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Short communication

Low-cost method for sodium borohydride regeneration and the energy efficiency of its hydrolysis and regeneration process

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HIGHLIGHTS

- The regeneration process for $NaBH_4$ is designed using MgH_2 with $NaBO_2$.
- The energy efficiency of the hydrolysis and regeneration of $NaBH_4$ is 49.91%.
- A cheap method for $NaBH_4$ regeneration was developed by reacting H–Mg_3La with $NaBO_2$.
- The mechanism of $NaBH_4$ regeneration by reacting Mg_3La hydride with $NaBO_2$ is revealed.

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ABSTRACT

Hydrolysis of sodium borohydride ($NaBH_4$) is one of the most attractive methods for energy generation of mobile systems used as hydrogen source because of the high gravimetric density and controllable hydrogen generation of $NaBH_4$. However, regeneration of $NaBH_4$ is a key issue that remains to be solved, and the energy efficiency of $NaBH_4$ is unknown. In the present study, the energy efficiency of $NaBH_4$ hydrolysis and the entire process of sodium metaborate ($NaBO_2$) regeneration via reaction with magnesium hydride (MgH_2) is determined through thermodynamics calculations. The maximum energy efficiency is 49.91%, indicating that $NaBH_4$ generation by reaction between MgH_2 and $NaBO_2$ during ball milling is feasible. An inexpensive high-energy ball milling method is employed to regenerate $NaBH_4$ by reaction of $NaBO_2$ with magnesium–lanthanum hydrides (H–Mg_3La). Products after ball milling are characterized through Fourier transform infrared spectroscopy and X-ray diffraction measurements. In the reaction of $NaBO_2$ with H–Mg_3La, MgH_2 reacts with $NaBO_2$ and then lanthanum hydride (LaH_3) reacts with $NaBO_2$ to produce $NaBH_4$.

1. Introduction

Because of the world energy crisis, replacement of fossil fuel has become a key issue. In this regard, hydrogen energy is an important alternative source of energy [1]. Unlike oil or natural gas, however, hydrogen is an energy carrier rather than a source of energy [2]. Appropriate methods for hydrogen generation and storage must therefore be developed to utilize it [3]. Hydrolysis is one of the most attractive methods of hydrogen generation because it obviates storage and produces a large amount of hydrogen. Among the hydrogen complexes that produce hydrogen by hydrolysis and function as storage material for hydrogen, sodium borohydride ($NaBH_4$) has been extensively studied. It has been utilized in hydrogen supply systems of fuel cells [4,5]. The nonhazardous characteristic and high gravimetric density (10.8wt%) [3] of $NaBH_4$ favor the use of this complex in hydrogen production. $NaBH_4$ hydrolyzes according to the following process:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \quad \Delta H = -75\ \text{kJ mol}^{-1}\ H_2 \qquad (1)$$

This highly controllable reaction generates pure hydrogen. Thus, it can be directly used in fuel cells [3,6]. The byproduct of this reaction, sodium metaborate ($NaBO_2$), is environmentally friendly

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and nontoxic. As $NaBH_4$ hydrolysis is irreversible, a key issue is discovering a means to convert $NaBO_2$ back to $NaBH_4$ [7]. For example, the less-expensive reducing metal, magnesium (or its hydride), has been used to produce $NaBH_4$ from dehydrated $NaBO_2$. Work on this approach was largely conducted by Kojima et al. [8]. They synthesized $NaBH_4$ by heating a mixture of dehydrated $NaBO_2$ and MgH_2 or a mixture of $NaBO_2$ and Mg under high H_2 pressure and elevated temperature. This synthesis proceeds through reactions described in Equations (2) and (3).

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

$$NaBO_2 + 2Mg + 2H_2 \rightarrow NaBH_4 + 2MgO \tag{3}$$

Other researchers further studied processes for converting $NaBO_2$ back to $NaBH_4$ through the above reaction [10,11]. Kojima et al. [8] synthesized $NaBH_4$ by heating dehydrated $NaBO_2$ and magnesium silicide (Mg_2Si) under high H_2 pressure at elevated temperature. However, energy consumption of such processes is very high. To achieve a new, economical route of $NaBH_4$ synthesis, Hsueh et al. [7], Çetin et al. [9], and Kong et al. [6] ball-milled dehydrated $NaBO_2$ and MgH_2 at room temperature. The yield of this process is 76%.

The U.S. Department of Energy advises against the use of $NaBH_4$ in on-board automotive hydrogen storage. One of the main reasons behind this advisory is the cost of $NaBH_4$ and the irreversible process of its hydrolysis [12]. We thus examined the energy efficiency and heat effect of the entire process of $NaBH_4$ recycling to determine the feasibility of hydrogen generation by $NaBH_4$ hydrolysis. $NaBO_2$ and MgH_2 were used to synthesize $NaBH_4$ by ball milling, and the energy efficiency of the entire recycling process was determined through thermodynamic calculations. The energy consumption of the regeneration procedure was discussed in accordance with the calculations. To reduce the cost and temperature of $NaBH_4$ synthesis, we reacted MgH_2 and lanthanum hydride (LaH_3) mixtures produced by hydrogenating magnesium–lanthanum alloy (Mg_3La) [13–15] with $NaBO_2$ by ball milling at room temperature. Our process avoids the use of MgH_2, which is synthesized by hydrogenation at a high temperature; it is thus an alternative route for the regeneration of $NaBH_4$ for industrial use.

