



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

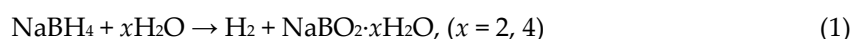
Hydrogen [1–3] has been widely accepted as a clear energy carrier [4–6] due to its high energy density (142 MJ/kg) [7–9] and its environmentally friendly byproduct (water) [10,11]. It can be generated via numerous strategies, such as the electrolysis of water [12–14] and photocatalytic water splitting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

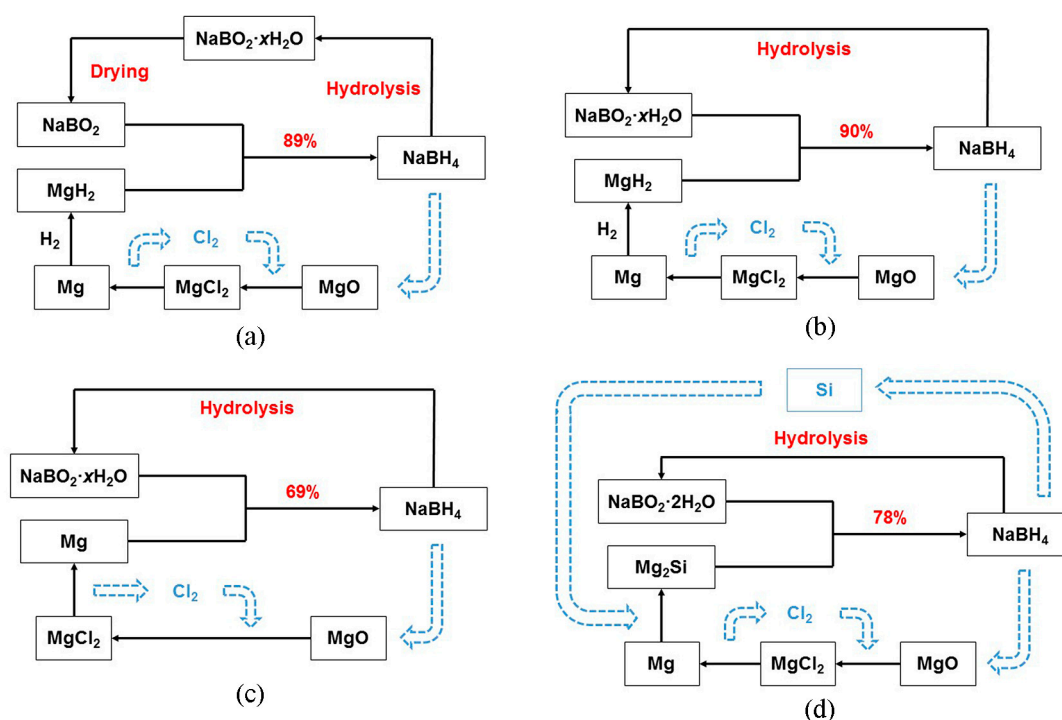
NaBH₄ hydrolysis is another promising system for hydrogen generation. It has relatively high hydrogen capacity (10.8 wt %) [46–48] and releases hydrogen with high purity at relatively low operational temperature with a controllable process [24,49,50]. Many studies have been focused on the hydrolysis 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:



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.



Scheme 1. Flowchart of (a) NaBH₄ regeneration via the reaction between MgH₂ and NaBO₂. (b) NaBH₄ regeneration via the reaction between MgH₂ and NaBO₂·xH₂O. (c) NaBH₄ regeneration via the reaction between Mg and NaBO₂·xH₂O. (d) NaBH₄ regeneration via the reaction between Mg₂Si and NaBO₂·2H₂O. Numbers indicate the yield of NaBH₄.

