a Netzsch STA 409 PC, Germany. X-ray diffraction (XRD) was performed on a Rigaku D/max 2400, Japan, with a CuKα radiation in the 2-Theta range from 10° to 90°. The XRD samples were smeared on

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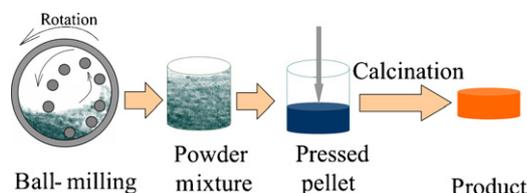
Scheme 1. The procedure for NaBH$_4$ synthesis based on a solid-state reaction.

a glass slide and then covered with Scotch tape to prevent the reaction with water and/or oxygen during measurements. Fourier transform infrared spectroscopy (FTIR) was performed on a Bruker Vector-22 spectrometer in the region of 4000–400 cm^{-1} with samples pressed into KBr pellets.

3. Results and discussion

3.1. Suppression of the decomposition of NaH by pressing

NaH can be thermally decomposed into Na and H$_2$, as described in reaction (2),

$$2NaH \rightarrow 2Na + H_2 \qquad (2)$$

This reaction is not desirable and should be avoided as much as possible during the synthesis of NaBH$_4$, which is found to be feasible by pressing NaH into pellet. Fig. 1 gives TG/DSC curves for pure NaH with and without the press. Without the press, the weight loss is about 3.83 wt.%, that is about 92 mol.% of the initial NaH being decomposed. After a press at 20 MPa, the weight loss is reduced to 3.08 wt.%, namely, 74 mol.% of the initial NaH is decomposed, much smaller than the value for the unpressed NaH. Moreover, the decomposition temperature shifts from 360 °C to 436 °C by 76 °C, indicating that the decomposition of NaH is suppressed.

3.2. Influence of the pressing on the reaction of the 4NaH–2SiO$_2$ and 4NaH–NaBO$_2$ binary mixtures

Prior to the study of the 4NaH–NaBO$_2$–2SiO$_2$ ternary mixture, the reactions in the binary mixtures consisting of 4NaH–2SiO$_2$ and 4NaH–NaBO$_2$ were examined, respectively. Fig. 2 gives the TG/DSC curves of these binary mixtures after being pressed at 20 MPa. In the case of the 4NaH–2SiO$_2$ mixture, the endothermic peak at around 356 °C in Fig. 2A (curve (a)) is due to the decomposition of NaH, as indicated in reaction (2). The prominent exothermic peak at 505 °C corresponds to the reaction between Na and SiO$_2$ [30,31], where Na derives from the decomposition of NaH. The reaction may be written as,

$$xNa + SiO_2 \rightarrow x/2Na_2SiO_3 + Si_{1-x/2}O_{2-3x/2} \qquad (3)$$

Fig. 2. TG/DSC curves for the binary mixtures of (a) 4NaH–2SiO$_2$ and (b) 4NaH–NaBO$_2$. Both samples were previously pressed at 20 MPa.

As to the 4NaH–NaBO$_2$ mixture (see Fig. 2A curve (b)), the peak for the NaH decomposition occurs at 460 °C. The exothermic peak at 480 °C attributes to the reaction between NaH and NaBO$_2$, as described in reaction (4),

$$NaBO_2 + 4NaH \rightarrow NaBH_4 + 2Na_2O \qquad (4)$$

Fig. 2B shows that over the temperature of 100–550 °C, the total weight loss for the 4NaH–2SiO$_2$ and 4NaH–NaBO$_2$ mixture is 0.96 and 0.80 wt.% (i.e., 68 and 39 mol.% of the initial NaH is decomposed), respectively, indicating that the decomposition of NaH is suppressed by pressing. This is in agreement with the results described in Section 3.1 and will favor the formation of NaBH$_4$.

3.3. Influence of the pressing on the reaction of the 4NaH–NaBO$_2$–2SiO$_2$ ternary mixture

Fig. 3A shows the DSC curves for the 4NaH–NaBO$_2$–2SiO$_2$ ternary mixture that was pressed under various pressures. In terms of the result in Fig. 2A, it is easy to identify that the endothermic peak at around 350 °C is from the decomposition of NaH, and that the exothermic peaks at around 505 °C from reaction (3). The peaks at around 480 °C can be ascribed to the formation of NaBH$_4$, which is predicted as:

$$4NaH + NaBO_2 + 2SiO_2 \rightarrow NaBH_4 + 2Na_2SiO_3 \qquad (5)$$

Moreover, with the increase of the pressing pressure from 0 MPa to 30 MPa, the peak at 480 °C becomes more pronounced while the peaks at 350 °C and 505 °C grow gradually weaker and are almost invisible at 30 MPa, indicating that the pressing step enhances the formation of NaBH$_4$, but suppresses the decomposition of NaH. The TG curves as shown in Fig. 3B provide the same information,

