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Review

A Recycling Hydrogen Supply System of $NaBH_4$ Based on a Facile Regeneration Process: A Review

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Abstract: $NaBH_4$ 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 $NaBH_4$ from anhydrous or hydrated $NaBO_2$ that is a byproduct of $NaBH_4$ hydrolysis. The anhydrous $NaBO_2$ can be regenerated effectively by MgH_2, whereas the production of MgH_2 from Mg requires high temperature to overcome the sluggish hydrogenation kinetics. Compared to that of anhydrous $NaBO_2$, using the direct hydrolysis byproduct of hydrated $NaBO_2$ as the starting material for regeneration exhibits significant advantages, i.e., omission of the high-temperature drying process to produce anhydrous $NaBO_2$ and the water included can react with chemicals like Mg or Mg_2Si to provide hydrogen. It is worth emphasizing that $NaBH_4$ could be regenerated by an energy efficient method and a large-scale regeneration system may become possible in the near future.

Keywords: sodium borohydride ($NaBH_4$); 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 MgH_2, ammonia borane (AB), and $NaBH_4$, 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 MgH_2 (7.6 wt %) [27–29], much attention has been paid to MgH_2 hydrolysis [30–32]. However, the reaction is interrupted easily by the formation of a magnesium hydroxide layer [33,34]. Compared with MgH_2, 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].

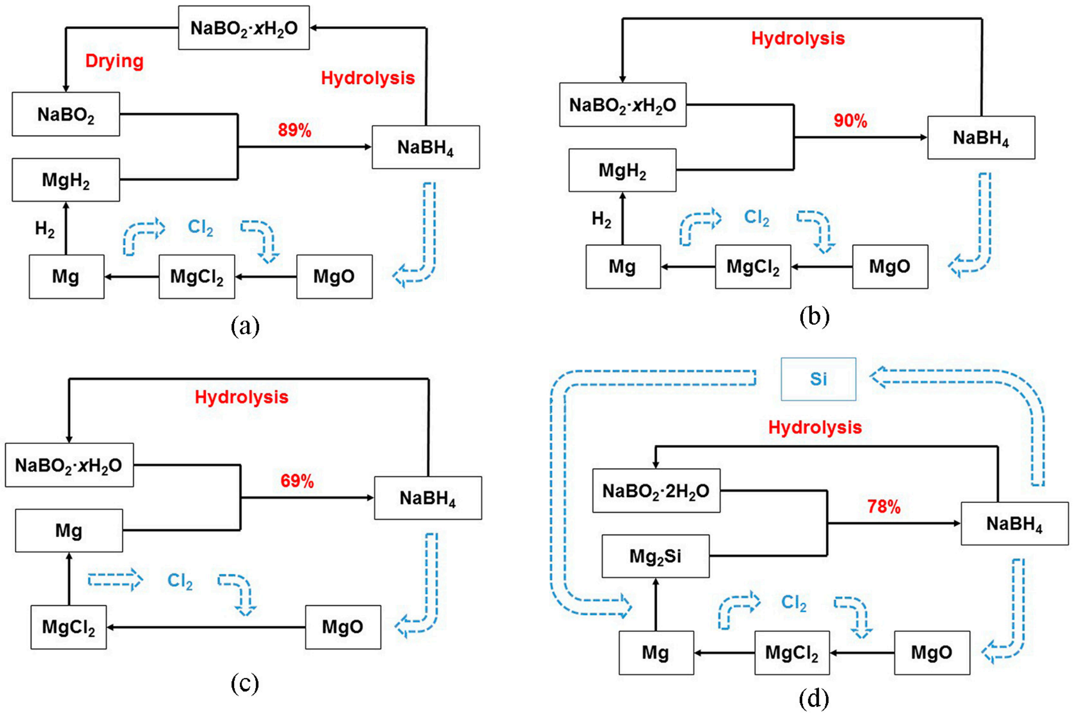
$NaBH_4$ hydrolysis is another promising system for hydrogen generation. It has relatively high hydrogen capacity (10.8 wt %) [46–48] and releases hydrogen with high purity at relatively low operational temperature with a controllable process [24,49,50]. Many studies have been focused on the hydrolysis property improvements [51–54]. Unfortunately, a no-go recommendation on $NaBH_4$ 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 $NaBH_4$ [56]. As a result, more focus was shifted into the synthesis and regeneration of $NaBH_4$. For commercial $NaBH_4$ production, the Brown-Schlesinger process [57] and the Bayer process [58] are the most popular methods. The Brown-Schlesinger process produces $NaBH_4$ via the reaction between trimethylborate ($B(OCH_3)_3$, TMB) and sodium hydride (NaH), which should be produced by reacting Na and H_2. Different from it, the Bayer process is based on the reaction among borax ($Na_2B_4O_7$), Na, H_2, and silicon oxide (SiO_2) at 700 °C to synthesize $NaBH_4$. Although the above methods are mature technologies and straightforward procedures, the raw materials are too expensive for $NaBH_4$ hydrolysis applications. Thus, the raw materials have been studied to develop suitable $NaBH_4$ synthesis methods. Instead of Na, MgH_2 was used to react with $Na_2B_4O_7$ to synthesize $NaBH_4$ by ball milling at room temperature. Here, Na_2CO_3 addition could increase $NaBH_4$ yield up to 78% [59]. This method provides not only a new reducing agent (MgH_2) for $NaBH_4$ synthesis, but also a new way of ball milling. Enlightened by it, ball milling became popular in $NaBH_4$ synthesis studies, in which Na and MgH_2 reacted with B_2O_3 by ball milling with the $NaBH_4$ yield of only 25% [60]. When Na was substituted by low-cost NaCl, $NaBH_4$ could also be produced [61]. Later, high-pressure ball milling was also tried to synthesize $NaBH_4$, for instance, NaH was reacted with MgB_2 by ball milling under 12 MPa hydrogen pressure with the $NaBH_4$ yield of about 18%.