2. NaBH₄ Regeneration via the Reaction between Metal or Other Hydrides and NaBO₂

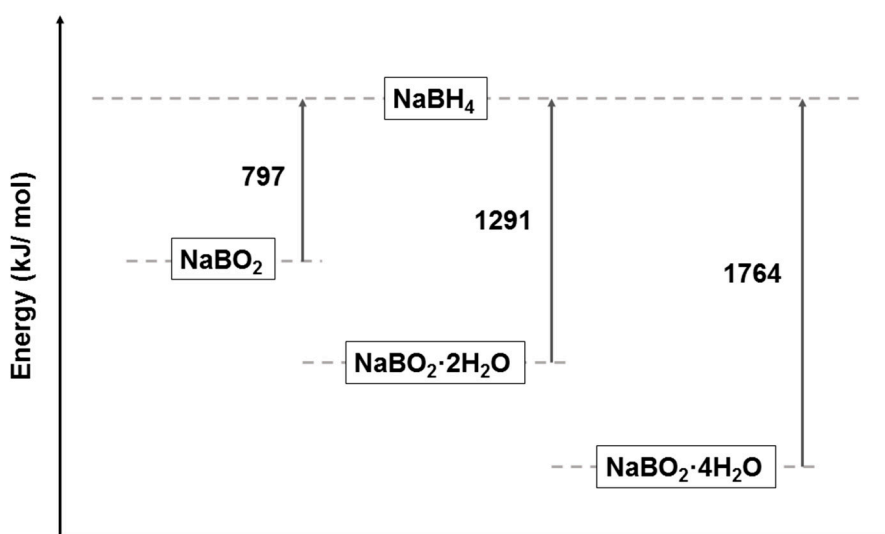
As the hydrolysis byproduct of NaBH₄, NaBO₂ is the main research object of NaBH₄ regeneration studies. Many approaches have been adopted to reduce NaBO₂ to NaBH₄ with different reducing agents. Among the reducing agent, MgH₂ is the most effective. Kojima et al. [66] reacted MgH₂ with NaBO₂ under 550 °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 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.

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 $\text{Na}_4\text{B}_2\text{O}_5$, the regeneration would succeed at 400 °C and 2.3 MPa pressure of hydrogen.

3. NaBH_4 Regeneration via using $\text{NaBO}_2 \cdot x\text{H}_2\text{O}$ 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 $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ [75], while for the solid NaBH_4 hydrolysis, the byproduct is $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$. 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.

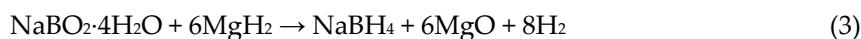
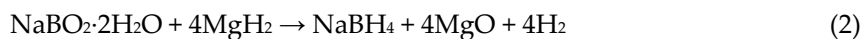


Scheme 2. Schematic energy diagram of the boron material for the recycling of NaBO_2 to NaBH_4 , $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ to NaBH_4 , and $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ to NaBH_4 .

3.1. NaBH_4 Regeneration via the Reaction between MgH_2 and $\text{NaBO}_2 \cdot x\text{H}_2\text{O}$

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 $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ 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 $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ 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

$\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ or $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ to react with MgH_2 directly via ball milling to regenerate NaBH_4 [77]. NaBH_4 was successfully regenerated (Figure 1b):



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].

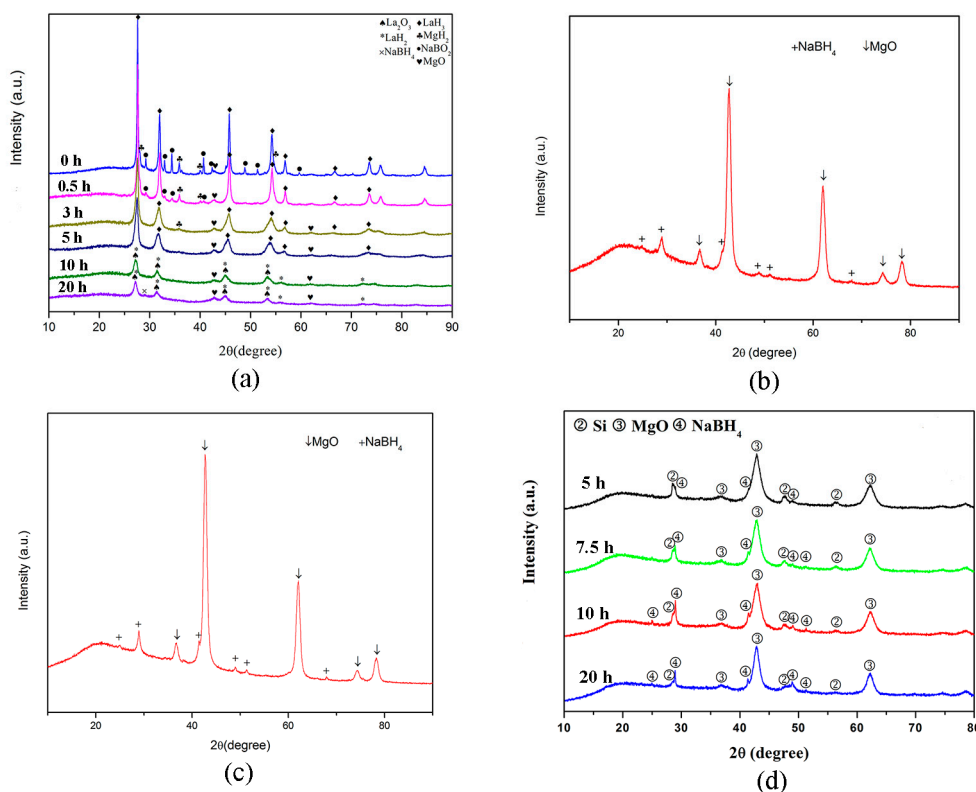
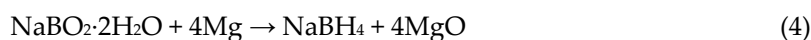


