Effective synthesis of magnesium borohydride via B-O to B-H bond conversion

Yongyang Zhu, [ad] Shaoyang Shen, [a] Liuzhang Ouyang, *[ab] Jiangwen Liu, [a] Hui Wang, [a] Zhenguo Huang*[c], and Min Zhu[a]

a: School of Materials Science and Engineering, Guangdong Provincial Key Laboratory of Advanced Energy Storage Materials, South China University of Technology, Guangzhou, 510641, People's Republic of China.

b: China-Australia Joint Laboratory for Energy & Environmental Materials, Key Laboratory of Fuel Cell Technology of Guangdong Province, Guangzhou, 510641, People's Republic of China.

c: School of Civil and Environmental Engineering, University of Technology Sydney, Sydney, NSW, 2007, Australia. Email: zhenguo.huang@uts.edu.au

d: Institute of Resources Utilization and Rare Earth Development, Guangdong Academy of Sciences, Guangzhou, 510650, People's Republic of China.

* Author to whom correspondence should be addressed.

Liuzhang Ouyang, E-mail address: meouyang@scut.edu.cn Tel: 86-20-87114253, Fax: 86-20-87114253 and Zhenguo Huang (zhenguo.huang@uts.edu.au)

Abstract

Magnesium borohydride ($Mg(BH_4)_2$) is widely regarded as a promising hydrogen storage material due to its high capacity; however, it is still challenging to synthesize $Mg(BH_4)_2$ with low cost. Traditionally, $Mg(BH_4)_2$ has been mainly produced using other borohydride as the starting materials via exchange reactions. Herein, we report an economical method to synthesize $Mg(BH_4)_2$ by converting B-O bonds in widely available borates or boric acid to B-H. The borates or boric acid is ball-milled with MgH_2 under ambient conditions to form $Mg(BH_4)_2$ with high yield (>80%). $Mg(BH_4)_2$ was also successfully generated by reacting low-cost Mg with boric acid. Compared with previous approaches, this method avoids expensive boron sources such as $LiBH_4$, $NaBH_4$, and B_2H_6, and does not require high pressure H_2 gas and high temperatures, and therefore significantly reduces costs. This method could be an alternative to the current $Mg(BH_4)_2$ synthesis processes.

Keywords: magnesium borohydride, boron compound, magnesium hydride, hydrogen storage

Introduction

A significant part of the world's energy demand could be fulfilled by hydrogen [1]. However, market acceptance of hydrogen fuel cell technology-related products, such as vehicles and portable devices, has been hindered by several critical problems, especially the challenge in developing safe hydrogen storage solutions that are able to supply/release hydrogen efficiently [2]. In the search for suitable hydrogen storage materials, complex hydrides, especially light weight borohydrides, have received great attention due to their high gravimetric and volumetric hydrogen capacities [3, 4]. Notably, magnesium borohydride ($Mg(BH_4)_2$), with high volumetric (147-145 g H_2/L) and gravimetric (14.9 wt%) capacities of hydrogen, has been identified as one of the most promising candidates to supply hydrogen to the fuel cells. Based upon the correlation between the thermodynamic stability of metal borohydrides and the Pauling electronegativity of cation, $Mg(BH_4)_2$, with a temperate decomposition enthalpy change of -39 kJ/mol H_2, should have lower theoretical hydrogen desorption temperatures than most other borohydrides [5, 6]. However, $Mg(BH_4)_2$ requires high temperatures (>300 °C) for hydrogen evolution due to kinetic barriers [7-11], and the hydrogen release cannot be fully accomplished under 500 °C [12]. Meanwhile, $Mg(BH_4)_2$ shows poor reversibility under mild conditions. Apart from thermolysis, $Mg(BH_4)_2$ hydrolysis can be an attractive way for hydrogen release since it has appealing features such as a high density (12.8 wt%), fast kinetics, and mild reaction conditions. However, hydrolytic reaction leads to the formation of highly stable borate and it is very challenging to convert the strong B-O back to B-H bonds.

So far, several approaches have been developed to prepare $Mg(BH_4)_2$, mostly based on a metathesis reaction between alkali borohydrides ($LiBH_4$ or $NaBH_4$) and magnesium halides ($MgCl_2$ or $MgBr_2$) in a suitable solvent (eg. diethyl ether, tetrahydrofuran) [12, 13] or in a ball mill [14, 15]. For example, Černý *et al.* [13] successfully synthesized $Mg(BH_4)_2$ by heating a mixture of $LiBH_4$ and $MgCl_2$ in diethyl ether under reflux for 3 days with a yield of 30%. However, unsolvated $Mg(BH_4)_2$ was contaminated with LiCl, Li_2MgCl_4 or $LiBH_4$, owing to similar radius between Li^+ and Mg^{2+} and LiCl and $LiBH_4$ being soluble in the solvents [12, 13]. $NaBH_4$ was also reacted with $MgCl_2$ under the same conditions but with a low yield of < 5% [13]. The reaction efficiency was improved by mechanochemical activation of the mixture of $NaBH_4$ and $MgCl_2$ through ball milling, leading to a yield of > 50% [14]. Pure $Mg(BH_4)_2$ was then obtained through desolvation. Note that dry mechanochemical milling $NaBH_4$ and $MgCl_2$ led to the formation of NaCl and $(Na,Mg)BH_4$ solid solution [16], which made it difficult to extract pure $Mg(BH_4)_2$. The key disadvantage of all these methods is the high cost of $LiBH_4$ or $NaBH_4$ making mass production less competitive.

$Mg(BH_4)_2$ was also produced by annealing MgB_2 under 90 MPa H_2 and at 390 °C for 72 h [17], or ball milling under 10 MPa H_2 for 100 h [18], or under 35 MPa H_2 for 50 h [19]. The high pressure H_2, high temperatures and long reaction time lead to high energy consumption, high cost, and hazards. Another synthesis is based on additive reaction of magnesium hydrides (MgH_2), magnesium alkyls or magnesium alkoxides with diborane (B_2H_6) or its derivatives [14, 20-22]. Owing to extreme flammability, high toxicity and high cost of B_2H_6 and its derivatives, these reactions are difficult to be employed to prepare $Mg(BH_4)_2$ in large scale, although relatively high yield and purity can be achieved.

Herein, we present a new approach for the synthesis of unsolvated $Mg(BH_4)_2$ with a high yield and low cost. It is a mechanochemical solid-state reaction between borate/boric acid and Mg/MgH_2, which converts B-O bond to B-H. Compared with previously reported procedures which require expensive boron source (eg. alkali borohydrides, B_2H_6 or its derivatives), high temperatures, and/or high-pressure H_2, this new approach operates under mild conditions and utilizes low-cost boron sources, which is suitable for cost-effective large-scale production of $Mg(BH_4)_2$. As the raw materials are composed of only Mg, O, B and H elements, common impurities observed in previous methods can be avoided. The by-products (oxides) and remaining reactants can be completely removed during purification, leading to high-purity $Mg(BH_4)_2$.

