Journal of Power Sources 261 (2014) 7–13

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Hydrogen generation behaviors of $NaBH_4$–NH_3BH_3 composite by hydrolysis

Yanmin Xu, Chaoling Wu*, Yungui Chen, Zhifen Huang, Linshan Luo, Haiwen Wu, Peipei Liu

College of Materials Science and Engineering, Sichuan University, Chengdu 610064, China

HIGHLIGHTS

- Hydrogen is generated via self-hydrolysis of $NaBH_4$-based composite ($x NaBH_4$–$y NH_3BH_3$) without any catalyst.
- More than 10 wt% hydrogen yield (taking reacted water into account) is achieved by optimized composition.
- The hydrolysis behaviors are affected by pH value, microstructure and the content of NH_3BH_3 in the composite.
- The detailed hydrolysis reaction processes were discussed.

ARTICLE INFO

Article history:
Received 21 December 2013
Received in revised form
27 January 2014
Accepted 13 March 2014
Available online 20 March 2014

Keywords:
Sodium borohydride
Ammonia borane
Hydrolysis
Composites
Ball-milling

ABSTRACT

In this work, NH_3BH_3 (AB) is used to induce hydrogen generation during $NaBH_4$ (SB) hydrolysis in order to reduce the use of catalysts, simplify the preparation process, reduce the cost and improve desorption kinetics and hydrogen capacity as well. $x NaBH_4$–$y NH_3BH_3$ composites are prepared by ball-milling in different proportions (from x:y = 1:1 to 8:1). The experimental results demonstrate that all composites can release more than 90% of hydrogen at 70 °C within 1 h, and their hydrogen yields can reach 9 wt% (taking reacted water into account). Among them, the composites in the proportion of 4:1 and 5:1, whose hydrogen yields reach no less than 10 wt%, show the best hydrogen generation properties. This is due to the impact of the following aspects: AB additive improves the dispersibility of SB particles, makes the composite more porous, hampers the generated metaborate from adhering to the surface of SB, and decreases the pH value of the composite during hydrolysis. The main solid byproduct of this hydrolysis system is $NaBO_2 \cdot 2H_2O$. By hydrolytic kinetic simulation of the composites, the fitted activation energies of the complexes are between 37.2 and 45.6 kJ mol^{-1}, which are comparable to the catalytic system with some precious metals and alloys.

1. Introduction

Energy is the driving force of human existence and social development. As a clean fuel, hydrogen is considered to be a potential alternative energy source with the increasing serious energy crisis and growing problem of environmental pollution. However, safe and effective on-board hydrogen storage and generation remain the main issues in the hydrogen economy [1].

Among various hydrogen storage materials, sodium borohydride ($NaBH_4$, denoted as SB) and ammonia borane (NH_3BH_3, denoted as AB) are high-profile due to their high theoretical hydrogen yields (THY) of 21.3 wt% and 19.5 wt% respectively by hydrolysis and without reacted water in calculation. Both of them belong to complex hydrides and have the following features: stable storage at ambient temperature and pressure, safe handling, ease of control for H_2 release [2]. There have been a lot of studies on their hydrolysis performance. SB can release hydrogen with a maximum mole ratio of $H_2/NaBH_4$ = 4.0 through hydrolysis and half of the hydrogen comes from H_2O, while AB can release hydrogen with a mole ratio of $H_2/NH_3 \cdot BH_3$ = 3.0 by hydrolysis [3]. Besides hydrogen, environmentally innocuous byproducts are produced in their hydrolysis process as well. The reactions with water can usually be described as:

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

$$NH_3BH_3 + 2H_2O \rightarrow NH_4^+ + BO_2^- + 3H_2 \quad (2)$$

* Corresponding author. Tel./fax: +86 28 85466916.
E-mail addresses: wuchaoling@scu.edu.cn, wmeimeiw07@163.com (C. Wu).

http://dx.doi.org/10.1016/j.jpowsour.2014.03.038
0378-7753/

Eqs. (1) and (2) are the ideal stoichiometry of aqueous hydrolysis. The THY of the system AB–H_2O is 8.98 wt% with reacted water in calculation, which is less than that of the system SB–H_2O, 10.81 wt%. But in practical applications, the reactions happen always in excessive water. This point accounts for the varying degrees of hydration of the solid by-products (i.e. hydrated metaborates) [4]. Hence, we characterize the hydrolysis by-products through XRD in order to discover the actual reaction process of the composites.

Low hydrogen productivity of either SB or AB at room temperature is regarded as a key barrier to their commercialization [5]. Catalytic hydrolysis accelerates hydrogen generation rate and achieves on-demand hydrogen production by controlling the contact of catalyst with aqueous solution [6]. Published literature has explored various catalysts such as noble [7–9] or non-noble metals [10,11], alloys [12–16] and acids [17,18]. At the same time, the following points have to be considered for practical applications: the low hydrogen yield caused by non-hydrolyzable catalysts, the high cost of noble metals, the relatively complex preparation process of some metal catalysts and alloys, corrosion resistance and long-term cyclic stability [11]. Besides the use of catalysts, there is also some research focusing on hydrolysis of solid SB with steam/water vapor at high temperatures [4]. Nevertheless, the operating conditions still need to be optimized.

