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Closing the loop for hydrogen storage: Facile regeneration of NaBH₄ from its hydrolytic product

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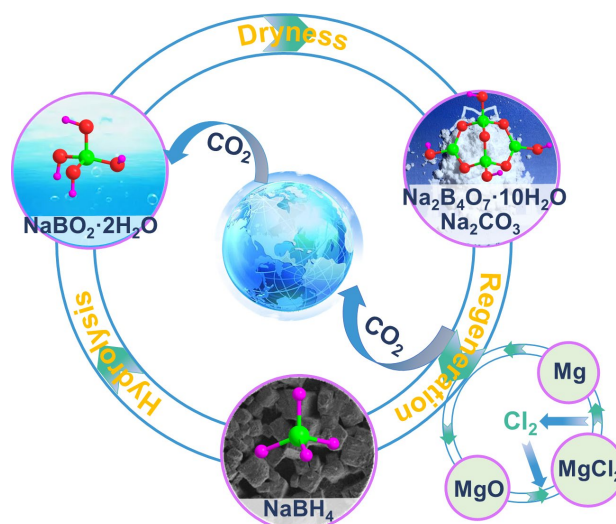
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Abstract:

Sodium borohydride (NaBH_4) is among the most studied hydrogen storage materials since it is able to deliver high purity H_2 at room temperature with controllable kinetics via hydrolysis, but its regeneration from the hydrolytic product has been challenging. Herein we report a facile method to regenerate NaBH_4 with high yield and low costs. The hydrolytic product NaBO_2 in aqueous solution reacts with CO_2 forming $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and Na_2CO_3 , both of which are ball milled with Mg under ambient conditions to form NaBH_4 with a high yield close to 80 %. Compared with previous studies, this new approach avoids expensive reducing agent such as MgH_2 , bypasses the energy-intensive dehydration procedure to remove water from $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, and does not require high-pressure H_2 gas, therefore leading to much reduced costs. This method is expected to effectively close the loop of NaBH_4 regeneration and hydrolysis, enabling a wide deployment of NaBH_4 for hydrogen storage.

Keywords: borohydride, regeneration, hydrolysis, hydrogen storage

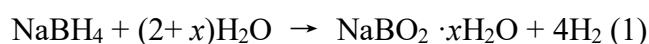
Graphical Abstract:



1 Introduction

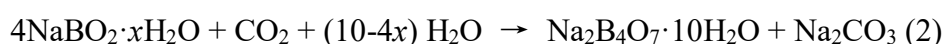
Hydrogen has been deemed as an ideal energy carrier due to its high energy density by weight, high abundance, and environmental friendliness [1-3]. However, wide utilization of hydrogen energy has been hampered by a few barriers with one of them associated with storage. Due to its low energy density by volume, hydrogen has been conventionally compressed or liquefied to improve the density. However, these physical processes cause large energy penalty and special care is always required when operating under high pressure or cryogenic conditions. Materials-based hydrogen storage has therefore received strong attention since it has attractive features such as higher capacity, better safety, and milder operation conditions.

Sodium borohydride (NaBH_4) is among the most studied candidates as a hydrogen storage material. NaBH_4 can release hydrogen via hydrolysis with good controllability, high hydrogen purity, high gravimetric hydrogen storage capacity and environmentally benign by-products [4-6]. The hydrolysis of NaBH_4 is typically expressed by the following reaction:



The spent fuel is normally hydrated sodium metaborate (NaBO_2) in aqueous solution [7]. The regeneration of NaBH_4 from the hydrolytic product so far has featured high costs and low yields.

NaBO_2 in aqueous solution reacts with CO_2 in air forming $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and NaCO_3 according to the following reaction:



$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ is the main constituent of naturally abundant borax mineral. It is therefore highly appealing to develop a simple, efficient and affordable approach to generate NaBH_4 from $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

Currently, two types of raw materials, H_2 (H°) and metal hydride (H^-) have been used as hydrogen sources in the (re)generation of NaBH_4 . For example, NaBH_4 can be synthesized by annealing $\text{Na}_2\text{B}_4\text{O}_7$ with Na and SiO_2 under high pressure H_2 (over 3 MPa) at elevated temperature (400–500°C) [8]. This method is of high cost because the reaction conditions are harsh and a considerable amount of sodium metal is needed. Recently, the preparation of NaBH_4 has been carried out by annealing the dehydrated borax ($\text{Na}_2\text{B}_4\text{O}_7$) with low-cost magnesium (Mg) at a high temperature (550°C) and high H_2 pressure (2.5MPa) [9]. However, this process is also energy intensive and dangerous. The process can be further optimized by ball milling $\text{Na}_2\text{B}_4\text{O}_7$ with magnesium hydrides (MgH_2) with a maximum yield of 78% [10, 11]. The use of expensive MgH_2 , however, makes mass production by this method less feasible. It should also note that high energy is required to obtain $\text{Na}_2\text{B}_4\text{O}_7$ by dehydrating $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ at approximately 600°C [12].