2 Experimental

2.1 Chemicals

Starting materials such as MgH_2 (≥99%), $MgCl_2$ (99%) and B_2O_3 (99.9%) were purchased from Aladdin. Mg (99.8%), $B(OH)_3$ (≥99.5%) and $Mg(BO_2)_2$ (98%) were purchased from Sigma-Aldrich, General-Reagent, and Shanghai Yuanye Bio-Technology, respectively. All these compounds were used as-received without any further treatment. Expendable graphite (XFNANO) in a graphite pot was treated in a muffle furnace at 970 °C for 1 min, and then cooled in air to obtain expanded graphite (EG). The morphology of the expendable and expanded graphite is shown in Fig. S1. Diethyl ether (Et_2O, AR, Guangzhou Chemical Reagent Factory) and H_2SO_4 (Aladdin, GR) were used for purification and quantification of $Mg(BH_4)_2$. Et_2O was distilled over sodium to remove water before use.

2.2 Synthesis of $Mg(BH_4)_2$

The experimental procedure is illustrated in Fig. 1. Firstly, totally 1 g of MgH_2 (or Mg) and B_2O_3 (or $B(OH)_3$, or $Mg(BO_2)_2$) with different molar ratios and 50 g of steel balls with two different sizes were put in a stainless steel jar in an argon filled glove box (MIKROUNA, China) with <0.1 ppm O_2 and H_2O. Mechanochemical reaction was conducted by milling the mixture in a planetary mill (QM-3SP4, Nanjing, China) at 500 revolutions per minute (rpm) or a shaker mill (QM-3C, Nanjing, China) at 1000 cycles per minute (cpm). The ball milling was conducted by alternating 0.5 h milling and 0.5 h rest to avoid excessive heating of the sample. Effects of molar ratios between reactants and milling time on the yield were investigated. To improve the yield of $Mg(BH_4)_2$, EG or $MgCl_2$ was tried as an additive in some experiments. After ball milling, 20 mL of dry Et_2O was added to the as-milled mixture to extract $Mg(BH_4)_2$. The $Mg(BH_4)_2$ solution and undissolved solids were separated by polytetrafluoroethylene membrane (0.45 μm in pore size). $Mg(BH_4)_2$ filtrate was then condensed under vacuum through a Schlenk line resulting in a viscous liquid. Finally, the solvated $Mg(BH_4)_2$ was heated to 200 °C for 24 h to remove ether. Resulting solid was ground and heat treated again to obtain desolvated $Mg(BH_4)_2$.

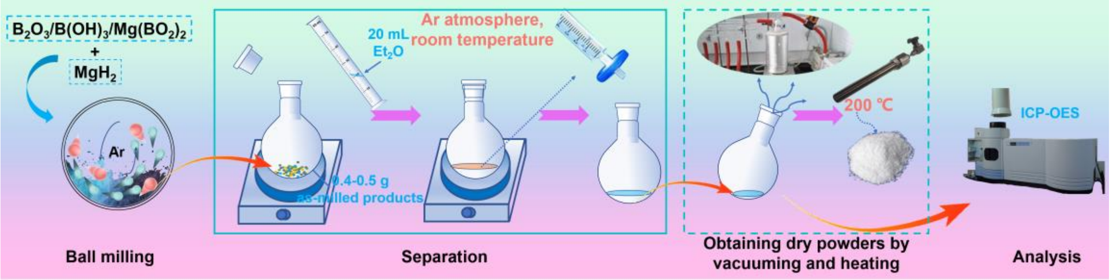

Fig. 1 Schematics of the experimental procedure.

2.3 Quantification of $Mg(BH_4)_2$

About 10 mL H_2O was added slowly to hydrolyze solvated $Mg(BH_4)_2$. Slowly with caution, 4 mol·L^{-1} H_2SO_4 solution was then added dropwise to dissolve the hydrolytic products (such as magnesium borates and magnesium hydroxide) and unhydrolyzed solvated $Mg(BH_4)_2$ [23]. The Mg concentration was determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Optima 8300). Based on the ICP-OES results, the mass of $Mg(BH_4)_2$ was calculated. The equation for the calculation of $Mg(BH_4)_2$ yield is as follows:

$$\text{Yield} = [(\text{obtained } Mg(BH_4)_2 \text{ mass})/(\text{theoretical } Mg(BH_4)_2 \text{ mass})] \times 100\% \quad (1)$$

Theoretical mass of $Mg(BH_4)_2$ was calculated based on the amount of B in the starting materials, meaning that 1 mol B_2O_3 or $Mg(BO_2)_2$ produces 1 mol $Mg(BH_4)_2$ and 1 mol $B(OH)_3$ yields 0.5 mol $Mg(BH_4)_2$.

2.4 Characterization

Various techniques are employed to characterize the as-milled products, including Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), solid-state ^{11}B nuclear magnetic resonance (NMR), and scanning electron microscope (SEM). More details can be found in previous studies [24, 25]. FTIR measurements were performed on a Nicolet IS50 spectrometer using the transmission mode in the region of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. $Mg(BH_4)_2$ powders were mixed with dry KBr powders (with a weight ratio of 1:99) in a glove box and then pressed into pellets under 20 MPa. The pellets were exposed to air for a short time (about 15 s) during measurement. Differential scanning calorimetry (DSC) was conducted on Setaram

SENSYS Evolution under Ar between 40 and 450°C with a heating rate of 5 K min^{-1}.

3 Results and discussion

3.1 Synthesis of $Mg(BH_4)_2$ by converting B-O to B-H

One key barrier in large-scale application of $Mg(BH_4)_2$ lies in its cost. Herein we developed an efficient method to synthesize $Mg(BH_4)_2$ based on a simple reaction where B-O bonds in low-cost starting materials were successfully converted to B-H through ball milling (Figs. 1, 2a). XRD patterns (Fig. 2b) and FTIR spectra (Fig. 2c) were collected on powders obtained after ball milling MgH_2-B_2O_3 (in a 4.5:1 molar ratio), MgH_2-$B(OH)_3$ (in a 7.785:2 molar ratio), and MgH_2-$Mg(BO_2)_2$ (in a 4.5:1 molar ratio) for 15 h in a shaker mill. After ball milling, the diffraction peaks of MgH_2 and boron compounds are nearly absent in all the systems, along with the appearance of strong diffraction peaks of MgO (Fig. 2b). The diffraction peaks of $Mg(BH_4)_2$ are invisible due to the poor crystallinity of the formed $Mg(BH_4)_2$ (Fig. 2b(1-3)), similar to previous reports where ball milling led to the formation of amorphous $Mg(BH_4)_2$ [26-28]. The characteristic IR bands of $Mg(BH_4)_2$ are highly visible in the FTIR spectra (Fig. 2c(1-3)), in particular the stretching and deformation IR bands of B-H at 2150-2400 cm^{-1} and 1100-1300 cm^{-1}, respectively [14]. The resonance at around -42 ppm in ^{11}B NMR spectra further confirms the existence of $Mg(BH_4)_2$ (Fig. S2) [29, 30]. Thus, B-H bonds have been successfully produced by ball-milling MgH_2 with B_2O_3, or $B(OH)_3$, or $Mg(BO_2)_2$ under ambient condition. The reaction conditions are milder compared with previous studies where $Mg(BH_4)_2$ was synthesized via ball milling MgB_2 under 10-35 MPa H_2 [18, 19] or annealing MgB_2 at 390 °C under 90 MPa H_2

[17].