In this work, a new approach is introduced for hydrogen generation, which uses AB with high hydrogen yield to induce the hydrolysis of SB with high hydrogen yield as well and does not require any other catalyst in the reaction process. The SB-based composites *x*SB–*y*AB used in this work were prepared simply and conveniently. These composites exhibited much higher hydrogen generation yields and better hydrolysis properties than pure SB or pure AB. The hydrolysis kinetics of the composites and the inducing mechanism of AB are discussed in various aspects, such as the change of activation energies, the evolution of pH values, etc.

2. Experimental

2.1. Sample preparation

In our experiments, $NaBH_4$ (SB, 99%) is used as received. NH_3BH_3 (AB) is synthesized by the procedure mentioned in the literature [19] and the purity is about 90%. All raw materials are stored and all manipulations are carried out in an argon glove box with <5 ppm O_2 and <10 ppm H_2O. An SPEX8000 high-energy ball miller is employed to prepare for *x*$NaBH_4$–*y*NH_3BH_3 composite samples in different *x*:y molar ratios ranged from 1:1 to 8:1 and with the ball-to-powder weight ratio of 30:1 under Ar atmosphere for 15 min.

2.2. Hydrolysis test

An experimental apparatus is designed to monitor the hydrogen generation amount/rate from the *x*SB–*y*AB composites, as was described in Ref. [20]. Predetermined quantity of the composites (0.2 g) is weighted in an argon-filled glove box and then transferred into a 250 ml round-bottom flask sealed by a dual-port tube with one water inlet plug and one hydrogen outlet plug. 10 ml water is injected into the flask through syringe pump, and the reaction is started by stirring the contents at different temperatures (25, 40, 50, 60 and 70 °C). The evolution of gas goes through $CuSO_4$ solution, a condenser and a dry tube with $CaCl_2$, respectively. These procedures aim at absorbing ammonia in the gas stream, separating steam emitted from the reaction and drying the gas, respectively. At last, the generated hydrogen is collected and measured in an inverted 1.5 L graduated cylinder immersed in a water-filled tray. The residual solution is immediately dried in a vacuum oven after reaction to obtain byproducts. Each experiment is performed twice in order to ensure the accuracy of the results.

2.3. Microstructure analysis

Powder X-ray diffraction (XRD) is used for characterizing the crystalline structure of the milled composite samples and the hydrolysis byproducts. The patterns are recorded on a DX-2600 diffractometer with CuKα radiation. The morphologies of the milled samples are detected by scanning electronic microscope (SEM), which is performed on a JSM-7500F scanning electron microscope.

3. Results and discussion

3.1. Hydrolysis performance of SB-AB composites and monomers

Fig. 1a reveals hydrogen generation curves of 4SB–AB composite in 1 h, and it's obviously seen that the chemical reaction rate is affected by temperature significantly. The higher the temperature, the quicker the hydrogen evolution rate, and the higher the hydrogen yield (note: the hydrogen yield mentioned in this work is considered for 1 h only). The H_2 yield increases from 3.28 wt% up to 10.41 wt% when the temperature rises from 25 to 70 °C, and the H_2 yield at 70 °C almost close to complete theoretical dehydrogenation. By contrast, the hydrolysis property of pure SB or pure AB is poor, as shown in Fig. 1b and c. The H_2 yields of the above monomers are lower than those of the composites at the same temperatures in the same time. Pure SB releases about 2.17 wt% and 8.86 wt% at 25 °C and 70 °C in 1 h, respectively. Pure AB only generates 0.63 wt% H_2 at 25 °C, and even at 70 °C, the highest H_2 amount is only 1.89 wt%, which is far less than the THY of 8.98 wt%.

The H_2 yields of *x*$NaBH_4$–*y*NH_3BH_3 composites at different temperatures can be seen in Table 1. As shown in both Fig. 1 and Table 1, it is obvious that the dehydrogenation property of the composites is superior to both pure AB and pure SB at any temperature, especially above 40 °C. It is demonstrated that the combination of the two compounds gives a synergetic effect. Meanwhile, the temperature has great effects on hydrolysis behaviors of these composites, and the mechanism is discussed in details in Section 3.3.1.

Aside from the temperature effect, the H_2 yield is also affected by the molar ratio of SB to AB. Fig. 2 shows the hydrogen release behaviors of a series of *x*SB–*y*AB composites by hydrolysis with magnetic stirring at 60 °C. All the curves have the same variation trend: there is a very fast reaction rate in the initial 10 min and then the rate slows down with the reaction proceeding. All composites can generate more than 3 wt% H_2 in 5 min, then continue to produce about 2 wt% more H_2 in 10 min. The amount of H_2 released in the first 10 min almost accounts for half of total H_2 yield in 1 h. The theoretical hydrogen yield of the composites increases with the rise of SB content (Table 1). However, the experimental results show that with the increase of the SB concentration from SB–AB to 8SB–AB, the actual H_2 yield increases first and then decreases. 4SB–AB and 5SB–AB have the highest H_2 yields of 9.42 wt% and 9.45 wt% respectively. The kinetics data of all *x*SB–*y*AB composites at different temperatures have the similar variation trend. Therefore, we only show the kinetics data for one temperature. More detailed information about the hydrolysis curves of each composite at other temperatures (25, 40, 50, and 70 °C) can be found in Fig. S1 in Supplementary data.

3.2. Analysis of SB-AB composites and hydrolysis by-products

Fig. 3 shows the XRD patterns of *x*SB–*y*AB composites with various molar ratios after ball milling under Ar atmosphere for