Herein, we present a new method where H^+ in the coordinate water in $\text{Na}_2\text{B}_4\text{O}_7$ can be directly used as a hydrogen source to prepare NaBH_4 . In the new procedure, a mixture of $\text{Na}_2\text{B}_4\text{O}_7 \cdot x\text{H}_2\text{O}$ ($x=5, 10$) and Na_2CO_3 is obtained by exposing NaBO_2 aqueous solution to CO_2 and then drying at a temperature of < 54 °C. Ball milling the mixture with Mg at room temperature and atmospheric pressure leads to the formation of NaBH_4 with a high yield of 78.9%. Compared with the literature procedures that

require dehydrated $\text{Na}_2\text{B}_4\text{O}_7$, MgH_2 , high pressure H_2 , and/or high temperatures, the new method utilize low cost materials and operate under mild reaction conditions, which allow for facile scaled up manufacturing.

2 Experimental

2.1 Materials

Sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and sodium tetraborate pentahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$) powders were purchased from Aladdin (Shanghai, China, ACS-grade) and Xiya Reagent (Shandong, China, 99% purity), respectively. Magnesium powder (Mg, 99.8% purity), sodium borohydride (NaBH_4 , $\geq 98\%$) and ethylenediamine ($\text{C}_2\text{H}_8\text{N}_2$, $\geq 99\%$ purity) were obtained from Sigma-Aldrich and stored and handled in a glove box (MIKROUNA, China) filled with argon with O_2 and H_2O concentrations below 0.1 ppm. Sulfuric acid (H_2SO_4 (GR)), sodium carbonate (Na_2CO_3 , 99.5% purity), sodium hydroxide (NaOH , $\geq 99\%$), potassium iodate (KIO_3 , AR-grade), potassium iodide (KI , $\geq 99\%$), starch indicator ($\geq 99\%$), and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$, AR-grade) were purchased from Aladdin. All reagents were used as received without further purification. DI water (18.25 $\text{M}\Omega$ resistance) obtained from a water purification system (Unique-S10, Guangzhou, China) was used to prepare aqueous solution.

2.2 Synthesis of NaBH_4

Mechano-chemical synthesis of NaBH_4 was carried out by ball milling $\text{Na}_2\text{B}_4\text{O}_7 \cdot x\text{H}_2\text{O}$ ($x=5, 10$), Na_2CO_3 and Mg in a shaker mill (QM-3C, Nanjing, China) at 1000 or 1200 cycle per min (CPM) under ambient temperature. For each experiment,

in a glove box filled with Ar, 1 g of reactants with a specific molar ratio was loaded in a 80 mL jar with a ball-to-powder weight ratio of 50:1. Two different sized steel balls were used. To prevent overheating, the milling process was performed by alternating 30 min of milling with 30 min of rest. NaBH₄ was extracted from the reaction products using anhydrous ethylenediamine under Ar atmosphere at room temperature. Ethylenediamine was added to the ball-milled product in a closed flask which was stirred by a magnetic stirrer. Polytetrafluoroethylene membrane (0.25 μm in pore size) was used to separate the solution from solids. The filtrate was dried in a freeze dryer (Martin Christ, Alpha 1-2LD plus, Germany) to obtain NaBH₄, whose quantity was determined using iodimetric analysis [13]. The yield of NaBH₄ was calculated according to the following equation [14]:

$$\text{Yield (NaBH}_4\text{)} = \frac{\text{obtained mass NaBH}_4}{\text{theoretical mass NaBH}_4} \times 100\%$$

The theoretical amount was based on a full conversion meaning that 1 mole Na₂B₄O₇·xH₂O (x=5, 10) is converted to 4 mole of NaBH₄.

2.3 Hydrolysis of NaBH₄

Hydrolysis of NaBH₄ was carried out using an apparatus (Fig. S1 in Supporting Information) described in one previous study [15]. About 0.05 g NaBH₄, synthesized or commercial, was hydrolysed in 1.0 mL aqueous solution with 2 wt% CoCl₂ at room temperature. NaBH₄ was first added into a glass tube and CoCl₂ aqueous solution was then injected into the glass tube. The hydrogen evolution was monitored via registering the weight of discharged water using an electronic scale connected to a computer.