Pure $Mg(BH_4)_2$ was isolated from the as-milled products by purification and desolvation, and its identity was studied using FTIR and XRD analysis. Thermal anneal can effectively remove diethyl ether, as evidenced by the absence of the FTIR bending vibration (at 2800 cm^{-1}) of C-H (Fig. 2d(3)). The FTIR bands at 2150-2400 cm^{-1} and 1100-1300 cm^{-1} correspond to the B-H stretching and deformation of pure $Mg(BH_4)_2$, respectively, in good agreement with those of commercial $Mg(BH_4)_2$ (Fig. 2d) [14]. The desolvated $Mg(BH_4)_2$ displays a XRD pattern similar to that of commercial $Mg(BH_4)_2$ (Fig. 2e), which is consistent with previous studies [28]. The unsolvated $Mg(BH_4)_2$ was also analyzed by DSC measurement (Fig. S3). DSC curve of the isolated $Mg(BH_4)_2$ is very similar to the reported [31], indicating the formation of $Mg(BH_4)_2$. According to the products and starting materials, the conversion reactions can be expressed in the following equations:

$$4MgH_2 + B_2O_3 \rightarrow Mg(BH_4)_2 + 3MgO \quad (2)$$

$$7MgH_2 + 2B(OH)_3 \rightarrow Mg(BH_4)_2 + 6MgO + 6H_2 \quad (3)$$

$$4MgH_2 + Mg(BO_2)_2 \rightarrow Mg(BH_4)_2 + 4MgO \quad (4)$$

The excess amount of MgH_2 used is 12.5% based on reaction equation (2-4). The excess amount of MgH_2 is calculated based upon the following reactions:

$$\text{Excess amount}=\frac{actual\ molar\ ratio\ \left(\frac{MgH2}{boron\ compound}\right)-stoichiometic\ ratio\left(\frac{MgH2}{boron\ compound}\right)}{stoichiometic\ ratio\left(\frac{MgH2}{boron\ compound}\right)}\times 100\%$$

(5)

In Fig. 2c, the intensities of the characteristic FTIR bands of $Mg(BH_4)_2$ obtained using

$B(OH)_3$ and $Mg(BO_2)_2$ are much weaker than those when B_2O_3 was used, which indicates that B_2O_3 are more conducive to the formation of $Mg(BH_4)_2$. This agrees with quantitative results (Fig. 2f), where B_2O_3 leads to the highest yield of 72.6%. Based on reaction equation (2-4), the B:O ratio in B_2O_3 (2:3) is higher than those in $B(OH)_3$ (1:3) and $Mg(BO_2)_2$ (1:2), which means for the same amount of B, more MgO will be formed during the reactions in the case of $B(OH)_3$ and $Mg(BO_2)_2$. The thicker layers of MgO slows down or even blocks mass transfer during the reaction, affecting the formation of $Mg(BH_4)_2$. Indeed, stronger MgO XRD peaks are observed when $B(OH)_3$ and $Mg(BO_2)_2$ were used (Fig. 2b).

To further reduce the cost, low-cost Mg instead of MgH_2 and $B(OH)_3$ as the hydrogen source were used. $Mg(BH_4)_2$ could be produced by ball milling Mg and $B(OH)_3$ in a 8.44:2 molar ratio for 20 h. The IR vibration of the B-H is visible (Fig. S4a), but the intensities are low, indicating a low yield of $Mg(BH_4)_2$ (0.14%). This is likely due to the low reactivity of Mg compared with MgH_2, and also a low ball-milling efficiency as evidenced by serious agglomeration of milled products (Fig. S5) and abrasion (Fe peeling off the balls and jar, Fig. S4b). To improve the milling efficiency, milling additives (EG and $MgCl_2$) were introduced. Although additives reduced Fe peeling off the jar and balls, the improvement in yield of $Mg(BH_4)_2$ was not obvious (Fig. S6). This is likely because EG and $MgCl_2$ decrease effective contact between Mg and $B(OH)_3$, and the oxygen containing group on EG also reacts with Mg. Efforts (discussed in later section) were therefore made to optimize the yield of $Mg(BH_4)_2$ by ball-milling B_2O_3 with MgH_2.

