A Recycling Hydrogen Supply System of NaBH₄ Based on a Facile Regeneration Process: A Review

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Received: 24 October 2017; Accepted: 5 January 2018; Published: 6 January 2018

Abstract: NaBH₄ hydrolysis can generate pure hydrogen on demand at room temperature, but suffers from the difficult regeneration for practical application. In this work, we overview the state-of-the-art progress on the regeneration of NaBH₄ from anhydrous or hydrated NaBO₂ that is a byproduct of NaBH₄ hydrolysis. The anhydrous NaBO₂ can be regenerated effectively by MgH₂, whereas the production of MgH₂ from Mg requires high temperature to overcome the sluggish hydrogenation kinetics. Compared to that of anhydrous NaBO₂, using the direct hydrolysis byproduct of hydrated NaBO₂ as the starting material for regeneration exhibits significant advantages, i.e., omission of the high-temperature drying process to produce anhydrous NaBO₂ and the water included can react with chemicals like Mg or Mg₂Si to provide hydrogen. It is worth emphasizing that NaBH₄ could be regenerated by an energy efficient method and a large-scale regeneration system may become possible in the near future.

Keywords: sodium borohydride (NaBH₄); hydrolysis; regeneration

1. Introduction

Hydrogen [1–3] has been widely accepted as a clear energy carrier [4–6] due to its high energy density (142 MJ/kg) [7–9] and its environmentally friendly byproduct (water) [10,11]. It can be generated via numerous strategies, such as the electrolysis of water [12–14] and photocatalytic water splitting [15–18]. Supplying hydrogen to end users on demand requires safe and efficient methods of hydrogen storage.

Hydrides, storing hydrogen in a safe and compact way without using high pressure, like 70 MPa, or extremely low temperature, like 20 K (liquid hydrogen), have attracted great interest as promising hydrogen storage materials. Though a great deal of progress has been achieved on the development of solid-state hydrogen storage materials in the previous decades, no material with reasonably good hydrogen absorption and desorption performance at near room temperature has been developed to meet all the requirements for onboard hydrogen storage [19–23]. Hydrolysis of hydrides, such as MgH₂, ammonia borane (AB), and NaBH₄, generating hydrogen with relatively high capacity at room temperature, is attracting increasing interest for hydrogen supply on demand [24–26]. Due to the low cost of Mg and the high capacity of MgH₂ (7.6 wt %) [27–29], much attention has been paid to MgH₂ hydrolysis [30–32]. However, the reaction is interrupted easily by the formation
of a magnesium hydroxide layer [33,34]. Compared with MgH₂, AB possesses higher hydrogen capacity (19.6 wt %) [35–37]. AB is stable in water and its solubility is as high as 33.6 g/100 mL [38,39], which provides a simple application of AB aqueous solution. Studies have been focused on the development of catalysts to accelerate and control the reaction [40–42]. However, the high cost of AB [43] and the difficulty of AB regeneration are major blocks for the application of AB hydrolysis [44,45].

NaBH₄ hydrolysis is another promising system for hydrogen generation. It has relatively high hydrogen capacity (10.8 wt %) [46–48] and releases hydrogen with high purity at relatively low operational temperature with a controllable process [24,49,50]. Many studies have been focused on the hydrolysis property improvements [51–54]. Unfortunately, a no-go recommendation on NaBH₄ hydrolysis for onboard applications was given by the US Department of Energy (DOE) [55]. One of the key reasons are the cost and the regeneration of NaBH₄ [56]. As a result, more focus was shifted into the synthesis and regeneration of NaBH₄. For commercial NaBH₄ production, the Brown-Schlesinger process [57] and the Bayer process [58] are the most popular methods. The Brown-Schlesinger process produces NaBH₄ via the reaction between trimethylborate (B(OCH₃)₃, TMB) and sodium hydride (NaH), which should be produced by reacting Na and H₂. Different from it, the Bayer process is based on the reaction among borax (Na₂B₄O₇), Na, H₂, and silicon oxide (SiO₂) at 700 °C to synthesize NaBH₄. Although the above methods are mature technologies and straightforward procedures, the raw materials are too expensive for NaBH₄ hydrolysis applications. Thus, the raw materials have been studied to develop suitable NaBH₄ synthesis methods. Instead of Na, MgH₂ was used to react with Na₂B₄O₇ to synthesize NaBH₄ by ball milling at room temperature. Here, Na₂CO₃ addition could increase NaBH₄ yield up to 78% [59]. This method provides not only a new reducing agent (MgH₂) for NaBH₄ synthesis, but also a new way of ball milling. Enlightened by it, ball milling became popular in NaBH₄ synthesis studies, in which Na and MgH₂ reacted with B₂O₃ by ball milling with the NaBH₄ yield of only 25% [60]. When Na was substituted by low-cost NaCl, NaBH₄ could also be produced [61]. Later, high-pressure ball milling was also tried to synthesize NaBH₄, for instance, NaH was reacted with MgB₂ by ball milling under 12 MPa hydrogen pressure with the NaBH₄ yield of about 18%.