From the point of cost reduction in synthesis and post-usage of $NaBH_4$, the regeneration of $NaBH_4$ from the byproduct of hydrolysis (see Equation (1) [62]) is in great need for the recycling of the hydrogen supply system of $NaBH_4$:

$$NaBH_4 + xH_2O \rightarrow H_2 + NaBO_2{\cdot}xH_2O,\ (x = 2, 4) \tag{1}$$

According to this, the Brown-Schlesinger process was modified using $NaBO_2$ as source of boric acid to synthesis of $NaBH_4$ [63], the drawback of which the byproduct $NaBO_2{\cdot}xH_2O$ of hydrolysis needs to be dried first. As another alternative, the electrochemical route was proposed for recycling $NaBO_2$ to $NaBH_4$. Direct electrolysis of a $NaBO_2$ solution was first proven feasible for regeneration of $NaBH_4$ with using palladium (Pd) or platinum (Pt) as electrodes, where the conversion ratio of $NaBO_2$ was about 17% within 48 h [64]. Later, an Ag electrode was also employed in the recycling of $NaBO_2$; unfortunately, the quantities of reborn $NaBH_4$ 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 $NaBO_2$ solution that is the main byproduct of $NaBH_4$ hydrolysis can be used directly without dehydration. Therefore, an efficient and simple route is most urgently needed for the cycling of $NaBO_2$ into $NaBH_4$.

In this paper, we discuss the state-of-the-art progress on the regeneration of $NaBH_4$ from anhydrous $NaBO_2$ or the direct byproduct $NaBO_2{\cdot}xH_2O$. In particular, the regeneration steps and the yield of $NaBH_4$ 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.



Scheme 1. Flowchart of (**a**) $NaBH_4$ regeneration via the reaction between MgH_2 and $NaBO_2$. (**b**) $NaBH_4$ regeneration via the reaction between MgH_2 and $NaBO_2 \cdot xH_2O$. (**c**) $NaBH_4$ regeneration via the reaction between Mg and $NaBO_2 \cdot xH_2O$. (**d**) $NaBH_4$ regeneration via the reaction between Mg_2Si and $NaBO_2 \cdot 2H_2O$. Numbers indicate the yield of $NaBH_4$.