2.4 Characterization

The phase composition of the solid powders was investigated by a wide-angle X-ray diffractometer (XRD). The X-ray diffraction patterns were recorded at ambient temperature using a Rigaku MiniFlex 300/600 in the range from 10 to 90° diffraction angle with CuK α radiation ($\lambda = 0.15418$ nm) at operating parameters of 40 mA and 45 kV. The samples were smeared on a glass slide in a home-made device and then covered with Scotch tape to prevent exposure to air. Fourier transform infrared spectroscopy (FTIR) was performed on a Nicolet IS50 spectrometer in the region of 4000-400 cm⁻¹. Solid-state ¹¹B magic angle spinning nuclear magnetic resonance (MAS NMR) (Bruker-AVANCE III HD 400) and solution-state (D₂O+0.5M NaOD) NMR (Bruker-AVANCE III HD 500) spectra were collected. The morphology of the samples was inspected by a scanning electron microscope (SEM) (Zeiss, Supra-40) and also a transmission electron microscope (TEM) (Jeol, JEM-2100). Identities of the gaseous products formed during ball milling were determined by a mass spectrometer (MS, Hiden-Qic 20).

3 Results and discussion

3.1 Regeneration and hydrolysis cycle

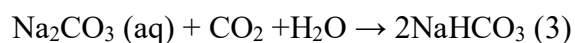
One key challenge in utilizing NaBH₄ for hydrogen storage lies in its regeneration. Herein we developed a facile procedure to regenerate NaBH₄ from its CO₂ treated hydrolytic product (Fig. 1a). NaBH₄ can be successfully synthesized by ball milling a mixture of Mg, Na₂B₄O₇·10H₂O, and Na₂CO₃ at ambient condition. Fig. 1b shows the XRD qualitative analysis of the powders after 20h milling of a mixture of Mg, Na₂B₄O₇·10H₂O, and Na₂CO₃ in a mole ratio of 24.75:1:1. The diffraction peaks are

indexed to NaBH₄ and MgO.

NaBH₄ was isolated from the as-milled product, and its identity and morphology were studied using XRD, FT-IR, NMR, SEM, and TEM. XRD pattern of commercial NaBH₄ (Fig. 1c(2)) show ten peaks at 25.1° , 28.9° , 41.4° , 49.0° , 51.3° , 60.0° , 66.0° , 68.0° , 75.5° , and 81.0° , corresponding to (111), (200), (220), (311), (222), (400), (331), (420), (422), and (511) of NaBH₄ (ICDD 00-009-0386), respectively. The synthesized NaBH₄ displays the same XRD pattern as the commercial NaBH₄ (Fig. 1c(3)). The FT-IR bands (2200-2400 and 1125 cm⁻¹, corresponding to the B-H stretching and deformation of pure NaBH₄, respectively [16-18]) of the isolated NaBH₄ are in good agreement with the those of commercial NaBH₄ (Fig. S2a). The XRD and FT-IR results are also consistent with the previous studies on NaBH₄ synthesis [18-21]. The BH₄⁻ anion is further confirmed by NMR analysis (Fig.S2b) [22]. Similar to commercial NaBH₄, the synthesized NaBH₄ exists in cubic particles with sizes of several microns (Fig. S3). Selected area electron diffraction (SAED) pattern also indicates the success in obtaining crystalline NaBH₄ (Fig. 1d and Fig. S4).

According to the results obtained from various techniques (XRD, FTIR, NMR, SEM, and TEM), we can conclude that high quality NaBH₄ with crystallography and microstructure similar to commercial NaBH₄ was successfully synthesized by directly ball milling Na₂B₄O₇·10H₂O and Na₂CO₃ with Mg in Ar at room temperature. The synthesis conditions are very mild compared with the previous studies in which NaBH₄ was produced via NaBO₂ reacting with Mg at 350°C under 7 MPa H₂ [23] or Na₂B₄O₇ reacting with Mg at 550°C under 2.5 MPa H₂ [9].

For a closed-loop application, hydrogen evolution performance of the regenerated NaBH₄ is particularly important. Fig. 1e shows the hydrogen production curves of prepared NaBH₄. The prepared NaBH₄ showed good hydrolysis properties and produced 2317 mL/g hydrogen totally in 1.8 min. After the hydrolytic aqueous solution was naturally dried up in air, solid Na₂B₄O₇·10H₂O (ICDD ref. 01-075-1078) powers were obtained, as evidenced by XRD patterns (Fig. 1f) and FT-IR spectra (Fig. S5). Another set of characteristic diffraction peaks can be indexed to Na₃H(CO₃)₂·2H₂O which is composed of Na₂CO₃ and NaHCO₃. The transformation of Na₂CO₃ into NaHCO₃ occurs in the following reaction:



NaHCO₃ can be avoided by regulating the exposure of the hydrolytic aqueous solution to air. This is supported by experiments that only Na₂B₄O₇·10H₂O and Na₂CO₃ can be obtained by tuning the exposure of NaBO₂ aqueous solution to CO₂ (Fig. S6).

