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Characterizations of composite $\text{NaNH}_2\text{--NaBH}_4$ hydrogen storage materials synthesized via ball milling

Chuan Wu*, Ying Bai, Jian-hu Yang, Feng Wu, Fei Long

Beijing Key Laboratory of Environmental Science and Engineering, School of Chemical Engineering and the Environment, Beijing Institute of Technology, Beijing 100081, China

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ABSTRACT

Composite $\text{NaNH}_2\text{--NaBH}_4$ (molar ratio of 2/1) hydrogen storage materials are prepared by a ball milling method with various ball milling times. The compositions and hydrogen generation characteristics are investigated by means of X-ray diffraction (XRD) and thermogravimetric-differential thermal analysis (TG-DTA). The structural characteristics imply that ball milling produces a new phase of $\text{Na}_3(\text{NH}_2)_2\text{BH}_4$, and mechanical energy accumulated in the ball milling process may be responsible for the phase change of $\text{Na}_3(\text{NH}_2)_2\text{BH}_4$. TG-DTA demonstrates that the phase change temperature of the composite $\text{NaNH}_2\text{--NaBH}_4$ (2/1) ball milled for 16 h is 141.8 °C, and the melting point is 197.3 °C; below 400 °C, composite hydrogen storage material is mainly decomposed to give hydrogen and Na_3BN_2 ; while above 400 °C, the previous by-product Na_3BN_2 continues to decompose so as to give metal Na gradually.

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1. Introduction

With the growing problems of environment and energy, people pay more and more attention on renewable and clean energy sources, such as hydrogen energy, wind energy, solar energy and the like. Among which, hydrogen energy is considered to be one of the most promising clean energy sources in 21st century owing to its high heating value, wide availability, and environmental friend. A hydrogen energy system comprises hydrogen generation, hydrogen storage, hydrogen transportation, hydrogen utilization and so on, wherein hydrogen storage is one of the main technical bottlenecks restricting application of hydrogen energy.

Ever since Chen et al. [1] discovered that Li_2NH and Ca_2NH can reversibly storage hydrogen in 2002, scientists have done extensive and in-depth research on amino-imino system, and

a series of amide-hydride or amide-coordination hydride composite hydrogen storage system [2], such as $\text{LiNH}_2\text{--LiH}$, $\text{NaNH}_2\text{--LiAlH}_4$, $\text{LiNH}_2\text{--CaH}_2$, $\text{Mg}(\text{NH}_2)_2\text{--LiH}$, $\text{Ca}(\text{NH}_2)_2\text{--NaH}$ and so on, have been investigated. Different components in these new systems can reduce stability of each other, thereby exhibiting high actual hydrogen-generation amount, thus become potential hydrogen supply sources for fuel cells. In recent years, people have also paid much attention to metal borohydride due to the high theoretical hydrogen storage amount. For example, hydrogen generation by means of thermal decomposition of solid metal borohydride [3–5] and hydrolysis of metal borohydride solution [6–12] are studied extensively.

Some composite hydrogen storage materials, which are composed of amide and borohydride, such as $\text{LiBH}_4\text{--LiNH}_2$, $\text{NaBH}_4\text{--NaNH}_2$, and so on, have theoretical hydrogen storage

* Corresponding author.

E-mail address: chuanwu@bit.edu.cn (C. Wu).

amounts of more than 7 wt%; and the gas product obtained after heating is mainly H₂. Because the hydrogen generation performances of the composite materials may be superior to that of pure borohydride or amide, they are regarded as a kind of potential hydrogen storage material. Investigation on the structure and reaction mechanism of this kind of composite materials is helpful for the selection of hydrogen storage systems with high hydrogen storage amount and good dynamics. In this paper, we are focusing on NaNH₂–NaBH₄ (molar ratio of 2/1), which is prepared by the ball milling method, and the composition and the hydrogen generation performance are investigated by XRD and TG-DTA.

2. Experimental

2.1. Preparation of composite hydrogen storage material

Herein, composite NaNH₂–NaBH₄ (2/1) samples are prepared by a ball milling method; NaBH₄ and NaNH₂ serve as raw materials. At first, NaNH₂ and NaBH₄ with a molar ratio of 2:1 are weighed in an argon-filled glove box (MBRAUN), then put into a ball milling jar where some steel balls with a diameter of 8 mm are enclosed, and the weight ratio of the steel balls to the raw materials is fixed as 20:1. After sealing and fixing, the ball milling jar is put into a planetary ball mill (QM-ISPO4). The rotate speed is selected 300 rpm; alternative operation is adopted, wherein operation in reverse is conducted after a pause of 0.2 h after every 1 h of operation. When an end time is reached, ball milling jar is removed from the ball mill and put into the glove box, and then the as-prepared sample is taken out. The samples with ball milling time of 1, 2, 4, 8, 16, and 32 h are named to be S1, S2, S4, S8, S16 and S32 respectively; and manually grinded sample with NaNH₂:NaBH₄ = 2:1 (molar ratio) is named to be S0. To avoid the raw materials and the as-prepared samples reacting with moisture and O₂, all the operations, excluding ball milling, were conducted in a glove box filled with high purity argon.