2. $NaBH_4$ Regeneration via the Reaction between Metal or Other Hydrides and $NaBO_2$

As the hydrolysis byproduct of $NaBH_4$, $NaBO_2$ is the main research object of $NaBH_4$ regeneration studies. Many approaches have been adopted to reduce $NaBO_2$ to $NaBH_4$ with different reducing agents. Among the reducing agent, MgH_2 is the most effective. Kojima et al. [66] reacted MgH_2 with $NaBO_2$ under 550 °C and 7 MPa hydrogen pressure to regenerate $NaBH_4$, and about 97% $NaBH_4$ 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 MgH_2 to react with $NaBO_2$ by ball milling under argon. All of their $NaBH_4$ yields were over 70%, which strongly indicated that ball milling is suitable for the reaction between MgH_2 and $NaBO_2$. 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 $NaBH_4$ yield by this method [71]. The highest $NaBH_4$ 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 MgH_2 is hard due to its sluggish kinetics, thus resulting in the high cost and high energy consumption in MgH_2 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 Mg_3La hydrides to react with $NaBO_2$ for its advantage of room temperature hydrogenation and low hydrogen purity requirement and found that $NaBH_4$ could be produced (Figure 1a) [70]. However, introduction of other elements influences the regeneration reaction of MgH_2. Directly using Mg and H_2 in the regeneration may solve the MgH_2 production problem. Kojima et al. [66] tried to directly react Mg with $NaBO_2$ 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 $NaBH_4$ yield and Liu et al. [72] found transition metals, like Ni, Fe, and Co, addition could also promote the $NaBH_4$ yield. However, both Si and transition metals keep their own elemental form after the reaction, indicating that such additions would reduce the absolute $NaBH_4$ 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 $NaBO_2$ to synthesize $NaBH_4$. After 1 h of ball milling of the reactants, about 69% yield was achieved under 600 °C and 5.5 MPa hydrogen pressure.

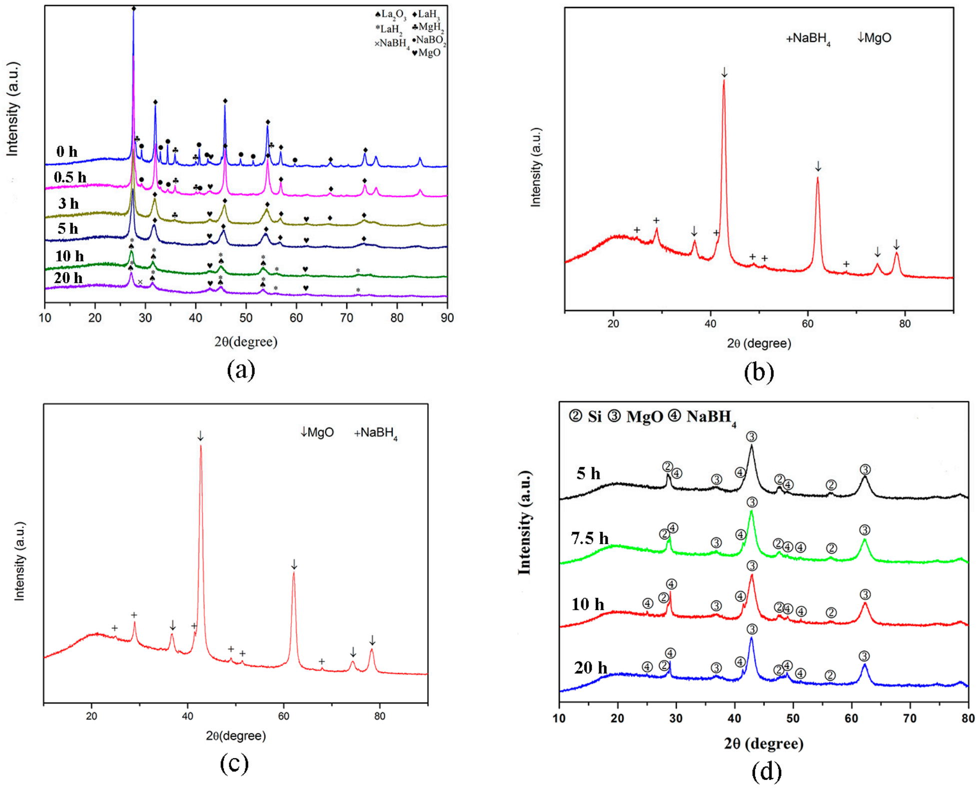
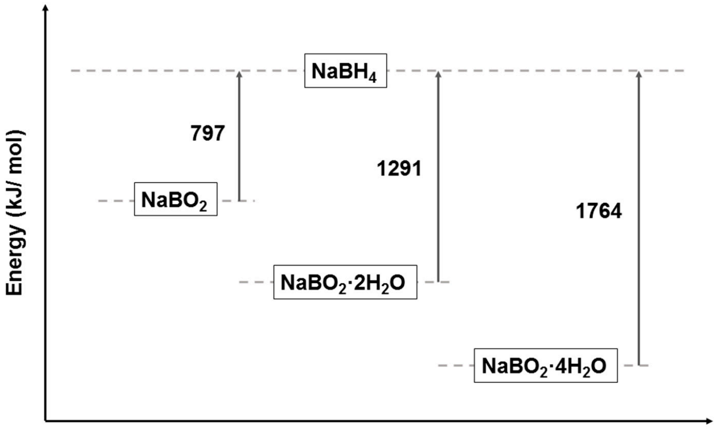