Fig. 1. TG/DSC curves for NaH before (a) and after (b) a press at 20 MPa.
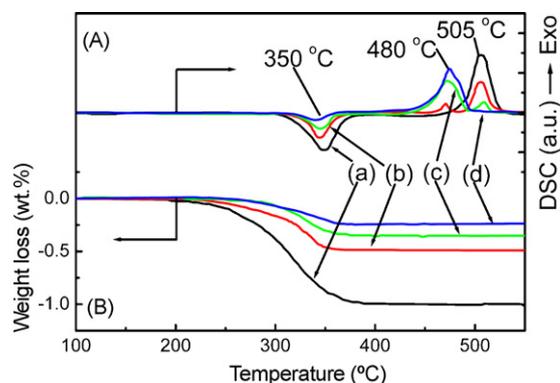
Fig. 3. TG/DSC curves for the 4NaH–NaBO$_2$–2SiO$_2$ ternary mixtures pressed at (a) 0 MPa, (b) 10 MPa, (c) 20 MPa and (d) 30 MPa, respectively.
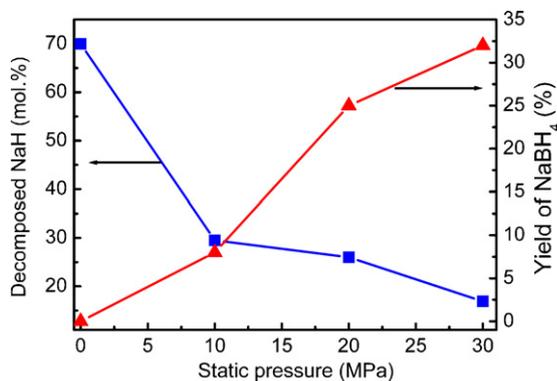
Fig. 4. Dependence of the amount for decomposed NaH and the NaBH$_4$ yield on the pressing pressures applied to the 4NaH–NaBO$_2$–2SiO$_2$ ternary mixtures. Samples were subject to calcination at 480 °C for 5 h under Ar atmosphere.

indicating that with the pressing pressure increase from 0 MPa to 30 MPa, the weight loss decreases from 0.99 wt.% to 0.24 wt.%. The onset temperature for the weight loss process complies with the DSC peak at around 350 °C, hence, the loss is certainly resulted from the decomposition of NaH. Converting the values for the weight loss into the mole loss, it is clear that the amount of decomposed NaH decreases greatly from 70 mol.% to 16.9 mol.% when the pressure is elevated from 0 MPa to 30 MPa (see Fig. 4), confirming that the decomposition of NaH was effectively suppressed.

The yield for NaBH$_4$ obtained after the calcination at 480 °C for 5 h under Ar atmosphere is also displayed in Fig. 4, showing that with the increase of pressure from 10 MPa to 30 MPa, the yield increases from 8% to 32%. Fig. 5 compares the XRD patterns for the 4NaH–NaBO$_2$–2SiO$_2$ ternary mixture before and after calcination. Fig. 5(a) shows that the freshly as-milled mixture consists of NaH, NaBO$_2$ and SiO$_2$ phases and no intermediate phase is formed during ball milling. Fig. 5(b–e) shows the XRD patterns for the as-received products after calcination. For unpressed sample, no peak for NaBH$_4$ is detected (see Fig. 5(b)). After pressing at 10 MPa (see Fig. 5(c)), three characteristic peaks of NaBH$_4$ are observed at 41.4°, 49° and 51.3°, respectively. With the increase of pressure further to 20 MPa and 30 MPa, the intensities of the three peaks increase gradually (see Fig. 5(d) and (e)), indicating the elevated yield for NaBH$_4$.

Fig. 6 presents the FTIR spectra for the as-received products. For unpressed samples, no signal for NaBH$_4$ is observed, as shown in Fig. 6(a). Once the mixture is pressed, the absorption peaks at 2291 cm^{-1} and 1125 cm^{-1}, (corresponding to the stretching and deformation vibration of the B–H in NaBH$_4$, respectively) are clearly visible in Fig. 6(b–d). The positions of these two peaks deviate
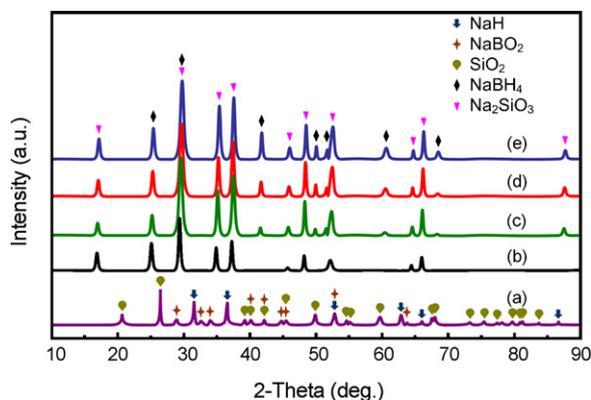
Fig. 6. FTIR spectra for the 4NaH–NaBO$_2$–2SiO$_2$ ternary mixtures. Samples were pressed at (a) 0 MPa, (b) 10 MPa, (c) 20 MPa and (d) 30 MPa, respectively, and then calcined at 480 °C for 5 h under Ar atmosphere.

slightly from the reported values of 2280 cm^{-1} and 1120 cm^{-1} [21], which may be caused by the disturbance of the by-product Na$_2$SiO$_3$.