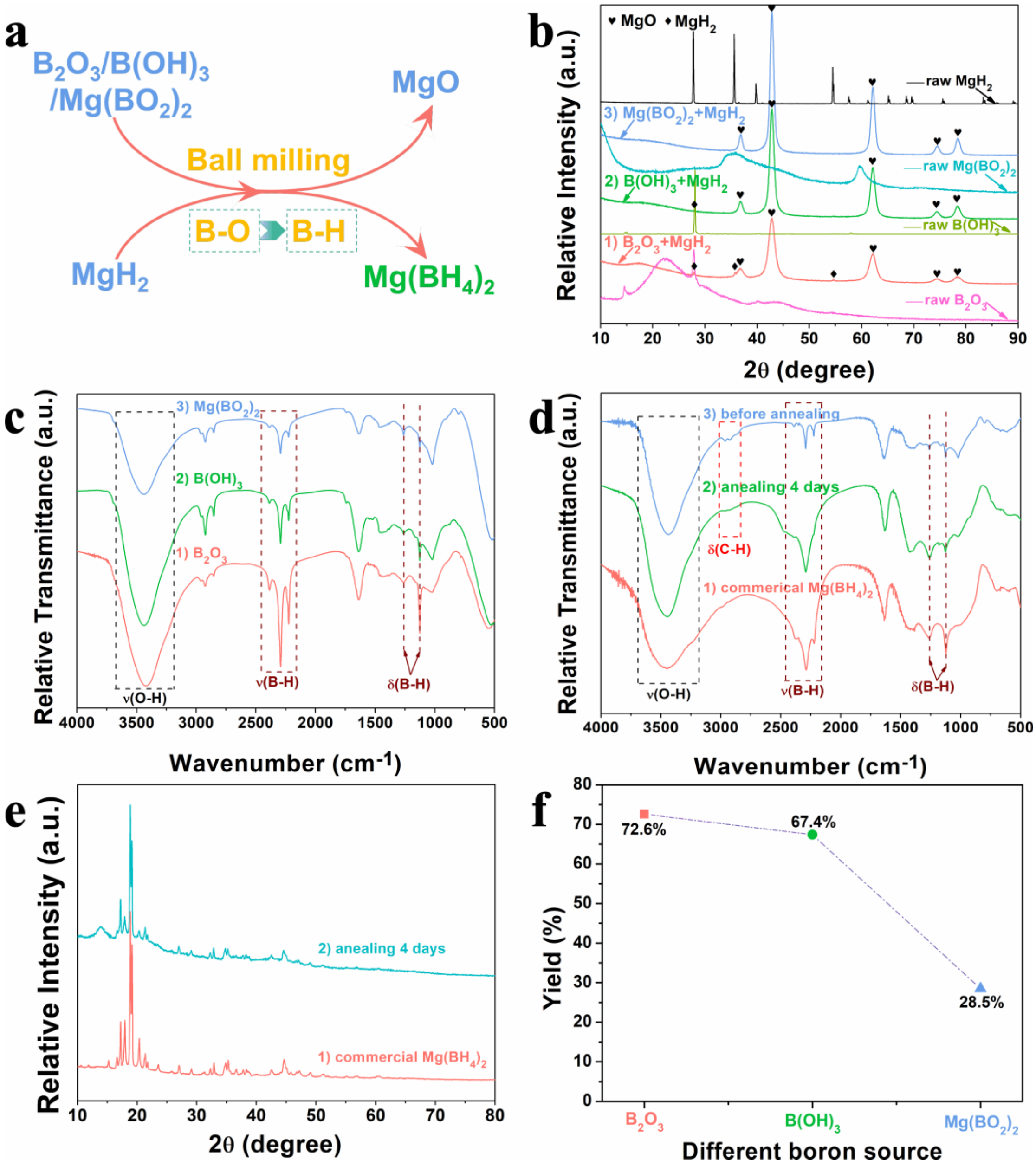

Fig. 2 (a) Schematics of synthesis by ball milling. (b) XRD patterns, (c) FTIR spectra of the products obtained via ball milling a mixture of 1) MgH_2 and B_2O_3 in a 4.5:1 molar ratio, 2) MgH_2 and $B(OH)_3$ in a 7.785:2 molar ratio and 3) MgH_2 and $Mg(BO_2)_2$ in a 4.5:1 molar ratio for 15 h. (d) FTIR spectra of 1) commercial $Mg(BH_4)_2$, 2) isolated product after annealing for 4 days, and 3) solvated product (before annealing). (e) XRD patterns of 1) commercial $Mg(BH_4)_2$ and 2) annealed product. f) Yields of $Mg(BH_4)_2$.

3.2 Yield of $Mg(BH_4)_2$

Based on previous reports that excess amount of MgH_2 is needed to improve the $NaBH_4$ yield [25, 32-34], 25 % more MgH_2 over the stoichiometric ratio (4:1) was loaded into reactions. Fig. 3a shows the XRD diffraction patterns of the as-milled products obtained after ball milling MgH_2 and B_2O_3 in a 5:1 molar ratio for various durations. After 1.25 h milling, the XRD diffraction peaks of B_2O_3 disappeared and the diffraction peaks of MgO appeared. Although the characteristic XRD peaks of $Mg(BH_4)_2$ were invisible, the FTIR bands of $Mg(BH_4)_2$ (2150-2400 cm^{-1}, 1100-1300 cm^{-1}) became highly visible, which indicates the formation of $Mg(BH_4)_2$ after 1.25 h milling (Fig. 3b (1)) [14]. The B-H stretching (2150-2400 cm^{-1}) and deformation (1100-1300 cm^{-1}) bands became stronger with increase in milling time [14]. The broad humps at 15-20° corresponding to amorphous $Mg(BH_4)_2$ also became stronger with longer ball milling (Fig. 3a). The as-milled products were purified by dissolution, filtration, and drying. The isolated dry $Mg(BH_4)_2$ product was then hydrolyzed in H_2O, followed by the addition of H_2SO_4 solution to dissolve the hydrolytic products and unhydrolyzed solvated $Mg(BH_4)_2$ [23]. The Mg concentration in the aqueous solution was determined using ICP-OES to quantify $Mg(BH_4)_2$, which is detailed in Experimental Section. The yield of $Mg(BH_4)_2$ increased quickly with milling time, and reached ~62.8% in 2.5 h (Fig. 3c). With the prolonged ball milling, the increase in yield slowed down. The yield reached 81.4% after 20 h of milling (Fig. 3c).

Considering the starting materials, B_2O_3 is low-cost so the cost of $Mg(BH_4)_2$ largely depends on the amount of MgH_2 used. The yield of $Mg(BH_4)_2$ increased when more MgH_2 was used, and reached 82.3% for a molar ratio of 5.5:1 (MgH_2:B_2O_3) (Fig.

3d). MgH_2 supplies H^- and Mg^{2+}, and high loading benefits mass transfer required during the reaction. However, on a per gram MgH_2 basis, yield of $Mg(BH_4)_2$ firstly increased and then decreased with increasing amounts of MgH_2, as shown in Fig.3d. Therefore, the optimal molar ratio of MgH_2 to B_2O_3 is around 4.5:1.

