



# Sodium borohydride regeneration via direct hydrogen transformation of sodium metaborate tetrahydrate

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## HIGHLIGHTS

- Hydrolysis byproduct is reduced without drying and work as the sole hydrogen sources.
- NaBH<sub>4</sub> is regenerated via ambient conditions ball milling with 74% yield.
- 26-fold reduction in cost is achieved compared to the study using MgH<sub>2</sub> as reductant.

## ARTICLE INFO

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## ABSTRACT

Irreversibility negatively impacts the application of NaBH<sub>4</sub> hydrolysis for hydrogen generation. Byproduct regeneration is key to solving this issue. In this work, the direct byproduct of aqueous NaBH<sub>4</sub> hydrolysis, NaBO<sub>2</sub>·4H<sub>2</sub>O, is reacted with Mg<sub>2</sub>Si to regenerate NaBH<sub>4</sub> via ball milling at room temperature under an argon atmosphere. In this process, the H<sup>-</sup> in NaBH<sub>4</sub> is exclusively from the H<sup>+</sup> in NaBO<sub>2</sub>·4H<sub>2</sub>O. The regenerated NaBH<sub>4</sub>, with a maximum yield of 74%, has the same physicochemical properties as a commercial sample. We also demonstrate that Mg<sub>2</sub>Si reacts with NaBO<sub>2</sub>·4H<sub>2</sub>O to generate NaBO<sub>2</sub>·2H<sub>2</sub>O, followed by a direct reaction between the residual Mg<sub>2</sub>Si and NaBO<sub>2</sub>·2H<sub>2</sub>O to produce NaBH<sub>4</sub>. The energy efficiency of this method is approximately 40%.

## 1. Introduction

As an alternative to fossil fuels, hydrogen can be utilized in fuel cell systems for portable power supplies [1]. Sodium borohydride (NaBH<sub>4</sub>) hydrolysis can be used for the hydrogen supply in a fuel cell system [2,3] because of its low toxicity, controllable hydrogen generation process [4], high hydrogen capacity (10.8 wt%) [5], and purity [6]. Recently, aqueous NaBH<sub>4</sub> hydrolysis was used for the hydrogen supply in small portable fuel cells [7]. The reaction is given by:



where  $x$  is the hydration factor [7] and the byproduct is a sodium metaborate (NaBO<sub>2</sub>) solution. It should be noted that from the NaBO<sub>2</sub>

solution, sodium metaborate tetrahydrate (NaBO<sub>2</sub>·4H<sub>2</sub>O) can be obtained below 54 °C, while dehydrated NaBO<sub>2</sub> can be obtained on treatment at > 350 °C [8]. However, the United States Department of Energy proposed a no-go recommendation for NaBH<sub>4</sub> hydrolysis for onboard system applications, mainly as a result of the high cost of NaBH<sub>4</sub> and its regeneration [9]. Therefore, the development of a low-cost and simple NaBH<sub>4</sub> regeneration method is imperative.

Currently, most of the studies on NaBH<sub>4</sub> regeneration focus on the dehydrated byproduct, NaBO<sub>2</sub>. For example, by annealing magnesium hydride (MgH<sub>2</sub>) and NaBO<sub>2</sub> at 550 °C, NaBH<sub>4</sub> can be successfully regenerated [10]. Ball milling of the same raw materials can also generate NaBH<sub>4</sub> with yields > 70% [11–14]. However, MgH<sub>2</sub> should be synthesized from its elements at ~350 °C [15], which is a waste of energy, and the cost of these methods is too high for utilization in industrial

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manufacture. Mg-based alloy hydrides were thus used to regenerate  $\text{NaBH}_4$  because of their low hydrogenation temperatures [16]. Use of Mg instead of  $\text{MgH}_2$  as a reducing agent in the annealing process could reduce the cost, but the  $\text{NaBH}_4$  yields were low [10,17]. When Si [10] or transition metals such as Fe, Co, and Ni [18,19] were added to the reaction, the yield increased. It should be noted that low-cost hydrogen is mainly produced from fossil fuels [20] and not renewable hydrogen sources, which further increases the regeneration cost. Recently, a new hydrogen source was identified. It was reported that H in the coordinated water of  $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$  could act as a hydrogen source, but the  $\text{NaBH}_4$  yield was only 12.3% via annealing of Mg and  $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$  under hydrogen pressure of 3 MPa [21]. As a consequence, current studies on  $\text{NaBH}_4$  regeneration are far from meeting United States Department of Energy targets.

