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$NaBH_4$ regeneration from $NaBO_2$ by high-energy ball milling and its plausible mechanism

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ABSTRACT

In this paper, we developed an easy and simple method (high-energy ball milling) for recycling $NaBO_2$ (the hydrolysis byproduct) back to $NaBH_4$ by a reaction with MgH_2. To optimize the yield of $NaBH_4$, we investigated the effect of four parameters, e.g. the ball milling time, the molar ratio of $MgH_2/NaBO_2$, H_2 pressure and addition of methanol, on the $NaBH_4$ regeneration. Accordingly, the maximum yield of $NaBH_4$ (89 wt. %) was achieved. The mechanism of $NaBH_4$ regeneration has been discussed. It is indicated that the $NaBH_4$ formation involves a two-step substitution in which $NaBOH_2$ is an intermediate confirmed by solid-state nuclear magnetic resonance (NMR).

Introduction

The established environmental impacts resulting from fossil fuel have stimulated urgent efforts to decarbonize our fuel sources. The hydrogen to be considered as an excellent alternative to fossil fuels has been suggested due to its abundance, high chemical energy, and pollution-free product [1–3]. However, the application of hydrogen as a fuel for transportation still confronts with some scientific and technical barriers, in which the safe and efficient hydrogen generation and storage on-board a vehicle is widely regarded as one of the most enormous challenges. Hydrolysis is one of the most attractive methods of hydrogen generation because it can obviate storage and produce a large amount of hydrogen [4–6]. Among the hydrogen complexes that produce hydrogen by hydrolysis and function as storage material for hydrogen, sodium borohydride ($NaBH_4$) has been extensively studied

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[7–9]. The hydrolysis reaction [10–13] can then be initiated on demand by bringing the aqueous $NaBH_4$ solution into contact with a heterogeneous catalyst, making the release of hydrogen very easy to control. The reaction Equation (1) is described as below [14]:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \quad \Delta H = -75kJ/mol\ H_2 \tag{1}$$

Despite the U.S. Department of Energy advises against the use of $NaBH_4$ in on-board automotive hydrogen storage due to two key concerns on the $NaBH_4$ cost and the irreversible process of its hydrolysis (convert $NaBO_2$ back to $NaBH_4$) [15], $NaBH_4$ is still a promising hydrogen carrier close to industrialization if the above two issues can be addressed.

In the past a few decades, several methods have been utilized to synthesize $NaBH_4$. The traditional manufacturing processes which have been applied to commercial production of $NaBH_4$ are the Brown-Schlesinger Process [16] and the Bayer Process [17,18]. The corresponding processes follow the equations below:

$$\text{Brown} - \text{Schlesinger Process}: \ 4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3 \tag{2}$$

$$\text{Bayer Process}: \ Na_2B_4O_7 + 16Na + 8H_2 + 7SiO_2 \rightarrow 4NaBH_4 + 7Na_2SiO_3 \tag{3}$$

However, the craft processes of these two methods are very complicated, and the reaction conditions are too harsh. Simultaneously, a considerable amount of metal (sodium) was consumed. All these mentioned factors can lead to a high price of $NaBH_4$. Presently, the market price of sodium borohydride is $55/kg which is too high as compared to gasoline. Therefore, it is highly desirable to explore alternative methods to synthesize $NaBH_4$ for reducing the use of sodium. Afterwards, magnesium (Mg) (or its hydride) as a less-expensive reducing agent, has been used to regenerate $NaBH_4$ from spent-$NaBH_4$ ($NaBO_2$) [19–23]. For instance, Kojima et al. proposed regeneration of $NaBH_4$ from $NaBO_2$ by means of thermochemical process with Mg/MgH_2 [20]. With this in mind, $NaBH_4$ can be synthesized by a reaction with Mg or MgH_2 according to the equations:

$$NaBO_2 + 2Mg + 2H_2 \rightarrow NaBH_4 + 2MgO \tag{4}$$

$$NaBO_2 + 2MgH_2 \rightarrow NaBH_4 + 2MgO \tag{5}$$

After that, great efforts also have been made to improve the yield and reduce cost of $NaBH_4$ regeneration [19,21–23]. However, either Mg or MgH_2 as the reducing agent, this process needs to be conducted under high temperature and high pressure to inspire the solid–solid reaction between Mg/MgH_2 and $NaBO_2$, leading to considerable energy consumption. In addition, harsh reaction conditions put forward higher requirements for the equipment, which is an obstacle for large-scale industrial production.