Figure 1. (**a**) XRD patterns of the $NaBO_2$–Mg_3La hydride mixture and the product after ball milling the $NaBO_2$–Mg_3La hydride mixture. (**b**) XRD pattern of products via ball-milling the mixture of $NaBO_2{\cdot}2H_2O$ and MgH_2 in 1:5.5 mol ratio for 15 h. (**c**) XRD pattern of products via ball-milling the mixture of $NaBO_2{\cdot}2H_2O$ and Mg in 1:5 mole ratio for 15 h. (**d**) XRD patterns of the products after ball milling Mg_2Si and $NaBO_2{\cdot}2H_2O$ mixtures (in 2:1 mol ratio).

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 $NaBH_4$ was regenerated. Another low cost and abundant metal reductant, Al, was studied by few researchers on $NaBH_4$ regeneration. The only work with respect to Al was reported by Liu et al. [74], expressing that Al could not react with $NaBO_2$ and H_2 to produce $NaBH_4$ because of the generated Al_2O_3. However, if $NaBO_2$ was exchanged to $Na_4B_2O_5$, the regeneration would succeed at 400 °C and 2.3 MPa pressure of of hydrogen.

3. $NaBH_4$ Regeneration via using $NaBO_2{\cdot}xH_2O$ as Raw Materials

In $NaBH_4$ regeneration, many studies have focused on anhydrous $NaBO_2$ reducing. However, it should be noted that the direct hydrolysis byproduct is hydrated $NaBO_2$. For the $NaBH_4$ aqueous solution hydrolysis, the byproduct is $NaBO_2{\cdot}4H_2O$ [75], while for the solid $NaBH_4$ hydrolysis, the byproduct is $NaBO_2{\cdot}2H_2O$. Anhydrous $NaBO_2$ should be produced by drying hydrated $NaBO_2$ 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 $NaBO_2$ and anhydrous $NaBO_2$ is shown in Scheme 2. Some studies thus worked on reducing hydrated $NaBO_2$ directly.



Scheme 2. Schematic energy diagram of the boron material for the recycling of $NaBO_2$ to $NaBH_4$, $NaBO_2·2H_2O$ to $NaBH_4$, and $NaBO_2·4H_2O$ to $NaBH_4$.