In this work, the regenerated hydrogen comes exclusively from the hydrolysis byproduct.  $\text{Mg}_2\text{Si}$  and  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$  mixtures are ball milled at room temperature under argon. There are no additional hydrogen sources introduced into the system. Renewable H in the coordinated water in  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$  acts as the sole hydrogen source and transforms to  $\text{H}^-$  in  $\text{NaBH}_4$  during the ball milling.  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$  can be easily obtained at a low temperature ( $< 54^\circ\text{C}$ ) by heating  $\text{NaBO}_2$  solution [8], which is an energy-saving process compared to the production of dehydrated  $\text{NaBO}_2$  ( $> 350^\circ\text{C}$ ). In addition, use of  $\text{Mg}_2\text{Si}$  as a reducing agent provides a remarkable reduction in cost. Investigation of the energy efficiency of this method indicates that this method is energy feasible. In summary, this method provides a sustainable route for  $\text{NaBH}_4$  and its mild conditions may be suitable for industrial  $\text{NaBH}_4$  regeneration.

## 2. Experimental

### 2.1. Chemicals

For  $\text{NaBH}_4$  synthesis,  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$  ( $> 99\%$ ) was purchased from Aladdin and  $\text{Mg}_2\text{Si}$  ( $\geq 99.5\%$ ) was purchased from Sigma-Aldrich. In the purification process, the ethylenediamine used as solvent ( $\geq 99\%$ ), was purchased from Sigma-Aldrich. Potassium iodate ( $\text{KIO}_3$ , AR grade), potassium iodide (KI,  $\geq 99\%$ ),  $\text{H}_2\text{SO}_4$  (98%), NaOH ( $\geq 99\%$ ), starch indicator ( $\geq 99\%$ ), and sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ , AR grade) were purchased from Aladdin and used without further purification.  $\text{Mg}_2\text{Si}$  and  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$  were stored and handled in a glove box (Mikrouna, China) filled with argon and equipped with a recirculation and regeneration system, which maintained the oxygen and water concentrations below 1 ppm.

### 2.2. Synthesis of $\text{NaBH}_4$

A mixture of  $\text{Mg}_2\text{Si}$  and  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$  was reacted in a shaker mill (QM-3C, Nanjing, China) at 1000 cycles per min. In each experiment,  $\sim 1$  g of the mixture was ball milled with a ball-to-powder ratio of 50:1 at room temperature under argon. The whole sample preparation process was performed in a glove box.

### 2.3. Purification, quantification, and hydrolysis of $\text{NaBH}_4$

A 20-mL aliquot of ethylenediamine was mixed with the product to dissolve the generated  $\text{NaBH}_4$ . A clear  $\text{NaBH}_4$  solution was obtained via filtration through a polytetrafluoroethylene filter. The  $\text{NaBH}_4$  solution was dried using a freeze dryer (Martin Christ, Alpha 1-2LD Plus, Germany). The white powder was collected in a flask and the solvent (ethylenediamine) was frozen in the cold trap of the freeze dryer. The iodate method was used to quantify the generated  $\text{NaBH}_4$  [22]. Approximately 0.1 g of the  $\text{NaBH}_4$  obtained was hydrolyzed in 0.225 mL of 5 wt%  $\text{CoCl}_2$  aqueous solution in a hydrolysis apparatus [25] at room temperature. The same method was used for hydrolysis of commercial  $\text{NaBH}_4$ .

## 2.4. Characterization

The phase composition of the raw materials and products was analyzed using X-ray diffraction (XRD) on an Rigaku MiniFlex 300/600 system with Cu  $\text{K}\alpha$  radiation at 45 kV and 40 mA. To prevent reaction between the products and air, liquid paraffin was used to cover the powder samples. FTIR analysis (IS50, Nicolet) was used to characterize chemical bonds in the products. Potassium bromide (KBr) pellets were prepared in a glove box with a sample/KBr ratio of 1:99. Solid-state  $^{11}\text{B}$  magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy (AVANCE III HD 400, Bruker) was used to identify the transformation of the raw materials during ball milling. The morphology of the products was determined via scanning electron microscopy (SEM; Supra-40, Zeiss) and TEM (JEM-2100, Jeol). The ball milling atmosphere was analyzed using mass spectrometry (MS; Qic-20, Hiden Analytical).