Figure 1. (a) XRD patterns of the $\text{NaBO}_2\text{-Mg}_3\text{La}$ hydride mixture and the product after ball milling the $\text{NaBO}_2\text{-Mg}_3\text{La}$ hydride mixture. (b) XRD pattern of products via ball-milling the mixture of $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ and MgH_2 in 1:5.5 mol ratio for 15 h. (c) XRD pattern of products via ball-milling the mixture of $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ and Mg in 1:5 mole ratio for 15 h. (d) XRD patterns of the products after ball milling Mg_2Si and $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ mixtures (in 2:1 mol ratio).

3.2. NaBH_4 Regeneration via the Reaction between Mg and $\text{NaBO}_2 \cdot x\text{H}_2\text{O}$

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 $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ 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 $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ and Mg mixture under argon (Figure 1c) [79] according to:



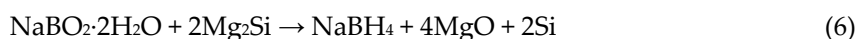
It should be noted that the regenerated H of NaBH₄ was completely from the coordinate water. On the other hand, the reaction between NaBO₂·4H₂O and Mg could also generate NaBH₄ by ball milling:



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:

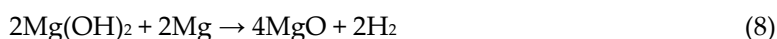
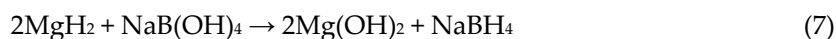


The highest NaBH₄ yield was increased to 78% when the Mg₂Si and NaBO₂·2H₂O mixture was ball milled for 20 h. By using Mg₂Si as a reducing agent, the NaBH₄ yield was promoted and the H was still from the coordinate water in NaBO₂·2H₂O. For the raw materials cost, this method is half of the commercial 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 [BH(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:



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. [B₃H₈][−] 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 NaBH_4 yield. In the situation of Mg, H in $[\text{OH}]^-$ first transfer to H in MgH_2 . Then it substitutes the $[\text{OH}]^-$ in NaB(OH)_4 to form NaBH_4 . The two-step reaction reduces the NaBH_4 yield. For the reaction between Mg_2Si and $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$, H in $[\text{OH}]^-$ 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.