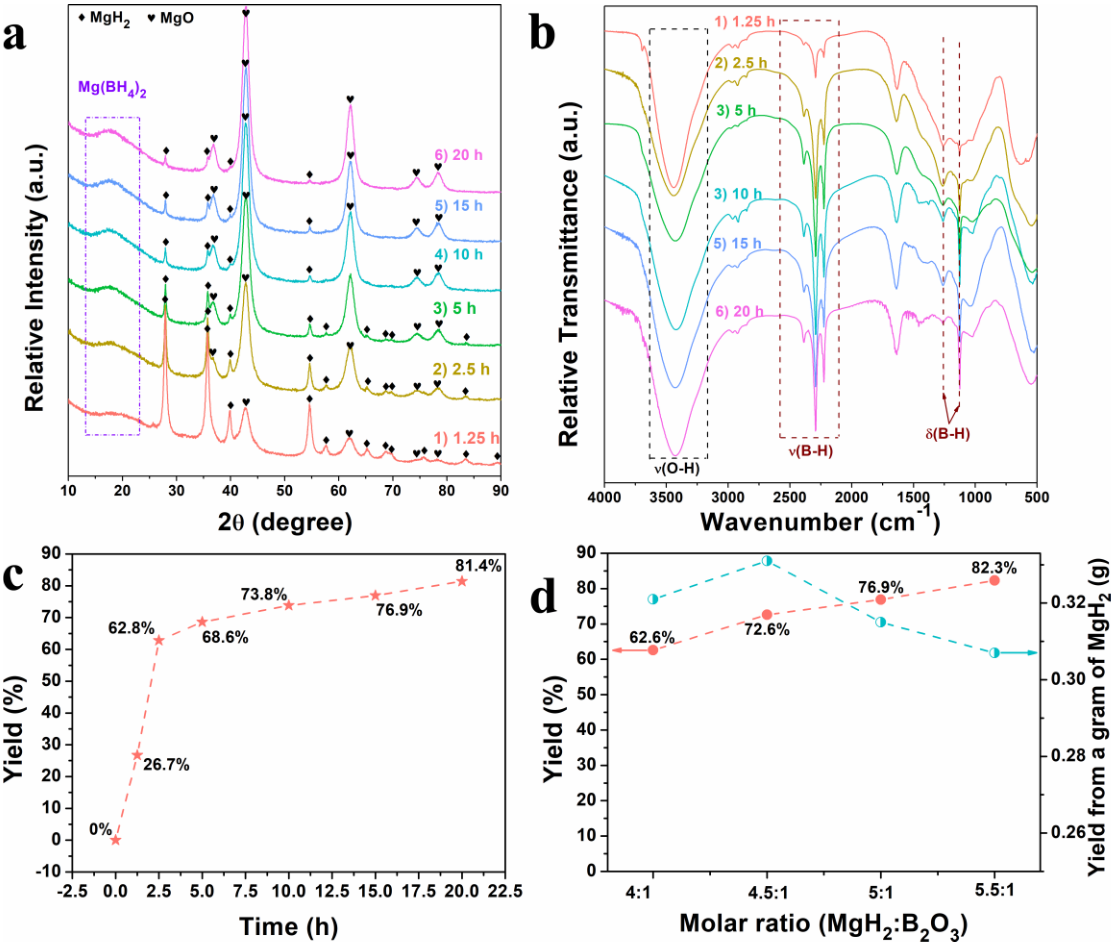

Fig. 3 (a) XRD patterns, (b) FTIR spectra, and (c) yield of $Mg(BH_4)_2$ obtained after ball milling MgH_2 and B_2O_3 mixtures (in a 5:1 molar ratio) for different durations using a shaker mill. (d) The correlation of yields with molar ratios after ball milling for 15 h.

We also investigated the effects of milling modes on the yield. A planetary mill (PM) was also tried since it enables higher materials loading, and therefore potentially larger outputs. Limited by the machine, milling was conducted at rotation speed of 500 rpm. The shaker mill (1000 cpm) is more effective in promoting the $Mg(BH_4)_2$

formation than the planetary mill, as evidenced by the stronger XRD peaks of MgO (Fig. 4a) and stronger FTIR peaks of $Mg(BH_4)_2$ (Fig. 4b). The improvement is likely associated with the energy provided by ball milling. The planetary mill with lower rotation speed supplies lower energy (in both shearing and impact modes), while the shaker mill generates mainly impact force with high energy. In addition, impact mode can help to break up MgO formed on the surface and consequently facilitate better contact between B_2O_3 and MgH_2. The yields of $Mg(BH_4)_2$ by the shaker mill are between 70% and 85% (Fig. 3d and Fig. 4c). In contrast, the $Mg(BH_4)_2$ yield by means of the planetary mill is less than 5% (Fig. 4c). As the planetary milling increased to 45 h, the yield of $Mg(BH_4)_2$ increased significantly and reached about 50% (Fig. 4c). This is consistent with the XRD and FTIR results where the intensity of XRD peaks of MgH_2 decreased significantly and stronger FTIR bands of $Mg(BH_4)_2$ appeared.

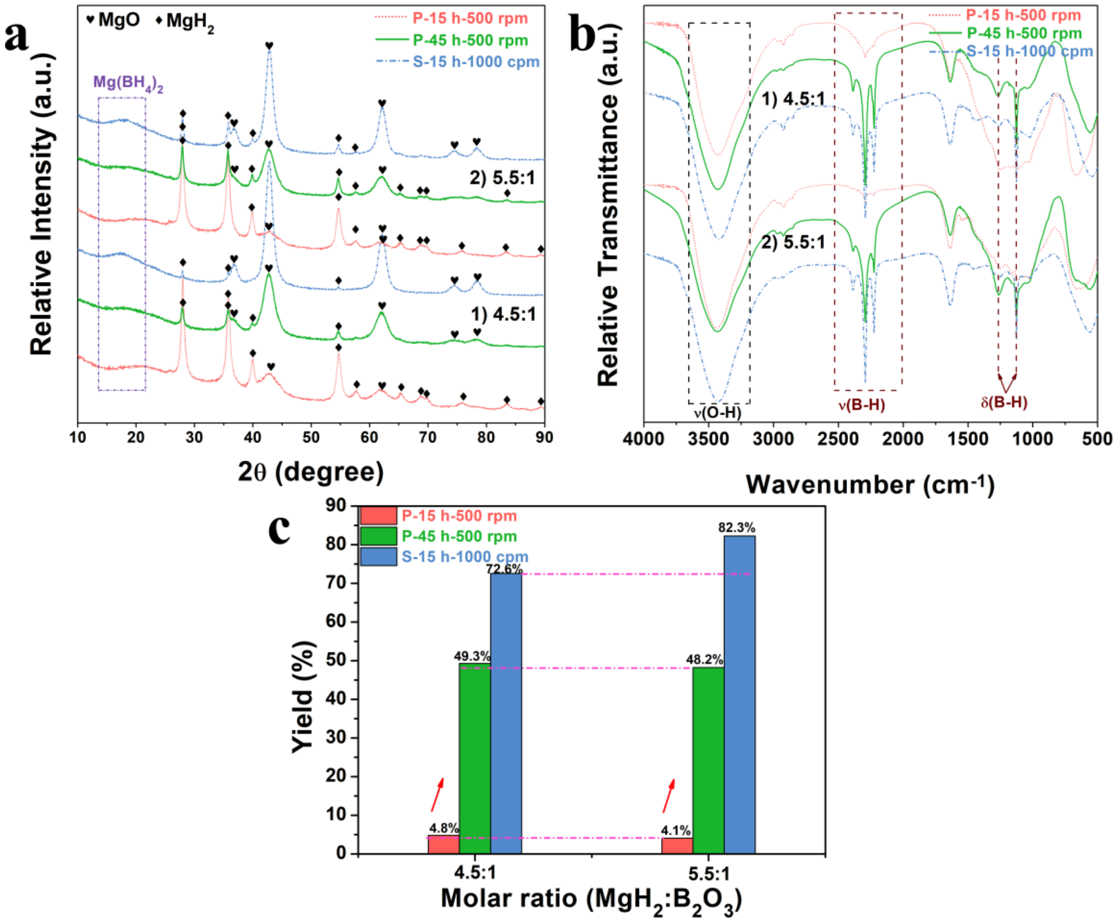

Fig. 4 (a) XRD patterns, (b) FTIR spectra, and c) yields of $Mg(BH_4)_2$ obtained after ball milling MgH_2 and B_2O_3 (in 4.5:1 or 5.5:1 molar ratio) for 15 h or 45 h at 500 rpm using a planetary mill, and for 15 h at 1000 cpm in a shaker mill.