## 3. Results and discussion

### 3.1. $\text{NaBH}_4$ synthesis

To regenerate  $\text{NaBH}_4$ ,  $\text{Mg}_2\text{Si}$  was reacted with  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$  under argon via ball milling. The XRD patterns (Fig. S1) indicated that the raw material was pure  $\text{Mg}_2\text{Si}$  and  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ . The red line in Fig. 1a shows the XRD pattern for the product of the  $\text{Mg}_2\text{Si}$  and  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$  mixture at a molar ratio of 3: and ball milled for 5 h. The peaks located at  $2\theta = 28.9^\circ$  and  $41.4^\circ$  are assigned to the (200) and (220) planes of  $\text{NaBH}_4$ . The other peaks are indexed to MgO and Si. The XRD pattern for the direct ball milled product demonstrates that  $\text{NaBH}_4$  was generated by this method. Here, the  $\text{NaBH}_4$  direct hydrolysis byproduct,  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ , is used to avoid the high-temperature dehydration process ( $> 350^\circ\text{C}$ ) [8]. The benefit of  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$  is that additional hydrogen sources, such as the  $\text{H}_2$  or hydrogen pressure [10,17,18] used in previous studies, are not required. The H in regenerated  $\text{NaBH}_4$  is exclusively from the coordinated water in  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ , which is a sustainable hydrogen source. Thus, this process effectively simplifies the regeneration.

The powder obtained was then mixed with ethylenediamine to produce a turbid solution. A clarified  $\text{NaBH}_4$  ethylenediamine solution was obtained by filtration through a polytetrafluoroethylene filter since among the ball milling products, only  $\text{NaBH}_4$  is soluble in ethylenediamine. Finally, a dried powder was obtained by freeze drying the clarified solution. The dried powder was characterized using XRD, liquid-state  $^{11}\text{B}$  NMR and FTIR spectroscopy to identify its phases, the chemical environment of boron, and the bonding. In the XRD pattern for the dried powder (Fig. 1b), the peaks located at  $2\theta = 25.1, 28.9, 41.4, 49.0, 51.3, 60.0, 66.0,$  and  $68.0^\circ$  are assigned to the (111), (200), (220), (311), (222), (400), (331), and (420) planes of  $\text{NaBH}_4$ . In Fig. 1c, the only resonance observed at around  $-40$  ppm indicates the sole existence of  $\text{BH}_4^-$ . In addition, the stretching vibrations (between 2200 and  $2400\text{ cm}^{-1}$ ) and bending vibrations ( $1125\text{ cm}^{-1}$ ) of B–H (Sigma) in the FTIR spectrum for the dried powder (Fig. 1d) are similar to those for commercial  $\text{NaBH}_4$ . All of the XRD patterns and NMR and FTIR spectra are consistent with previous studies on  $\text{NaBH}_4$  [23,24], confirming that pure  $\text{NaBH}_4$  was regenerated by the above method. SEM was used to further identify the morphology of the reduced  $\text{NaBH}_4$ . As shown in Fig. 1e, there are the holes and gaps on the surface of the particles, and the particles are likely to be composed of smaller particles. The morphology is similar to that of the  $\text{NaBH}_4$  bought from Sigma-Aldrich. The hydrolysis of the generated  $\text{NaBH}_4$  was also compared to that of commercial  $\text{NaBH}_4$ . Approximately 0.1 g of generated  $\text{NaBH}_4$  was hydrolyzed in 0.225 mL of 5 wt%  $\text{CoCl}_2$  aqueous solution. Compared to commercial  $\text{NaBH}_4$  hydrolyzed under the same conditions (Fig. S3), the hydrogen generation kinetics of the generated  $\text{NaBH}_4$  is faster, with a hydrogen conversion rate of 93% in 5 min, which demonstrates that the generated  $\text{NaBH}_4$  has similar hydrolysis property to the commercial

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