From the point of cost reduction in synthesis and post-usage of NaBH₄, the regeneration of NaBH₄ from the byproduct of hydrolysis (see Equation (1) [62]) is in great need for the recycling of the hydrogen supply system of NaBH₄:

\[
\text{NaBH}_4 + x\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{NaBO}_2\cdot x\text{H}_2\text{O}, \quad (x = 2, 4)
\]

(1)

According to this, the Brown-Schlesinger process was modified using NaBO₂ as source of boric acid to synthesis of NaBH₄ [63], the drawback of which the byproduct NaBO₂·xH₂O of hydrolysis needs to be dried first. As another alternative, the electrochemical route was proposed for recycling NaBO₂ to NaBH₄. Direct electrolysis of a NaBO₂ solution was first proven feasible for regeneration of NaBH₄ with using palladium (Pd) or platinum (Pt) as electrodes, where the conversion ratio of NaBO₂ was about 17% within 48 h [64]. Later, an Ag electrode was also employed in the recycling of NaBO₂; unfortunately, the quantities of reborn NaBH₄ were too low to be measured [65]. In contrast to the commercial gas-solid methods, the electrochemical method possesses ultra-low efficiency and complex processes, using precious metal electrodes, although the NaBO₂ solution that is the main byproduct of NaBH₄ hydrolysis can be used directly without dehydration. Therefore, an efficient and simple route is most urgently needed for the cycling of NaBO₂ into NaBH₄.

In this paper, we discuss the state-of-the-art progress on the regeneration of NaBH₄ from anhydrous NaBO₂ or the direct byproduct NaBO₂·xH₂O. In particular, the regeneration steps and the yield of NaBH₄ in each process are summarized in Scheme 1 and the facile regeneration process is also proposed. This review can provide important insights for the recycling hydrogen supply system with high efficiency.
2. NaBH₄ Regeneration via the Reaction between Metal or Other Hydrides and NaBO₂

As the hydrolysis byproduct of NaBH₄, NaBO₂ is the main research object of NaBH₄ regeneration studies. Many approaches have been adopted to reduce NaBO₂ to NaBH₄ with different reducing agents. Among the reducing agent, MgH₂ is the most effective. Kojima et al. [66] reacted MgH₂ with NaBO₂ under 550 °C and 7 MPa hydrogen pressure to regenerate NaBH₄, and about 97% NaBH₄ yield was achieved, while the high reaction temperature and high hydrogen pressure leads to a high energy consumption. Therefore, the thermochemistry method was substituted by room temperature ball milling in this reaction. Hsueh et al. [67], Kong et al. [68] and Çakanyildirim et al. [69] used MgH₂ to react with NaBO₂ by ball milling under argon. All of their NaBH₄ yields were over 70%, which strongly indicated that ball milling is suitable for the reaction between MgH₂ and NaBO₂. Based on the thermodynamics calculation, we found the maximum energy efficiency of the cycle was 49.91% [70]. Recently, we found that the addition of hydrogen pressure and methanol could further increase the NaBH₄ yield by this method [71]. The highest NaBH₄ yield could be increased to 89%. In addition to the energy consumption, raw material is another issue that should be considered. Hydrogenation of Mg to produce MgH₂ is hard due to its sluggish kinetics, thus resulting in the high cost and high energy consumption in MgH₂ production. By modifying the hydrogenation of Mg using Mg-based alloy, the above issue can be partly solved. Following this observation, we tried to use Mg₃La hydrides to react with NaBO₂ for its advantage of room temperature hydrogenation and low hydrogen purity requirement and found that NaBH₄ could be produced (Figure 1a) [70]. However, introduction of other elements influences the regeneration reaction of MgH₂. Directly using Mg and H₂ in the regeneration may solve the MgH₂ production problem. Kojima et al. [66] tried to directly react Mg with NaBO₂ under hydrogen, but the yield was extremely low, which may have resulted from the produced MgO obstruction. To promote the yield, Kojima et al. [66] found that Si addition could remarkably increase the NaBH₄ yield and Liu et al. [72] found transition metals, like Ni, Fe, and Co,
addition could also promote the NaBH₄ yield. However, both Si and transition metals keep their own elemental form after the reaction, indicating that such additions would reduce the absolute NaBH₄ yield. A pre-milling of the reactants was then found that could also promote the yield. Eom et al. [73] proposed a large-scaled method for reacting Mg with NaBO₂ to synthesize NaBH₄. After 1 h of ball milling of the reactants, about 69% yield was achieved under 600 °C and 5.5 MPa hydrogen pressure.