We propose a pathway to close the cycle of NaBH₄ hydrolysis and regeneration (Fig. 1a). Comparing with the literature methods, current procedure features low-cost starting materials, mild reactions at room temperature, and requiring no high pressure H₂. The energy efficiency of regeneration can be estimated by systematic modeling, which is beyond the scope of the current work. One important step in the complete cycle is the reformation of Mg metal. Although electrochemical process of extracting Mg is energy intensive, it is widely adopted industrially. Overall, this represents a promising cycle pathway for large-scale application of NaBH₄ as a hydrogen carrier.

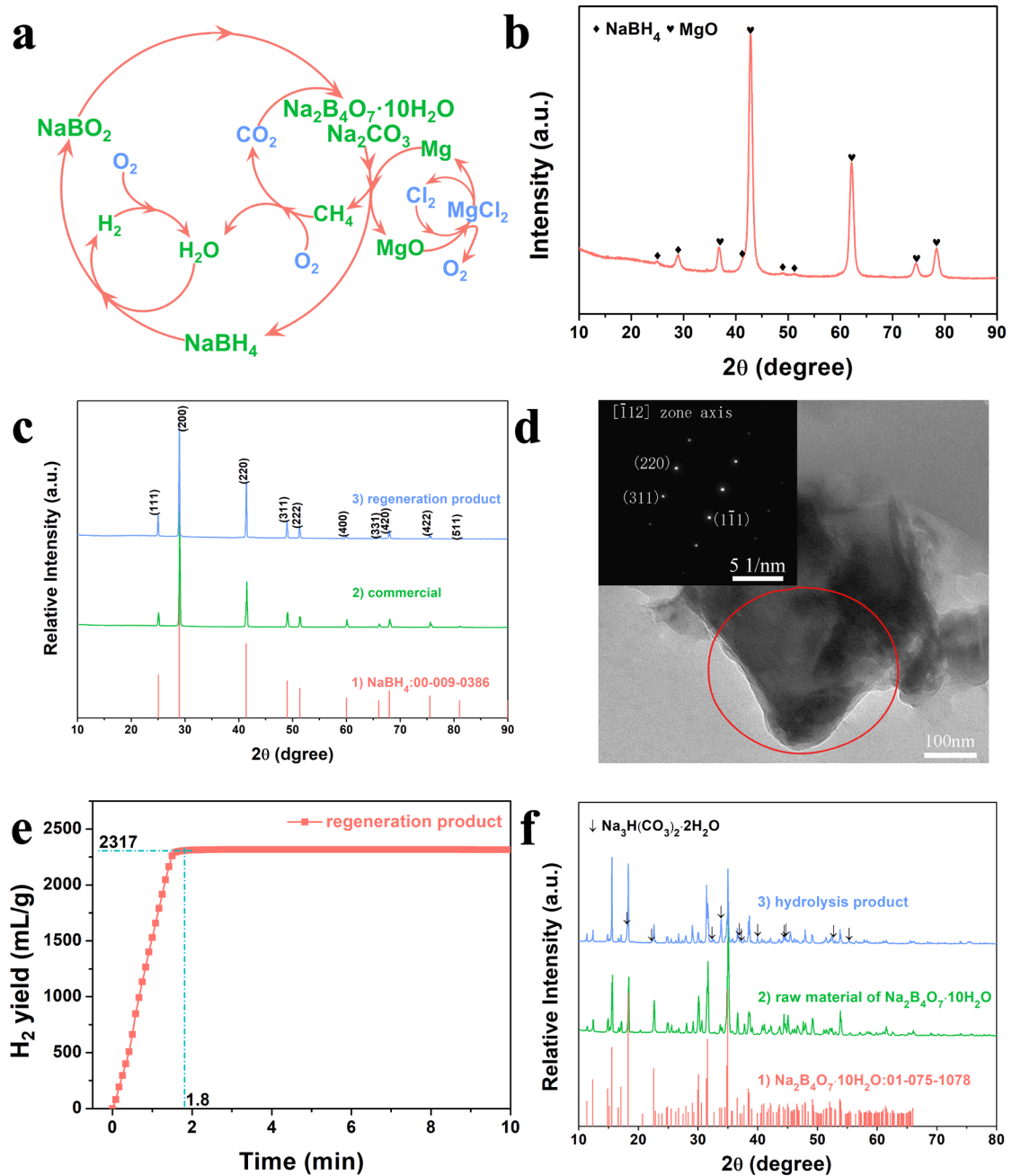


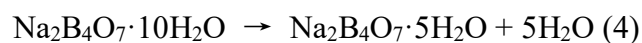
Fig. 1 (a) A closed system of NaBH₄ hydrolysis and regeneration. (b) XRD pattern of products obtained via ball milling a mixture of Mg, Na₂B₄O₇·10H₂O, and Na₂CO₃ in 24.75:1:1 molar ratio for 20 h at 1000 CPM. (c) XRD patterns of 1) standard PDF card of NaBH₄, 2) commercial and 3) synthesized NaBH₄. (d) TEM image and SAED pattern of synthesized NaBH₄. (e) Hydrolysis curve of the prepared NaBH₄ in 2 wt% CoCl₂ aqueous solution. (f) XRD patterns of 1) standard PDF card of Na₂B₄O₇·10H₂O, 2) raw Na₂B₄O₇·10H₂O, and 3) compounds obtained after hydrolytic aqueous

solution naturally dried up in air.

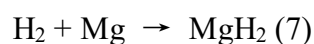
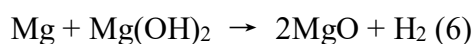
3.2 Reaction mechanism

To understand the reaction, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, Na_2CO_3 , and Mg mixtures were ball milled for relatively short periods. The XRD diffraction peaks of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ become invisible after 5 min milling, along with the appearance of diffraction peaks of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ (Fig. 2a), in agreement with FT-IR results (Fig. 2b(2) and Fig. S7). The actual formula of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ are $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 3\text{H}_2\text{O}$ and $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$, respectively, according to the chemical structures [24]. Hydrogen can be detected in this period from the MS of the gas atmosphere (Fig. S8). After 10 min of ball