3.1. $NaBH_4$ Regeneration via the Reaction between MgH_2 and $NaBO_2·xH_2O$

For directly using hydrated $NaBO_2$ as the regeneration raw material, a thermochemistry method was tried. Liu et al. [76] reported that $NaBH_4$ can be regenerated by annealing Mg and $NaBO_2·2H_2O$ 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 $NaBO_2·2H_2O$ 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 $NaBO_2·4H_2O$ or $NaBO_2·2H_2O$ to react with MgH_2 directly via ball milling to regenerate $NaBH_4$ [77]. $NaBH_4$ was successfully regenerated (Figure 1b):

$$NaBO_2·2H_2O + 4MgH_2 \rightarrow NaBH_4 + 4MgO + 4H_2 \tag{2}$$

$$NaBO_2·4H_2O + 6MgH_2 \rightarrow NaBH_4 + 6MgO + 8H_2 \tag{3}$$

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 $NaBO_2·xH_2O$

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 $NaBO_2·2H_2O$ 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 $NaBO_2·2H_2O$ and Mg mixture under argon (Figure 1c) [79] according to:

$$NaBO_2·2H_2O + 4Mg \rightarrow NaBH_4 + 4MgO \tag{4}$$

It should be noted that the regenerated H of $NaBH_4$ was completely from the coordinate water. On the other hand, the reaction between $NaBO_2·4H_2O$ and Mg could also generate $NaBH_4$ by ball milling:

$$NaBO_2·4H_2O + 6Mg \rightarrow NaBH_4 + 6MgO + H_2 \tag{5}$$

Currently, the highest $NaBH_4$ yield of the reaction between Mg and $NaBO_2{\cdot}2H_2O$ 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 MgH_2 and $NaBO_2$ in terms of the raw materials required [79].

3.3. $NaBH_4$ Regeneration via the Reaction between Mg_2Si and $NaBO_2{\cdot}2H_2O$

Via ball milling hydrated $NaBO_2$ and Mg, $NaBH_4$ was regenerated and the energy efficiency was further increased. However, the highest $NaBH_4$ yield by this method was 68.55%, which did not reach the general yield of regenerated $NaBH_4$ (~76%) [67,68]. According to Kojima et al. [66], with Si added, the $NaBH_4$ yield was increased in the reaction between $NaBO_2$ and Mg under a hydrogen atmosphere. Therefore, Mg_2Si is possible to react with $NaBO_2{\cdot}2H_2O$ to regenerate $NaBH_4$ and improve the $NaBH_4$ yield. We have attempted the above idea in our previous study [80] and found that $NaBH_4$ was regenerated (Figure 1d) according to:

$$NaBO_2{\cdot}2H_2O + 2Mg_2Si \rightarrow NaBH_4 + 4MgO + 2Si \tag{6}$$

The highest $NaBH_4$ yield was increased to 78% when the Mg_2Si and $NaBO_2{\cdot}2H_2O$ mixture was ball milled for 20 h. By using Mg_2Si as a reducing agent, the $NaBH_4$ yield was promoted and the H was still from the coordinate water in $NaBO_2{\cdot}2H_2O$. For the raw materials cost, this method is half of the commercial method and about 30-fold lower than the method using MgH_2 and $NaBO_2$ [80].

4. Mechanism of $NaBH_4$ Regeneration Using $NaBO_2{\cdot}xH_2O$ as Raw Materials

The above three works [77,79,80] are new discoveries for direct regeneration of $NaBH_4$ from the hydrated $NaBO_2$ 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 $[BH_3(OH)]^-$ [81]. Such an intermediate was likely to generate from $[BH(OH)_3]^-$ and $[BH_2(OH)_2]^-$. Conjecturing from the above intermediates, $[BH_4]^-$ was likely to generate from a step-by-step substitution process of $[OH]^-$ in $[B(OH)_4]^-$ by $[H]^-$. The $[H]^+$ in $NaBO_2{\cdot}xH_2O$ thus transformed to $[H]^-$ in this process.