For other reducing agents, the Gibbs free energy of the reaction using Ca is much lower than that of Mg. In addition, we found that the energy efficiency of the cycle using Ca is about 43%. For the experiment, Eom et al. tried to substitute Mg by Ca [73], but few NaBH₄ was regenerated. Another low cost and abundant metal reductant, Al, was studied by few researchers on NaBH₄ regeneration. The only work with respect to Al was reported by Liu et al. [74], expressing that Al could not react with NaBO₂ and H₂ to produce NaBH₄ because of the generated Al₂O₃. However, if NaBO₂ was exchanged to Na₄B₂O₅, the regeneration would succeed at 400 °C and 2.3 MPa pressure of of hydrogen.

3. NaBH₄ Regeneration via using NaBO₂·xH₂O as Raw Materials

In NaBH₄ regeneration, many studies have focused on anhydrous NaBO₂ reducing. However, it should be noted that the direct hydrolysis byproduct is hydrated NaBO₂. For the NaBH₄ aqueous solution hydrolysis, the byproduct is NaBO₂·4H₂O [75], while for the solid NaBH₄ hydrolysis, the byproduct is NaBO₂·2H₂O. Anhydrous NaBO₂ should be produced by drying hydrated NaBO₂ at 350 °C. If the drying process was omitted, more energy could be saved and the price can be lowered. The energy of the hydrated NaBO₂ and anhydrous NaBO₂ is shown in Scheme 2. Some studies thus worked on reducing hydrated NaBO₂ directly.

Figure 1. (a) XRD patterns of the NaBO₂–Mg₃La hydride mixture and the product after ball milling the NaBO₂–Mg₃La hydride mixture. (b) XRD pattern of products via ball-milling the mixture of NaBO₂·2H₂O and MgH₂ in 1:5.5 mol ratio for 15 h. (c) XRD pattern of products via ball-milling the mixture of NaBO₂·2H₂O and Mg in 1:5 mole ratio for 15 h. (d) XRD patterns of the products after ball milling Mg₂Si and NaBO₂·2H₂O mixtures (in 2:1 mol ratio).
was tried. Liu et al. [76] reported that NaBH$_4$ can be regenerated by annealing Mg and NaBO$_2$·2H$_2$O under hydrogen atmosphere with only 12.3% yield. The low NaBH$_4$ yield may result from the obstruction of the thick generated MgO layer. However, they found that the coordinate water in NaBO$_2$·2H$_2$O was likely to be the hydrogen source. Considering the generated oxide layer, ball milling might be suitable to break the layer and continue the reaction. Therefore, we tried to used NaBO$_2$·2H$_2$O or NaBO$_2$·2H$_2$O to react with MgH$_2$ directly via ball milling to regenerate NaBH$_4$ [77]. NaBH$_4$ was successfully regenerated (Figure 1b):

\[
\text{NaBO}_2\cdot2\text{H}_2\text{O} + 4\text{MgH}_2 \rightarrow \text{NaBH}_4 + 4\text{MgO} + 4\text{H}_2
\]  

(2)

\[
\text{NaBO}_2\cdot4\text{H}_2\text{O} + 6\text{MgH}_2 \rightarrow \text{NaBH}_4 + 6\text{MgO} + 8\text{H}_2
\]  

(3)

The energy efficiency calculated in Section 2 could be improved by approximately 5.2%. Furthermore, a high NaBH$_4$ yield of 89.78% was achieved by this method, which is the highest compared with previous studies [67,69,78].