milling, the intensity of diffraction peaks of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ decreases significantly. As the milling increases to 30 min, XRD diffraction peaks of MgO become highly visible while those of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ and Na_2CO_3 almost disappear. Although the diffraction peaks of NaBH_4 are invisible, the B-H group can be detected by FT-IR (Fig. 2b(4)). The absorption bands of BO_3^{3-} ($1500\text{-}1300\text{ cm}^{-1}$) and BO_4^{5-} ($1150\text{-}950\text{ cm}^{-1}$) originally present in $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$, and of CO_3^{2-} ($1450\text{-}1400\text{ cm}^{-1}$, 877 cm^{-1}) originally present in Na_2CO_3 become very weak and then vanish completely from the spectra (Fig. 2b). As the milling time reaches 5 h, the (200) diffraction peak of NaBH_4 appears.

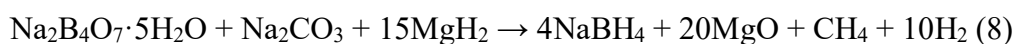
Considering the observation of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ and H_2 after 5 min, the first step of the reaction is assumed as follows:



Under the experiment conditions, the following reactions will subsequently occur [25, 26]:



With increasing milling time, NaBH₄, MgO, and also CH₄ (Fig. S8 and Fig. S9) were observed which is associated with this reaction:



The overall reaction equation is therefore can be expressed in the following equation:



This reaction is calculated to be favourable in thermodynamics ($\Delta G_{298\text{k}}^\circ = -1326.18$ kJ/mol of NaBH₄).

In this closed-loop regeneration (Fig. 1a), CH₄ can be collected and converted to CO₂, which is then used to produce Na₂CO₃. Mg can be regenerated via the commercial method, where MgO is first converted to MgCl₂ and Mg is obtained by electrolysis of MgCl₂.

MgH₂ was not observed in this study, probably because it was consumed *in-situ* due to its high activity. This is in agreement with a previous study where MgH₂ was proposed as an intermediate during NaBH₄ regeneration via ball milling NaB(OH)₄ and Mg [17]. The formation of methane is likely due to the reaction between Na₂CO₃ and

MgH₂ [27, 28]. H₂ was not in the overall reaction (eqn 9) but was observed by MS, which is due to the nature of gas-solid reaction between H₂ and Mg, where it is hard to achieve 100 % conversion.