3.4. The reaction pathway and the role of additive SiO$_2$

According to the TG/DSC and XRD results for the 4NaH–NaBO$_2$–2SiO$_2$ ternary mixture that was pressed under different pressures, the reaction pathway is suggested and illustrated in Scheme 2. For unpressed samples, the NaH and NaBO$_2$ particles are physically separated, and when the mixture is heated, NaH decomposes to H$_2$ and Na followed by the reaction between Na and SiO$_2$. As a result, the formation of NaBH$_4$ is not observed. For pressed samples, reactant particles experience more physical contact, and NaH prefers to react with NaBO$_2$ to produce NaBH$_4$ before thermal decomposition. Meanwhile, the generated Na$_2$O is absorbed by SiO$_2$.

The added SiO$_2$ plays important roles in the synthesis procedure. On the one hand, the Gibbs free energy (ΔG) of reaction (4) is 146 kJ mol^{-1} under the standard state [32], indicating that NaBH$_4$ synthesis through the reaction of NaBO$_2$ and NaH is thermodynamically impossible. When SiO$_2$ is added, as shown in reaction (5), the ΔG is -311 kJ mol^{-1}, indicating that the synthesis reaction occurs spontaneously. On the other hand, as indicated in Scheme 2, with the improvement of the pressure, the role of SiO$_2$ changes from the

Fig. 5. XRD patterns for 4NaH–NaBO$_2$–2SiO$_2$ ternary mixtures: (a) the freshly as-milled sample, (b–e) the samples being pressed at 0 MPa, 10 MPa, 20 MPa and 30 MPa, respectively, and then calcined at 480 °C for 5 h under Ar atmosphere.
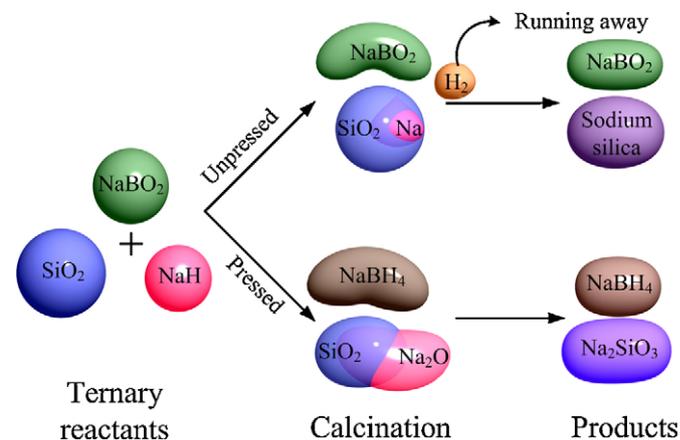
Scheme 2. Illustrations of the plausible reaction route for NaBH$_4$ synthesis. In the unpressed sample, the NaH and NaBO$_2$ particles are physically separated, thus during the calcination, NaH decomposes to H$_2$ and Na, followed by the reaction between SiO$_2$ and Na, leading to the further decomposition of NaH, rather than the formation of NaBH$_4$. In the pressed sample, however, the NaH and NaBO$_2$ particles are in physical contact, thus, NaH reacts with NaBO$_2$ to produce NaBH$_4$ and Na$_2$O during the calcination. The generated Na$_2$O further reacts with SiO$_2$ to form Na$_2$SiO$_3$, which enhances the NaBH$_4$ formation.

absorber of Na for unpressed sample which facilitates the decomposition of NaH to an absorber of Na_2O for pressed samples which facilitates the formation of $NaBH_4$.

4. Conclusions

The present work proposes a synthesis route for the preparation of $NaBH_4$ based on a solid-state reaction, i.e., by calcining the $4NaH–NaBO_2–2SiO_2$ ternary mixture. It is found that $NaBH_4$ is successfully synthesized under Ar, instead of H_2 atmosphere. The pressure applied to the reactant pellet is of crucial for the reaction pathway: for unpressed samples, NaH decomposes to H_2 and Na; for the pressed samples, the reaction route changes gradually to the formation of $NaBH_4$ with the increase of the pressing pressure. When the pressing pressure is elevated from 10 MPa to 30 MPa, the yield for $NaBH_4$ is increased from 8% to 32%. A higher yield can be expected with a further increase in the pressure. Moreover, the role of SiO_2 changes from the absorber of Na for the unpressed samples to the absorber of Na_2O for the pressed samples.

Acknowledgments

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