3.3 Reaction Mechanism

We attempted to understand the reaction mechanism by ball milling MgH_2 and B_2O_3 for different periods. The XRD peaks of B_2O_3 became invisible after 10 min, whereas a peak at ~26° likely associated with intermediates appeared (Fig. 5a(2)). With the extension in milling, the XRD peaks of MgH_2 became weaker, while those of MgO grew stronger (Fig. 5a). This is consistent with the FTIR results (Fig. 5b) where the FTIR bands of MgH_2 (500-750 cm^{-1}) and B-O (780 cm^{-1}, 1190 cm^{-1}, 1460 cm^{-1}) became weaker with the increase in ball-milling time, while the intensity of B-H in $Mg(BH_4)_2$ (2150-2400 cm^{-1}, 1100-1300 cm^{-1}) increased continuously [14, 35, 36]. The O-H bands at 3400 cm^{-1} observed in all the FTIR spectra are due to H_2O adsorbed from air on the pellets surface during measurements (Fig. 2c,d, Fig. 3b, Fig. 4b, and Fig. 5b).

Since XRD and FTIR fail to identify the intermediate, solid-state ^{11}B magic-angle spinning (MAS) NMR analysis was used to analyze the milled products. The intensity of resonance corresponding to B_2O_3 (13 ppm) decreased with time (Fig. 5c). For products milled for 30 min (Fig. 5c(2)) and 2 h (Fig. 5c(3)), the resonance at around -13.8 ppm can be assigned to an intermediate $[BOH_2]^-$ [24, 37, 38] and the one at -41.9 ppm to $[BH_4]^-$ [29, 30]. Hydrogen has weaker electron withdrawing capability than oxygen, which therefore leads to higher electron cloud density around boron (B), causing stronger shielding effect and upfield chemical shift (δ). The upfield shift from 13 ppm for B_2O_3 to -13.8 ppm for $[BOH_2]^-$, and then to -41.9 ppm for $[BH_4]^-$ indicates the stepwise transformation from B-O to B-H bond. Based upon the XRD, FTIR, and NMR results, it can be deduced that "-B-O-B-" in B_2O_3 firstly breaks, and B then bonds with H in MgH_2 to form B-H and O bonds with Mg leading to "B-O-Mg-H" (Fig. 5d). The B-O and Mg-H bonds in "B-O-Mg-H" then break, leading to MgO and B-H, since MgO is more stable than B_2O_3 ($\Delta G_f°$ of B_2O_3: -398.1 kJ mol^{-1} oxygen; $\Delta G_f°$ of MgO: -569.3 kJ mol^{-1} oxygen). This is why $[BOH_2]^-$ was observed. Finally, O^{2-} in $[BOH_2]^-$ is replaced by two H^- from MgH_2 forming $Mg(BH_4)_2$ and MgO.

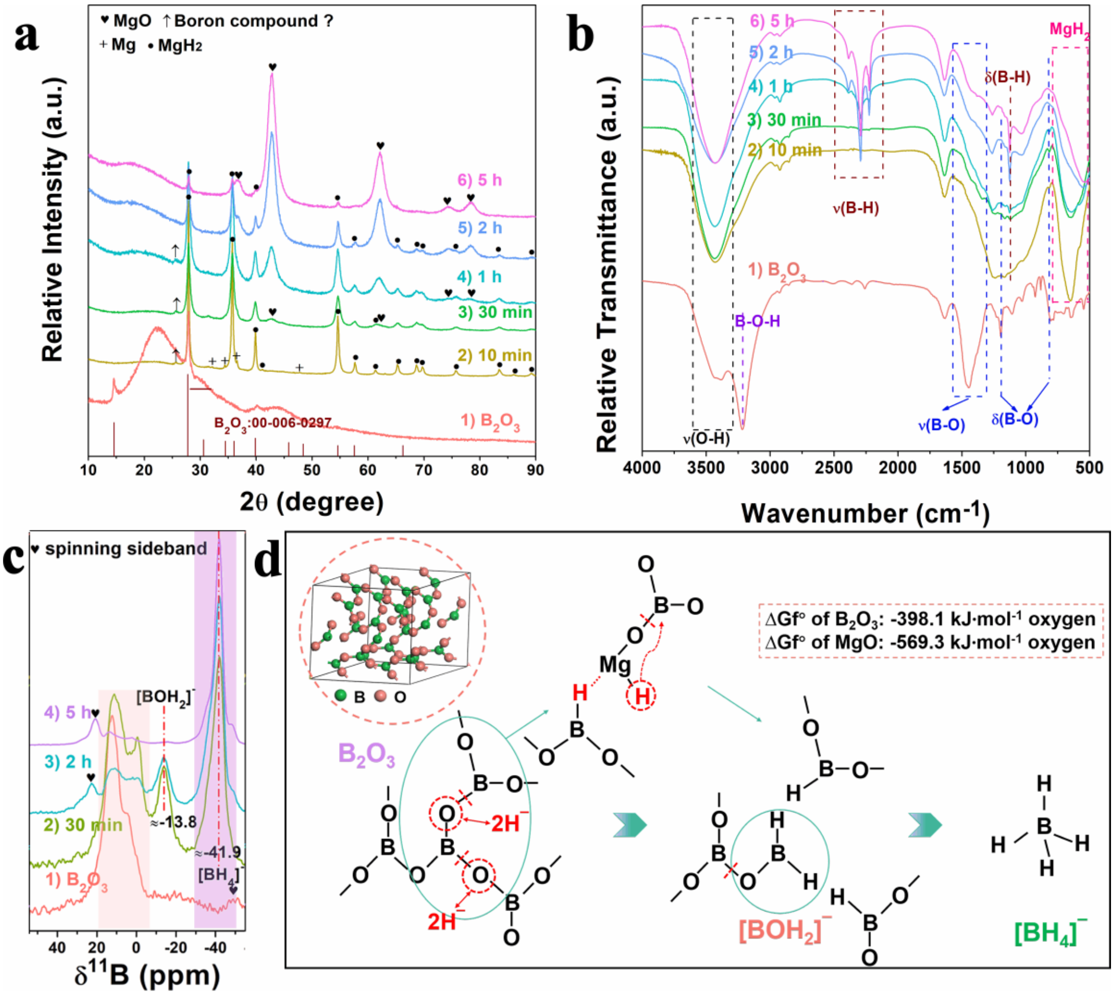

Fig. 5 (a) XRD patterns, (b) FTIR spectra, and (c) solid-state ^{11}B NMR spectra of B_2O_3 and the products obtained after ball milling MgH_2 and B_2O_3 (in a 4:1 molar ratio) for different durations using a shaker mill. (d) The proposed mechanism for the conversion of B-O bonds to B-H.