To further elucidate the reaction mechanism, the ball milled products were characterized by solid-state ¹¹B magic-angle spinning (MAS) NMR (Fig. 2c). After 10 min of ball milling, only [B₄O₅(OH)₄]²⁻ is detected (Fig. 2c(2)). The resonance observed at ≈-13.4 ppm in Fig. 2c(3) after 30 min milling demonstrates the formation of intermediate H₂BOH [21, 29]. The reaction transformation of [B₄O₅(OH)₄]²⁻ is therefore proposed as shown in Fig. 2d. The unit of [B₄O₅(OH)₄]²⁻ contains two BO₄ tetrahedra and two BO₃ triangles as showed in Fig. 2d(1). The B-O bond (average bond length: 1.3683 Å) in BO₃ triangles is stronger than the one (average bond length: 1.4418 Å) in BO₄ tetrahedra [30]. Thus, the B-O in BO₄ tetrahedra preferentially breaks, and B forms bond with the H in MgH₂ and the O forms bond with Mg. It is reasonable to assume that three intermediates are formed (Fig. 2d(2-4)). Thermodynamically, Mg is more likely to bond with oxygen to form a more stable compound, MgO (ΔG_f^o of MgO: -569.3 kJ/mol oxygen; ΔG_f^o of B₂O₃: -398.1 kJ/mol oxygen) [31]. Therefore, B-O and Mg-H in the B-O-Mg-H intermediate break and the B-H and MgO are formed (Fig. 2d(2,4)). The breaking of the (B)-O-H (O bonded with sp² boron) in Fig. 2d(5) results into formation of intermediate “H₂BOH”, which is detected in NMR spectra (Fig. 2c(3)). According to the literature [21], B in “H₂BOH” is Lewis acidic and could accept H⁻ from MgH₂. As a result, “BH₄⁻” and MgO are generated. In addition, the “OH⁻” that is bonded with sp³ boron (Fig. 2d(3,4)), is substituted by H⁻ in MgH₂ forming “BH₄⁻”,

which agrees with previous studies [17].

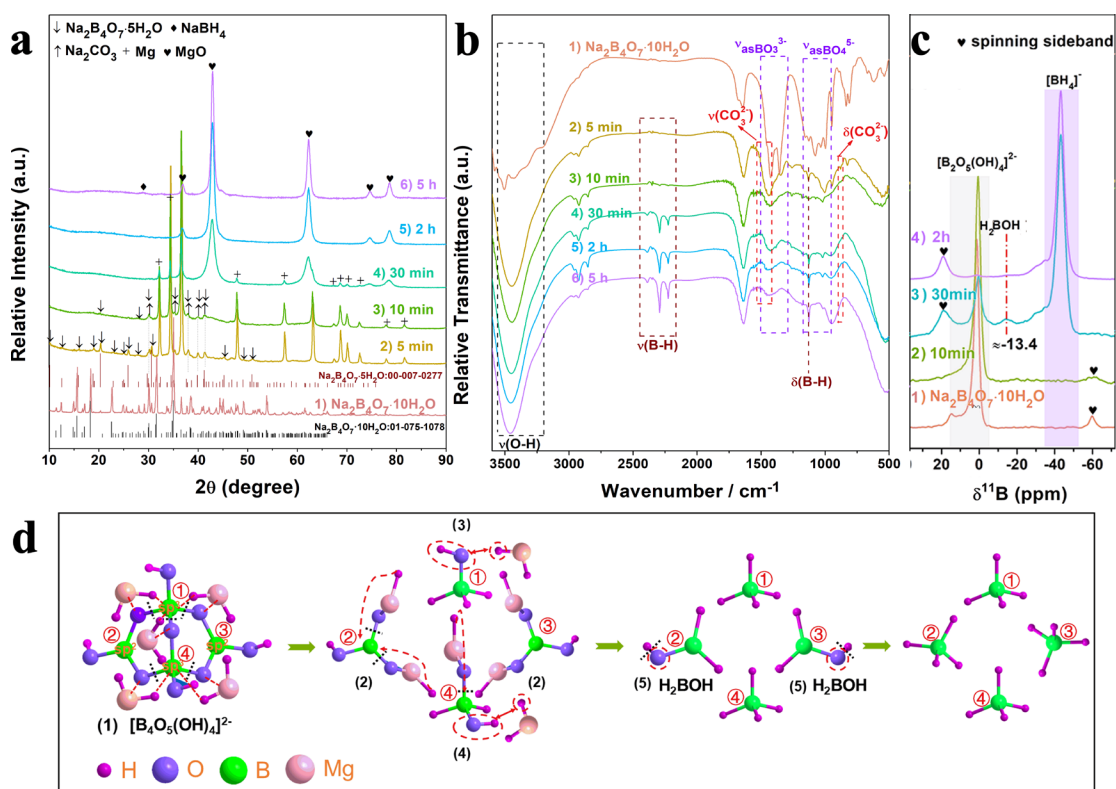


Fig. 2. (a) XRD patterns and (b) FT-IR spectra of 1) raw Na₂B₄O₇·10H₂O; products obtained after ball milling Mg, Na₂B₄O₇·10H₂O, and Na₂CO₃ mixtures (in 18:1:1 molar ratio) at 1200 CPM for different durations 2) 5 min, 3) 10 min, 4) 30 min, 5) 2 h and 6) 5 h. (c) Solid-state ¹¹B NMR spectra of 1) raw Na₂B₄O₇·10H₂O; products obtained after ball milling for different durations 2) 10 min, 3) 30 min, 4) 2 h. (d) Proposed reaction mechanism between Mg, Na₂CO₃, and Na₂B₄O₇·10H₂O to form NaBH₄.