For the reaction between MgH_2 and $NaBO_2{\cdot}2H_2O$, the hydrogen transformation was realized by the substitution of the $[OH]^-$ in $NaBO_2{\cdot}xH_2O$ by $[H]^-$ in MgH_2. For the reaction of Mg and $NaBO_2{\cdot}2H_2O$, $Mg(OH)_2$ and MgH_2 were generated as intermediates and the reactions can be written as:

$$2MgH_2 + NaB(OH)_4 \rightarrow 2Mg(OH)_2 + NaBH_4 \tag{7}$$

$$2Mg(OH)_2 + 2Mg \rightarrow 4MgO + 2H_2 \tag{8}$$

$$2H_2 + 2Mg \rightarrow 2MgH_2 \tag{9}$$

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 MgH_2. During the substitution process, a side reaction may happen. $[B_3H_8]^-$ was generated and then may react with MgH_2 and Na^+ to form another part of $NaBH_4$ [82]. In the reaction between Mg_2Si and $NaBO_2{\cdot}2H_2O$, 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 MgH_2 as a reducing agent, H in MgH_2 directly substitutes $[OH]^-$ in $NaB(OH)_4$. This direct process contributes to the high $NaBH_4$ yield. In the situation of Mg, H in $[OH]^-$ first transfer to H in MgH_2. Then it substitutes the $[OH]^-$ in $NaB(OH)_4$ to form $NaBH_4$. The two-step reaction reduces the $NaBH_4$ yield. For the reaction between Mg_2Si and $NaBO_2{\cdot}2H_2O$, H in $[OH]^-$

first transfers to H in Si–H and then it transfers to $NaBH_4$. Although this process is also two steps, the more active Si–H benefits from the higher $NaBH_4$ yield. Therefore, all of the reactions are H transfer processes.

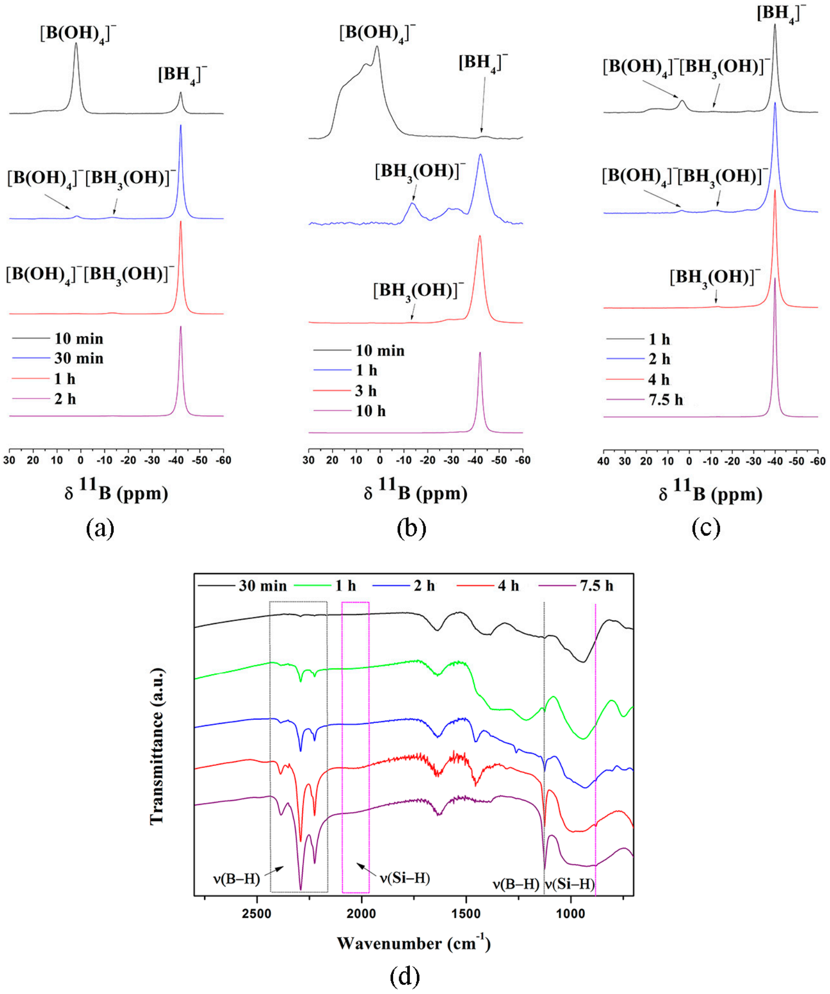


Figure 2. (**a**) Solid-state ^{11}B NMR spectra of products after ball milling MgH_2 and $NaBO_2{\cdot}2H_2O$ mixtures (in 5.0:1 mol ratio). (**b**) Solid-state ^{11}B NMR spectra of products after ball milling Mg and $NaBO_2{\cdot}2H_2O$ mixtures (in 5.0:1 mole ratio). (**c**) ^{11}B MAS NMR spectra of the products after ball milling Mg_2Si and $NaBO_2{\cdot}2H_2O$ mixtures (in 2:1 mol ratio). (**d**) FT-IR spectra of the products after ball milling Mg_2Si and $NaBO_2{\cdot}2H_2O$ mixtures (in 2:1 mol ratio).