2. Experimental

2.1. Sample preparation

MgH_2 powder (98% purity) was purchased from Alfa Aesar (USA). Mg_3La was prepared by induction melting of Mg (99.9%) and lanthanum (99.9%) in an alumina crucible under an argon atmosphere. The alloys were milled for 0.5 h in a QM-2SP planetary ball mill at a ball-to-powder mass ratio of 20:1. The $NaBO_2$ powder was dried at 280 °C to obtain anhydrous $NaBO_2$. To prevent samples and raw materials from oxidation and/or hydroxide formation, they were stored and handled in an Ar-filled glove box equipped with a recirculation system.

2.2. Synthesis of $NaBH_4$

Hydrogenation of Mg_3La was performed for 0.5 h at room temperature. MgH_2–$NaBO_2$ mixtures (2:1 mole ratio) and magnesium hydride–lanthanum hydride ($3MgH_2$–LaH_3)–$NaBO_2$ mixtures (4.4:9 mole ratio) were prepared. The mixtures were processed in a high-speed vibrating mill (QM-3C) using two sizes of balls.

2.3. Purification of $NaBH_4$

Purification of $NaBH_4$ was accomplished by extracting $NaBH_4$ with anhydrous ethylenediamine (99% purity) from the products after milling and then separating the extracted solution from the byproducts and remaining reactants through a polytetrafluoroethylene filter. The filtrate was dried in a vacuum oven at 50 °C to obtain $NaBH_4$.

2.4. Sample characterization

H–Mg_3La, as well as products after reaction and after purification were characterized by using a Philips X'Pert MPD X-ray diffractometer with Cu Kα radiation. Patterns in the 2θ range of 10°–90° were recorded at a scanning rate of 0.02° s^{-1}. The reaction products were analyzed by Fourier transformed infrared (FT-IR) spectroscopy (Bruker Vector33).

3. Results and discussion

3.1. Regeneration of $NaBH_4$ using $NaBO_2$ and MgH_2

To obtain a cyclical process with $NaBH_4$ hydrolysis and regeneration for hydrogen generation, $NaBH_4$ was regenerated by using $NaBO_2$ and MgH_2. Fig. 1 presents X-ray diffraction (XRD) patterns of the products after ball milling for different durations. Peaks of the XRD pattern of the product after 0.5 h of ball milling (Fig. 1(a)) could be indexed to MgH_2, $NaBH_4$ [16], and MgO. According to the phase analysis mentioned above, $NaBH_4$ and the by-product MgO were produced after 0.5 h of ball milling. Peaks of the XRD pattern of the product after 2 h of ball milling (Fig. 1(c)) could be indexed to $NaBH_4$ and MgO. In contrast to the XRD patterns in Fig. 1(a) and (b), the pattern in Fig. 1(c) does not have diffraction peaks of MgH_2. Stronger diffraction peaks of $NaBH_4$ in Fig. 1(c) compared with peaks in Fig. 1(d) suggest that part of the MgH_2 phase reacted with $NaBO_2$ and part of it became refined. Peaks of the XRD pattern of the product after 4 h of ball milling (Fig. 1(e)) could be indexed to $NaBH_4$ and MgO. The energy input for the vibrating mill used in this process of $NaBH_4$ regeneration was omitted in the subsequent calculation.

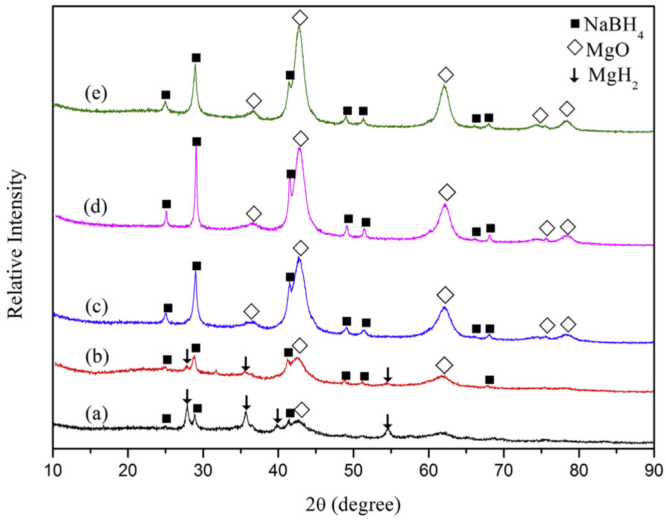

Fig. 1. XRD patterns of the powders produced after shaker milling the MgH_2–$NaBO_2$ mixture (in 2:1 mol ratio) for different durations (a) 30 min (b) 1 h (c) 2 h (d)3 h (e) 4 h.