3.3 Yield of NaBH₄

Efforts have been made to optimize the yield of NaBH₄ by ball milling CO₂ treated hydrolytic products (a mixture of Na₂B₄O₇·10H₂O and Na₂CO₃) with Mg. Fig. 3a shows the XRD patterns of the products obtained by ball milling Mg, Na₂B₄O₇·10H₂O, and Na₂CO₃ in a 18:1:1 molar ratio for different durations. After 2.5 h of ball milling,

the diffraction peaks of raw materials disappear, along with the appearance of strong diffraction peaks of MgO. Although the diffraction peaks of NaBH₄ are invisible, the typical BH₄ bands (2200-2400 and 1125 cm⁻¹) are detectable by FT-IR (Fig. 3b(1)), which indicates the formation of NaBH₄ after 2.5h ball milling. As milling time increases to 10h, the diffraction peaks assigned to Fe₂B become visible (Fig. 3a(3)). With further increase in milling time, the diffraction peaks of Fe₂B become stronger while the characteristic FT-IR bands of NaBH₄ become weaker. The FT-IR results indicate that the yield of NaBH₄ firstly increases and then decreases with the milling time (Fig. 3b). Iodometric analysis was carried to quantify NaBH₄ after its isolation from the ball-milled product. The relationship between the yield and milling time is consistent with FT-IR results (Fig. 3b, c), reflecting the fact that NaBH₄ is decomposed after long-time ball-milling. This is likely due to the reaction between NaBH₄ and Fe (peeling off the balls and jar after long-time ball-milling), as evidenced by the formation of more Fe₂B as milling time increases (Fig. 3a). The highest yield among the five durations for the mixture with 18:1:1 molar ratio is about 17.4% after 5 h of ball milling (Fig. 3c).

The impact of Mg loading on the yield was also studied (Fig. 3d). For 20h milling, the yield increased when more Mg was used, and it was ~46.9% for a molar ratio of 20.25:1:1 (Mg: Na₂B₄O₇·10H₂O: Na₂CO₃), and reached the maximum of 75.7% for a ratio of 24.75:1:1. The highest yield of 78.9% was obtained after 30 h of ball milling for the sample with 24.75:1:1 mole ratio (Fig. 3c). For this particular batch, the yield after 5 h (38.0%) is already much higher than that with 18:1:1, and the XRD diffraction

peaks of NaBH_4 are clearly visible (Fig. 3f). Yields can be improved by increasing the amount of Mg used, which is consistent with previous studies [10, 11, 14, 19, 31, 32]. With a high loading of Mg, powders do not stick to the jar and balls, resulting in better the ball-milling efficiency. In addition, more Mg leads to better contact among all the reactants resulting in favorable yield. Limited by the ball mill machine, only two milling speeds, 1000 and 1200 CPM, were tried, which proves that ball mill speed, ie energy, does impact the yield. Although the energy is higher at 1200 CPM, we fail to obtain better yields under any circumstances, especially for a low molar ratio (Fig. 3d). This is because more Fe peels off the balls and jar for small amount of Mg at high speed and promotes NaBH_4 decomposition (Fig. 3e).

We have also found that when $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ were ball milled simultaneously with Na_2CO_3 and Mg in a molar ratio of 0.6:0.4:1:22, NaBH_4 was also successfully synthesized (Fig. S10). Mg can also be replaced by Al or Ca to synthesize NaBH_4 (Fig. S11). More research is needed to optimize the yields of NaBH_4 from these reactions.