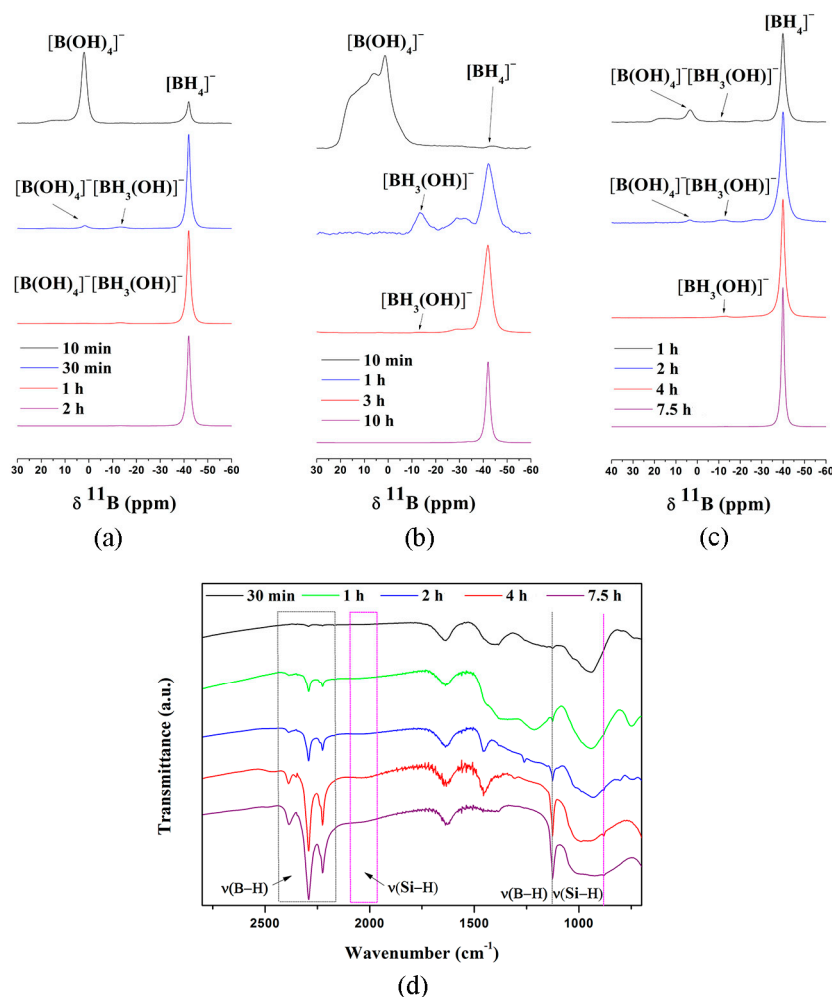


Figure 2. (a) Solid-state ^{11}B NMR spectra of products after ball milling MgH_2 and $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ mixtures (in 5.0:1 mol ratio). (b) Solid-state ^{11}B NMR spectra of products after ball milling Mg and $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ mixtures (in 5.0:1 mole ratio). (c) ^{11}B MAS NMR spectra of the products after ball milling Mg_2Si and $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ mixtures (in 2:1 mol ratio). (d) FT-IR spectra of the products after ball milling Mg_2Si and $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ mixtures (in 2:1 mol ratio).

5. Hydrolysis Property of Regenerated NaBH_4 Using $\text{NaBO}_2 \cdot x\text{H}_2\text{O}$ 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 $\text{NaBO}_2 \cdot x\text{H}_2\text{O}$ 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 $\text{NaBO}_2 \cdot x\text{H}_2\text{O}$. A system hydrogen capacity of 6.33 wt % and 6.3 wt % could also be obtained. Furthermore, the hydrolysis byproduct was indexed to be $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ (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.

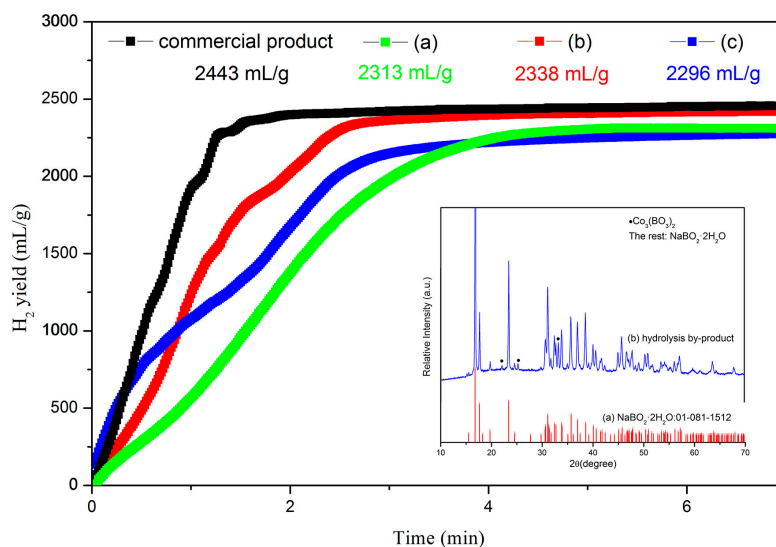


Figure 3. Hydrolysis curves of (a) the regeneration product (MgH_2 and $\text{NaBO}_2 \cdot x\text{H}_2\text{O}$). (b) The regeneration product (Mg and $\text{NaBO}_2 \cdot x\text{H}_2\text{O}$). (c) The purified product (Mg_2Si and $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$) and the commercial NaBH_4 in 5 wt % CoCl_2 aqueous solution. Inset: XRD patterns of (a) a standard PDF card of $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ 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 $[\text{H}]^+$ in the hydrated NaBO_2 may directly transform to the $[\text{H}]^-$ 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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