3.2. NaBH$_4$ Regeneration via the Reaction between Mg and NaBO$_2$·xH$_2$O

Hydrated NaBO$_2$ could be directly used in NaBH$_4$ regeneration, saving the energy consumption on the dehydration to produce anhydrous NaBO$_2$. However, production of MgH$_2$ from Mg requires high temperature to overcome the sluggish hydrogenation kinetics, resulting in the increased cost. In other words, the energy efficiency could be further promoted and the regeneration cost could be reduced, if the high-temperature hydrogenation process to produce MgH$_2$ can be avoided. According to Liu et al. [76], H in NaBO$_2$·2H$_2$O could transform to be the H of the regenerated NaBH$_4$. As a result, directly reacting Mg with hydrated NaBO$_2$ was possible to regenerate NaBH$_4$ and avoided the high-temperature hydrogenation process. We found that NaBH$_4$ could be produced by ball milling the NaBO$_2$·2H$_2$O and Mg mixture under argon (Figure 1c) [79] according to:

\[
\text{NaBO}_2\cdot2\text{H}_2\text{O} + 4\text{Mg} \rightarrow \text{NaBH}_4 + 4\text{MgO}
\]  

(4)

It should be noted that the regenerated H of NaBH$_4$ was completely from the coordinate water. On the other hand, the reaction between NaBO$_2$·4H$_2$O and Mg could also generate NaBH$_4$ by ball milling:

\[
\text{NaBO}_2\cdot4\text{H}_2\text{O} + 6\text{Mg} \rightarrow \text{NaBH}_4 + 6\text{MgO} + \text{H}_2
\]  

(5)
Currently, the highest NaBH₄ yield of the reaction between Mg and NaBO₂•2H₂O is only 68.55%. The energy efficiency needs to be further promoted. Note that the cost of this method is 34-fold lower than the method using MgH₂ and NaBO₂ in terms of the raw materials required [79].

3.3. NaBH₄ Regeneration via the Reaction between Mg₂Si and NaBO₂•2H₂O

Via ball milling hydrated NaBO₂ and Mg, NaBH₄ was regenerated and the energy efficiency was further increased. However, the highest NaBH₄ yield by this method was 68.55%, which did not reach the general yield of regenerated NaBH₄ (~76%) [67,68]. According to Kojima et al. [66], with Si added, the NaBH₄ yield was increased in the reaction between NaBO₂ and Mg under a hydrogen atmosphere. Therefore, Mg₂Si is possible to react with NaBO₂•2H₂O to regenerate NaBH₄ and improve the NaBH₄ yield. We have attempted the above idea in our previous study [80] and found that NaBH₄ was regenerated (Figure 1d) according to:

NaBO₂•2H₂O + 2Mg₂Si → NaBH₄ + 4MgO + 2Si (6)

The highest NaBH₄ yield was increased to 78% when the Mg₂Si and NaBO₂•2H₂O mixture was ball milled for 20 h. By using Mg₂Si as a reducing agent, the NaBH₄ yield was promoted and the H was still from the coordinate water in NaBO₂•2H₂O. For the raw materials cost, this method is half of the commercial method and about 30-fold lower than the method using MgH₂ and NaBO₂ [80].

4. Mechanism of NaBH₄ Regeneration Using NaBO₂•xH₂O as Raw Materials

The above three works [77,79,80] are new discoveries for direct regeneration of NaBH₄ from the hydrated NaBO₂ with high yield. Some common points were found in their mechanism studies. In all of the three works, a resonance at approximately -11.4 ppm was observed in the NMR spectra (Figure 2), which belongs to intermediate [BH₃(OH)]⁻ [81]. Such an intermediate was likely to generate from [BHi(OH)₃]⁻ and [BH₂(OH)₂]⁻. Conjecturing from the above intermediates, [BH₄]⁻ was likely to generate from a step-by-step substitution process of [OH]⁻ in [B(OH)₄]⁻ by [H]⁺. The [H]⁺ in NaBO₂•xH₂O thus transformed to [H]⁻ in this process.