4. Conclusions

Herein, we report a cost-effective method to produce $Mg(BH_4)_2$ via ball milling borates/boric acid-MgH_2 mixtures under ambient conditions. A high $Mg(BH_4)_2$ yield of 82.3% was achieved. $Mg(BH_4)_2$ was also successfully generated by using low-cost Mg to react with $B(OH)_3$. The method is highly advantageous in terms of cost compared with reported methods where expensive borohydrides or boranes were used as the source of boron. Furthermore, the reaction conditions are quite mild in comparison with high temperatures and/or high pressure H_2 commonly used in most literature studies. This newly developed synthesis could be suitable for large-scale production of $Mg(BH_4)_2$ and promotes its wide application for hydrogen storage and as raw materials in chemical synthesis.

Acknowledgement

This work was financially supported by the Foundation for Innovative Research Groups of the National Natural Science Foundation of China (No. NSFC51621001). Z.H. acknowledges financial support from the Australian Research Council's Future Fellowship (project number FT190100658).

References

[1] L. Schlapbach, Z. A, Hydrogen-storage materials for mobile applications, Nature 414 (2001) 353-358. https://doi.org/10.1038/35104634.

[2] P. Jena, Materials for hydrogen storage: past, present, and future, J. Phys. Chem. Lett. 2 (2011) 206-211. https://doi.org/10.1021/JZ1015372.

[3] G. Zhang, D. Morrison, G. Bao, H. Yu, C.W. Yoon, T. Song, J. Lee, A.T. Ung, Z. Huang, An amine–borane system featuring room-temperature dehydrogenation and regeneration, Angew. Chem. Int. Ed. 60 (2021) 11725-11729. https://doi.org/10.1002/ANIE.202017302.

[4] Z. Huang, S. Wang, R.D. Dewhurst, N.V. Ignat'Ev, M. Finze, H. Braunschweig, Boron: Its role in energy-related processes and applications, Angew. Chem. Int. Ed. 59 (2020) 8800-8816. https://doi.org/10.1002/ANIE.201911108.

[5] Y. Nakamori, H. Li, K. Miwa, S.I. Towata, S.I. Orimo, Syntheses and hydrogen desorption properties of metal-borohydrides $M(BH_4)_n$ (M=Mg, Sc, Zr, Ti, and Zn; n=2–4) as advanced hydrogen storage materials, Mater. Trans. 47 (2006) 1898-1901. https://doi.org/10.2320/MATERTRANS.47.1898.

[6] Y. Nakamori, H.W. Li, K. Kikuchi, M. Aoki, K. Miwa, S. Towata, S. Orimo, Thermodynamical stabilities of metal-borohydrides, J. Alloys Compd. 446-447 (2007) 296-300. https://doi.org/10.1016/J.JALLCOM.2007.03.144.

[7] O. Zavorotynska, A. El-Kharbachi, S. Deledda, B.C. Hauback, Recent progress in magnesium borohydride $Mg(BH_4)_2$: Fundamentals and applications for energy storage, Int. J. Hydrogen Energy, 41 (2016) 14387-14403. https://doi.org/ 10.1016/J.IJHYDENE.2016.02.015 .

[8] O. Zavorotynska, S. Deledda, B.C. Hauback, Kinetics studies of the reversible partial decomposition reaction in $Mg(BH_4)_2$, Int. J. Hydrogen Energy, 41 (2016) 9885-9892. https://doi.org/ 10.1016/j.ijhydene.2016.02.153.

[9] I. Saldan, C. Frommen, I. Llamas-Jansa, G.N. Kalantzopoulos, S. Hino, B. Arstad, R.H. Heyn, O. Zavorotynska, S. Deledda, M.H. Sørby, H. Fjellvåg, B.C. Hauback, Hydrogen storage properties of γ–$Mg(BH_4)_2$ modified by MoO_3 and TiO_2, Int. J. Hydrogen Energy, 40 (2015) 12286-12293. https://doi.org/ 10.1016/j.ijhydene.2015.07.082.

[10] O. Zavorotynska, S. Deledda, J.G. Vitillo, I. Saldan, M.N. Guzik, M. Baricco, J.C. Walmsley, J. Muller, B.C. Hauback, Combined X-ray and raman studies on the effect of cobalt additives on the decomposition of magnesium borohydride, Energies, 8 (2015) 9173-91901. https://doi.org/10.3390/en8099173.

[11] I. Saldan, S. Hino, T.D. Hamphries, O. Zavorotynska, M. Chong, C.M. Jensen, S. Deledda, B.C. Hauback, Structural changes observed during the reversible hydrogenation of $Mg(BH_4)_2$ with Ni-based additives, J. Phys. Chem. C, 118 (2014) 23376-23384. https://doi.org/ 10.1021/jp5066677.

[12] G.L. Soloveichik, M. Andrus, Y. Gao, J.C. Zhao, S. Kniajanski, Magnesium borohydride as a hydrogen storage material: Synthesis of unsolvated $Mg(BH_4)_2$, Int. J. Hydrogen Energy 34 (2009) 2144-2152. https://doi.org/10.1016/j.ijhydene.2008.12.053.

[13] R. Černý, Y. Filinchuk, H. Hagemann, K. Yvon, Magnesium borohydride: synthesis and crystal structure, Angew. Chem. Int. Ed. 46 (2007) 5765-5767. https://doi.org/10.1002/ANIE.200700773.

[14] K. Chłopek, C. Frommen, A. Léon, O. Zabara, M. Fichtner, Synthesis and properties of magnesium tetrahydroborate, $Mg(BH_4)_2$, J. Mater. Chem. 17 (2007) 3496-3503. https://doi.org/10.1039/B702723K.

[15] Y. Nakamori, K. Miwa, A. Ninomiya, H. Li, N. Ohba, S.-i. Towata, A. Züttel, S.-i. Orimo, Correlation between thermodynamical stabilities of metal borohydrides and cation electronegativites: First-principles calculations and experiments, Phys. Rev. B 74 (2006) 45126-45126. https://doi.org/10.1021/10.1103/PHYSREVB.74.045126.

[16] R.A. Varin, C. Chiu, Z.S. Wronski, Mechano-chemical activation synthesis (MCAS) of disordered $Mg(BH_4)_2$ using $NaBH_4$, J. Alloys Compd. 462 (2008) 201-208. https://doi.org/10.1016/J.JALLCOM.2007.07.110.

[17] R.J. Newhouse, V. Stavila, S.-J. Hwang, L.E. Klebanoff, J.Z. Zhang, Reversibility and improved hydrogen release of magnesium borohydride, J. Phys. Chem. C 114 (2010) 5224-5232. https://doi.org/10.1021/JP9116744.

[18] C. Pistidda, S. Garroni, F. Dolci, E.G. Bardají, A. Khandelwal, P. Nolis, M. Dornheim, R. Gosalawit, T. Jensen, Y. Cerenius, S. Suriñach, M.D. Baró, W. Lohstroh, M. Fichtner, Synthesis of amorphous $Mg(BH_4)_2$ from MgB_2 and H_2 at room temperature, J. Alloys Compd. 508 (2010) 212-215. https://doi.org/10.1016/J.JALLCOM.2010.07.226.