Recently, high-energy ball milling as a convenient technique has been used to regenerate $NaBH_4$ by the reaction of Mg/MgH_2 and $NaBO_2$ [24–28]. $NaBH_4$ can be synthesized through ball milling the mixed powder of MgH_2 and $NaBO_2$ at room temperature. Here, as reducing agent, MgH_2 possesses extreme surface properties which could transfer H^- into $NaBO_2$ and displace the site of O^{2-}. The reaction equation is as follows.

$$NaBO_2 + 2MgH_2 \xrightarrow{ball\ \ milling} NaBH_4 + 2MgO \tag{6}$$

In addition, to improve the yield of $NaBH_4$, Çakanyıldırım et al. [26] attempted to add some additives in starting materials such as Na, Al and Na_2CO_3, but the effect was not obvious. Hsueh et al. achieved an extreme value of 76% by detailing experiments of milling time and molar ratio of $MgH_2/NaBO_2$ [24], but the mechanism of $NaBH_4$ formation needs further investigations. There are also other ways to synthesize $NaBH_4$, such as nuclear process [29,30], microwave process [31,32], electrosynthesis process [33–35], etc. However, so far these methods are still need to be further studied [36].

In this paper, we used the high-energy ball milling for synthesizing $NaBH_4$ from $NaBO_2$ and MgH_2. We achieved a record yield of $NaBH_4$ (89 wt. %) by this process via optimizing the experimental parameters (milling time: 8 h; hydrogen pressure: 3 MPa; the molar ratio of $MgH_2/NaBO_2$: 2.7) and with adding additives (0.15 mL methanol to 1 g starting materials). The synthesized $NaBH_4$ shows impressive hydrolysis rate (~400 mL/g per min) as compared to commercial $NaBH_4$, illustrating that the $NaBH_4$ regenerated by this approach is the same as the currently commercialized $NaBH_4$. Our research may open a new opportunity for future $NaBH_4$ fabrication.

Experimental

MgH_2 (Sigma Aldrich, 95%) was used as reducing agent. Anhydrous sodium metaborate ($NaBO_2$) was obtained by drying sodium metaborate tetrahydrate ($NaBO_2 \cdot 4H_2O$: Sigma Aldrich, ≥95%), i.e., the $NaBO_2 \cdot 4H_2O$ was heated to 400 °C at a slow heating rate of 2°/min under vacuum to prevent its undesirable expansion and kept that temperature for 20 h. Then, anhydrous sodium metaborate was obtained when the treated material was cooled to room temperature. Methanol (99.5% purity) was purchased from Tianjin Caiyunfei Chemical Sales Co., Ltd and used without further purification.

The mixed powder was milled in a vibrating high energy ball mill (QM-3C, Nanjing University Instrument Plant, China) at a ball-to-powder mass ratio of 50:1. Ethylenediamine (Sigma Aldrich, ≥99%) was used to separate $NaBH_4$ from as-milled powder. Also, the corresponding calculation formula of yield was given as below.

$$Yield(\%) = \frac{obtained\ \ mass_{(\ NaBH_4\ )}}{theoretical\ mass_{(\ NaBH_4\ )}} \times 100\% \tag{7}$$

The ball milled product was analyzed by a Mini Flex 600 X-ray diffractometer using Cu Ka radiation and a iS50 Fourier transform infrared spectrometer, respectively. Hydrolysis experiment of $NaBH_4$ was conducted in 2wt% $CoCl_2$ solution. ^{11}B NMR experiments were performed at a spin speed of 10 kHz on a Bruker AVANCE III HD 400 spectrometer using 4 mm ZrO_2 rotors. All sample handling was performed in an Ar-filled glovebox.

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