For the reaction between MgH₂ and NaBO₂•2H₂O, the hydrogen transformation was realized by the substitution of the [OH]⁻ in NaBO₂•xH₂O by [H]⁻ in MgH₂. For the reaction of Mg and NaBO₂•2H₂O, Mg(OH)₂ and MgH₂ were generated as intermediates and the reactions can be written as:

2MgH₂ + NaB(OH)₄ → 2Mg(OH)₂ + NaBH₄ (7)

2Mg(OH)₂ + 2Mg → 4MgO + 2H₂ (8)

2H₂ + 2Mg → 2MgH₂ (9)

Since four moles of MgO were generated in this reaction (Equation (4)), it was a strong exergonic reaction. The reaction could be described as a substitution process of [OH]⁻ through the [H]⁻ from the produced intermediate MgH₂. During the substitution process, a side reaction may happen. [B₃H₆]⁻ was generated and then may react with MgH₂ and Na⁺ to form another part of NaBH₄ [82]. In the reaction between Mg₂Si and NaBO₂•2H₂O, Si–H was found (Figure 2d). It was speculated that an intermediate consisting of Mg, O, Si, and H was generated. The [OH]⁻ was transformed to [H]⁻ through a Mg–O–Si–H intermediate. Therefore, though Si was generated with an elemental state after the reaction, Si played an important role in H⁻ formation. Consequently, the substitution process of [OH]⁻ through [H]⁻ was a direct process.

In conclusion, two forms of hydrogen molecules exist in the regeneration. They are H in [OH]⁻ and H in [H]⁻. When using MgH₂ as a reducing agent, H in MgH₂ directly substitutes [OH]⁻ in NaB(OH)₄. This direct process contributes to the high NaBH₄ yield. In the situation of Mg, H in [OH]⁻ first transfer to H in MgH₂. Then it substitutes the [OH]⁻ in NaB(OH)₄ to form NaBH₄. The two-step reaction reduces the NaBH₄ yield. For the reaction between Mg₂Si and NaBO₂•2H₂O, H in [OH]⁻...
first transfers to H in Si–H and then it transfers to NaBH₄. Although this process is also two steps, the more active Si–H benefits from the higher NaBH₄ yield. Therefore, all of the reactions are H transfer processes.

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5. Hydrolysis Property of Regenerated NaBH₄ Using NaBO₂∙xH₂O as Raw Materials

Hydrolysis is the main application of the regenerated NaBH₄. By the catalysis of CoCl₂ [83], NaBH₄ could fast hydrolyze with stoichiometry H₂O. It was found that the regenerated NaBH₄ from NaBO₂∙xH₂O had an excellent hydrolysis property, which was similar to the commercial NaBH₄. According to Figure 3, the highest system hydrogen capacity (containing water and catalyst) was 6.75 wt %, which was the highest compared with previous studies [67,69,78]. It was produced by the reaction between MgH₂ and NaBO₂∙xH₂O. A system hydrogen capacity of 6.33 wt % and 6.3 wt % could also be obtained. Furthermore, the hydrolysis byproduct was indexed to be NaBO₂∙2H₂O (inset, Figure 3), which was the raw material of our regeneration. As a result, it was demonstrated that a complete cycle of NaBH₄ hydrolysis could be achieved by existing works, which was suitable for sustainable application.
Acknowledgments:

via ball milling, and the highest NaBH$_4$ yield reaches 90%. This process using hydrated NaBO$_2$ exhibits significant advantages, whereby the dehydration process at 350 °C to obtain anhydrous NaBO$_2$ can be omitted and, more importantly, the water included can react with chemicals like Mg and Mg$_2$Si to provide hydrogen instead of using MgH$_2$. As a result, low cost metal (such as Mg, Ca, or Al) becomes possible to be the reducing agent for the NaBH$_4$ regeneration reaction via ball milling, because the [H$^+$] in the hydrated NaBO$_2$ may directly transform to the [H$^-$] in the hydrated NaBH$_4$. These reactions could operate without extra hydrogen inputs, which provides the possibility of a low-cost and sustainable regeneration. Furthermore, this strategy may also be promoted to other areas, such as LiBH$_4$ production.

Conflicts of Interest: The authors declare no conflict of interest.

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