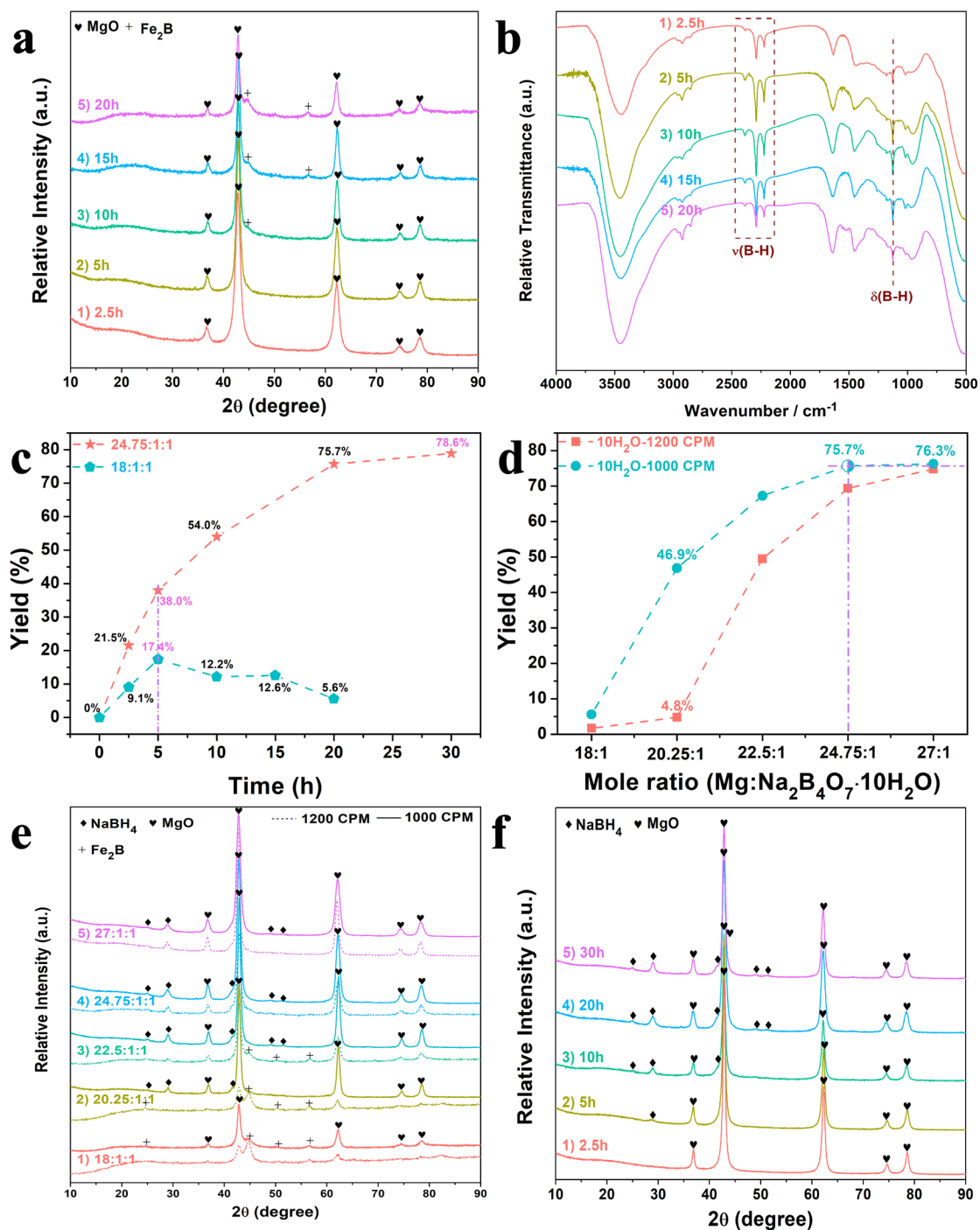


Fig. 3. (a) XRD patterns and (b) FT-IR spectra of the products obtained after ball milling Mg, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, and Na_2CO_3 mixtures (in 18:1:1 molar ratio) at 1000 CPM for different durations. (c) Yields of NaBH_4 with reactants in different molar ratios at 1000 CPM for different durations. (d) Yields of NaBH_4 and (e) XRD patterns of the products obtained after ball milling Mg and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in different molar ratios ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and Na_2CO_3 were fixed at 1:1 molar

ratio) for 20h at 1000 CPM and 1200 CPM, respectively. (f) XRD patterns of the products obtained via ball milling Mg, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, and Na_2CO_3 in a molar ratio of 24.75:1:1 at 1000 CPM for different durations.

4. Conclusions

In summary, we present a closed pathway for utilizing NaBH_4 for hydrogen storage. The regeneration of NaBH_4 can be achieved by ball milling its CO_2 treated hydrolytic product ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and Na_2CO_3) and Mg under ambient condition, with the yield being among the highest reported so far. This process outperforms the literature methods in several key aspects. First of all, the current yield is the best among the reported literatures [10, 14, 19, 33-35] (Table S1). Secondly, the direct use of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ avoids high temperatures (over 600°C [12]) required to dehydrate $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. Thirdly, this process does not need expensive MgH_2 , which is usually obtained by high-temperature reaction between Mg and H_2 . When comparing this method with reported process using MgH_2 , Na_2CO_3 and $\text{Na}_2\text{B}_4\text{O}_7$ [10], the cost of the raw materials in this method is reduced by 24-fold (Table S2). This indicates a promising pathway for large-scale application of NaBH_4 as a hydrogen carrier.

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