[19] S. Gupta, I.Z. Hlova, T. Kobayashi, R.V. Denys, F. Chen, I.Y. Zavaliy, M. Pruski, V.K. Pecharsky, Facile synthesis and regeneration of $Mg(BH_4)_2$ by high energy reactive ball milling of MgB_2, Chem. Commun. 49 (2012) 828-830. https://doi.org/10.1039/C2CC36580D.

[20] J. Plesek, S. Hermanek, Chemistry of boranes. IV. Preparation, properties and behavior of magnesium borohydride towards Lewis bases, Chem. Commun. 31 (1966) 3845-3858. https://doi.org/10.1135/CCCC19663845.

[21] R. Koster, Neue praparative methoden zur herstellung und umwandlung von borwasserstoff-verbindungen, Angew. Chem. Int. Ed. 69 (1957) 684-684.

[22] P. Zanella, L. Crociani, N. Masciocchi, G. Giunchi, Facile high-yield synthesis of pure, crystalline $Mg(BH_4)_2$, Inorganic Chemistry 46 (2010) 9039-9041.

https://doi.org/10.1021/IC701436C.

[23] M.V. Solovev, O.V. Chashchikhin, P.V. Dorovatovskii, V.N. Khrustalev, A.S. Zyubin, T.S. Zyubina, O.V. Kravchenko, A.A. Zaytsev, Y.A. Dobrovolsky, Hydrolysis of $Mg(BH_4)_2$ and its coordination compounds as a way to obtain hydrogen, J. Power Sources 377 (2018) 93-102. https://doi.org/10.1016/J.JPOWSOUR.2017.11.090.

[24] Y. Zhu, L. Ouyang, H. Zhong, H. Wang, H. Shao, Z. Huang, M. Zhu, Closing the loop for hydrogen storage: Facile regeneration of $NaBH_4$ from its hydrolytic product, Angew. Chem. Int. Ed. 59 (2020) 8623-8629. https://doi.org/10.1002/ANIE.201915988.

[25] Y. Zhu, L. Ouyang, H. Zhong, H. Wang, H. Shao, Z. Huang, M. Zhu, Efficient synthesis of sodium borohydride: balancing reducing agents with intrinsic hydrogen source in hydrated borax, ACS Sustainable Chem. Eng. 8 (2020). https://doi.org/10.1021/ACSSUSCHEMENG.0C04354.

[26] H.-W. Li, K. Kikuchi, Y. Nakamori, K. Miwa, S. Towata, S. Orimo, Effects of ball milling and additives on dehydriding behaviors of well-crystallized $Mg(BH_4)_2$, Scr. Mater., 57 (2007) 679-682. https://doi.org/10.1016/j.scriptamat.2007.06.052.

[27] O. Friedrichs, A. Remhof, A. Borgschulte, F. Buchter, S.I. Orimo, A. Züttel, Breaking the passivation—the road to a solvent free borohydride synthesis, Phys. Chem. Chem. Phys., 12 (2010) 10919-10922. https://doi.org/10.1039/c0cp00022a.

[28] X. Wang, X. Xiao, J. Zheng, X. Huang, M. Chen, L. Chen, In-situ synthesis of amorphous $Mg(BH_4)_2$ and chloride composite modified by NbF_5 for superior reversible hydrogen storage properties, Int. J. Hydrogen Energy, 45 (2020) 2044-2053. https://doi.org/10.1016/j.ijhydene.2019.11.023.

[29] G.L. Soloveichik, Y. Gao, J. Rijssenbeek, M. Andrus, S. Kniajanski, R.C. Bowman Jr., S.-J. Hwang, J.-C. Zhao, Magnesium borohydride as a hydrogen storage material: Properties and dehydrogenation pathway of unsolvated $Mg(BH_4)_2$, Int. J. Hydrogen Energy, 34 (2009) 916-928. https://doi.org/ 10.1016/j.ijhydene.2008.11.016.

[30] G. Severa, E. Rönnebro, C.M. Jensen, Direct hydrogenation of magnesium boride to magnesium borohydride: demonstration of >11 weight percent reversible hydrogenstorage, Chem. Commun., 46 (2010) 421-423. https://doi.org/10.1039/B921205A.

[31] J. Zheng, H. Cheng, X. Xiao, M. Chen, L. Chen, Enhanced low temperature hydrogen desorption properties and mechanism of $Mg(BH_4)_2$ composited with 2D MXene, Int. J. Hydrogen Energy 44 (2019) 24292-24300. https://doi.org/10.1016/J.IJHYDENE.2019.07.177.

[32] W. Chen, L. Ouyang, J. Liu, X. Yao, H. Wang, Z.W. Liu, M. Zhu, Hydrolysis and regeneration of sodium borohydride ($NaBH_4$) – A combination of hydrogen production and storage, J. Power Sources, 359 (2017) 400-407. https://doi.org/ 10.1016/j.jpowsour.2017.05.075.

[33] Z.P. Li, N. Morigazaki, B.H. Liu, S. Suda, Preparation of sodium borohydride by the reaction of MgH_2 with dehydrated borax through ball milling at room temperature, J. Alloys Compd., 349 (2003) 232-236. https://doi.org/10.1016/S0925-8388(02)00872-1.

[34] C.-L. Hsueh, C.-H. Liu, B.-H. Chen, C.-Y. Chen, Y.-C. Kuo, K.-J. Hwang, J.-R. Ku, Regeneration of spent-$NaBH_4$ back to $NaBH_4$ by using high-energy ball milling,

Int. J. Hydrogen Energy 34 (2009) 1717-1725. https://doi.org/10.1016/j.ijhydene.2008.12.036.

[35] Y. Wang, X. Chen, H. Zhang, G. Xia, D. Sun, Y. X., Heterostructures built in metal hydrides for advanced hydrogen storage reversibility, Adv. Mater. 32 (2020) 2002647. https://doi.org/10.1002/ADMA.202002647.

[36] O.M. Moon, B.-C. Kang, S.-B. Lee, J.-H. Boo, Temperature effect on structural properties of boron oxide thin films deposited by MOCVD method, Thin Solid Films 464-465 (2004) 164-169. https://doi.org/10.1016/J.TSF.2004.05.107.

[37] A.C. Stowe, W.J. Shaw, J.C. Linehan, B. Schmid, T. Autrey, In situ solid state ^{11}B MAS-NMR studies of the thermal decomposition of ammonia borane: mechanistic studies of the hydrogen release pathways from a solid state hydrogen storage material, Phys. Chem. Chem. Phys. 9 (2007) 1831-1836. https://doi.org/10.1039/B617781F.

[38] K. Shimoda, Y. Zhang, T. Ichikawa, H. Miyaoka, Y. Kojima, Solid state NMR study on the thermal decomposition pathway of sodium amidoborane $NaNH_2BH_3$, J. Mater. Chem. 21 (2011) 2609-2615. https://doi.org/10.1039/C0JM02828B.