In this study, the hydrogen generation performance of the composite NaNH₂–NaBH₄ (2/1) samples are tested by TG-DTA, so that the used amounts of the samples in the test are in milligram level, and the mass of solid products after decomposition by heating is extremely less, which is difficult to collect and detect. In order to characterize the structural evolutions of the decomposed samples, 2 g sample under the protection of argon is heated to a preconcerted temperature in a tubular furnace, and the final product thereof is characterized by XRD.

2.2. X-ray diffraction

Crystal structures of the as-prepared samples are characterized by a Rigaku DMAX2400 X-ray diffractometer adopting Cu-K_α radiation. The tube voltage is 40 kV and the tube current is 20 mA. The scanning range is from 10° to 90°, while the scanning rate is 8°/min.

2.3. TG-DTA test

The TG-DTA test is conducted with a ZCT-A thermo gravimetric analyser/differential thermal analyzer (Beijing Jingyi

High-tech Instrument Co., Ltd.). 5–10 mg sample is weighed and put into a corundum crucible in the glove box, and then quickly transferred into the TG-DTA instrument. High purity argon (99.999%) serves as a protective gas; the flow rate is 10 ml/min; TG range is 10 mg; DTA range is 50 UV; sampling interval is 1 s; thus the samples are measured from room temperature to 450 °C with a heating rate of 10 °C/min.

3. Result and discussion

3.1. Crystal structure of composite NaNH₂–NaBH₄

Fig. 1 shows the XRD pattern of sample S0 after manually grinding 2:1 of NaNH₂ and NaBH₄. It is evident that there are new diffraction peaks at $2\theta = 15.513, 31.41, 38.13,$ and 55.46 in addition to diffraction peaks of NaNH₂ [13] and NaBH₄ [14] in the manually grinded sample S0. Compared with the compounds in the JCPDS database, which contain elements Na, N, B, and H, the new peaks have been found to be matched none of them. However, according to Chater et al. [15] and Somer et al. [16], a new phase of Na₂BH₄NH₂ was detected when the NaNH₂–NaBH₄ (1/1) system is heat-treated. Additionally, Pinkerton et al. [6] obtained a new phase by ball-milling LiNH₂ and LiBH₄ (molar ratio of 2:1); although there is no standard diffraction data for contrast, they believe that Li₃N₂BH₈ should have been yielded because the synthesized substance is a pure phase. Similarly, it is reasonable to predict that a new phase of Na₃(NH₂)₂BH₄ should have been yielded by manually grinding in this work.

Furthermore, with increasing ball milling time, the crystal structures of the composite hydrogen storage materials change as well, as shown in Fig. 2. Two new peaks at $2\theta = 15.513$ and 31.41 increase first and then decrease, and after 16 h of ball milling, the new peaks almost disappear; while the diffraction peaks at $2\theta = 38.13$ and 55.46 have no obvious change. Meanwhile, the ball milling results in more new diffraction peaks at $2\theta = 10.22, 12.64, 18.91, 26.84, 37.01,$ and 43.01 ; the diffraction peaks at $2\theta = 10.22, 12.64, 18.91, 37.01$ appear after 1 h of ball milling, and become very strong after 8 h and 16 h ball milling. The diffraction peaks at $2\theta = 26.84$

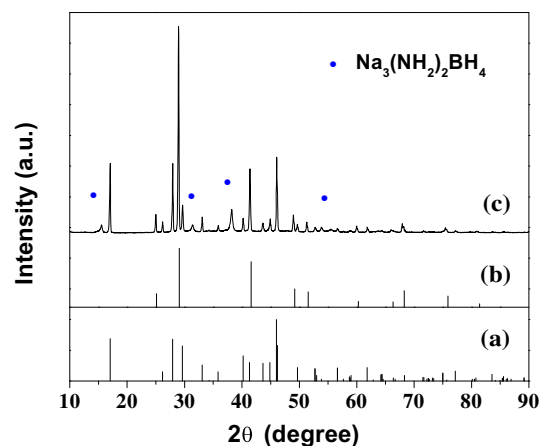


Fig. 1 – XRD patterns of (a) NaNH₂, (b) NaBH₄, and (c) NaNH₂–NaBH₄ (2/1).

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