5. Hydrolysis Property of Regenerated $NaBH_4$ Using $NaBO_2{\cdot}xH_2O$ as Raw Materials

Hydrolysis is the main application of the regenerated $NaBH_4$. By the catalysis of $CoCl_2$ [83], $NaBH_4$ could fast hydrolyze with stoichiometry H_2O. It was found that the regenerated $NaBH_4$ from $NaBO_2{\cdot}xH_2O$ had an excellent hydrolysis property, which was similar to the commercial $NaBH_4$. 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 MgH_2 and $NaBO_2{\cdot}xH_2O$. A system hydrogen capacity of 6.33 wt % and 6.3 wt % could also be obtained. Furthermore, the hydrolysis byproduct was indexed to be $NaBO_2{\cdot}2H_2O$ (inset, Figure 3), which was the raw material of our regeneration. As a result, it was demonstrated that a complete cycle of $NaBH_4$ hydrolysis could be achieved by existing works, which was suitable for sustainable application.

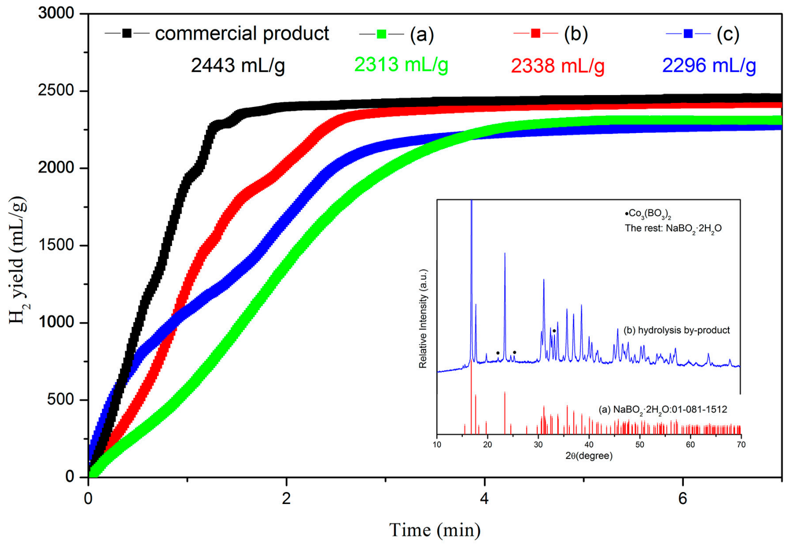


Figure 3. Hydrolysis curves of (**a**) the regeneration product (MgH_2 and $NaBO_2 \cdot xH_2O$). (**b**) The regeneration product (Mg and $NaBO_2 \cdot xH_2O$). (**c**) The purified product (Mg_2Si and $NaBO_2 \cdot 2H_2O$) and the commercial $NaBH_4$ in 5 wt % $CoCl_2$ aqueous solution. Inset: XRD patterns of (**a**) a standard PDF card of $NaBO_2 \cdot 2H_2O$ and (**b**) the hydrolysis byproduct.

6. Summary and Perspective

Application of $NaBH_4$ hydrolysis is limited by its effective regeneration. $NaBH_4$ synthesis and regeneration thus become attractive research topics, especially for the recycling of byproduct $NaBO_2$. For the anhydrous $NaBO_2$ recycling, MgH_2 has the best reducing result. However, its high cost, resulting from the high hydrogenation temperature of Mg, limits the application of such methods. For the hydrolysis byproduct hydrated $NaBO_2$, it can also be reduced by MgH_2, Mg, or Mg_2Si 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_2Si 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.

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