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Breaking the Passivation: Sodium Borohydride Synthesis by Reacting Hydrated Borax with Aluminium

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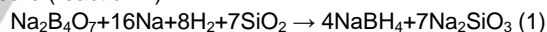
Abstract: A significant obstacle in the large-scale applications of sodium borohydride (NaBH₄) for hydrogen storage is its high cost. Herein, we report a new method to synthesize NaBH₄ by ball milling hydrated sodium tetraborate (Na₂B₄O₇·10H₂O) with low-cost Al or Al₈₈Si₁₂, instead of Na, Mg or Ca. An effective strategy is developed to facilitate mass transfer during the reaction by introducing NaH to enable the formation of NaAlO₂ instead of dense Al₂O₃ on Al surface, and by using Si as a milling additive to prevent agglomeration and also break up passivation layers. Another advantage of this process is that hydrogen in Na₂B₄O₇·10H₂O serves as a hydrogen source for NaBH₄ generation. Considering the low cost of the starting materials and simplicity in operation, our studies demonstrate the potential of producing NaBH₄ in a more economical way than the commercial process.

Introduction

Transition from fossil fuels to renewables as primary energy sources is important for solving energy and environmental problems and realizing sustainable future.^[1] In this regard, hydrogen (H₂) is considered as a suitable candidate for an energy carrier in view of its high energy density, and generating electrical and thermal power with zero greenhouse gas emission. However, the lack of safe and efficient means to store large amounts of hydrogen is a major barrier to wide deployment of hydrogen. Sodium borohydride (NaBH₄) as a hydrogen source for direct fuel cell (DFC)^[2] or as a hydrogen storage material^[3] has attracted great attention owing to its high hydrogen storage density (10.8 wt%)^[4]. However, its high cost poses a significant obstacle in large-scale applications. Thus, developing cost-effective NaBH₄ synthesis becomes highly desirable.

Previously, significant efforts have been mainly devoted to synthesizing NaBH₄ from anhydrous sodium metaborate (NaBO₂) recycled from the hydrolytic product of NaBH₄^[5] or

anhydrous sodium tetraborate (Na₂B₄O₇) obtained from naturally abundant borax^[6]. In those reactions, strong reducing agents such as alkaline metal or metal hydride are typically employed to convert B-O to B-H. High pressure hydrogen gas is often needed for the formation of B-H. One traditional method, Bayer process, involves heating up Na₂B₄O₇, sodium (Na) and silicon dioxide (SiO₂) at high temperature (700°C) under high hydrogen pressure (reaction 1):^[6a]



The consumption of a considerable amount of Na and high pressure H₂ at high temperature leads to the high price of NaBH₄. Therefore, it is necessary to develop alternative methods to reduce the cost. Non-Na based reducing agents such as magnesium hydride (MgH₂)^[5a] and calcium hydride (CaH₂)^[5b] have been used to synthesize NaBH₄ from NaBO₂. For example, NaBH₄ was successfully obtained via annealing MgH₂ and NaBO₂ at 550°C under 7 MPa H₂.^[5a] Due to the high cost of MgH₂, Mg was used as a substitute but the yield was only 10%, which is due to the agglomeration of Mg powders and consequently reduced reaction activity.^[5a] To improve the yield, various additives such as Si, Ni, Fe and Co were introduced to this system to help with either the dispersion of Mg^[5a] or activation of H₂ molecules^[5c, 5d, 5h]. In addition, Mg was also used to react with Na₂B₄O₇ under high-pressure H₂ (2.5 MPa) via thermochemical method (550°C) to prepare NaBH₄.^[6b]

The methods mentioned above are energy inefficient and special safety measures are required when handling highly corrosive/flammable chemicals at high temperatures and under high H₂ pressure. The H₂ is mainly generated from fossil fuels, which is not environmentally friendly and also adds raw materials cost. Alternatively, NaBH₄ has been successfully synthesized through a mechano-chemical reaction at room temperature. MgH₂ was used as the reducing agent to react with NaBO₂^[5e-g] or Na₂B₄O₇^[6c, 6d] facilitated by high-energy ball milling with the maximum NaBH₄ yield of 76% and 78%, respectively. The low temperature is certainly an operational

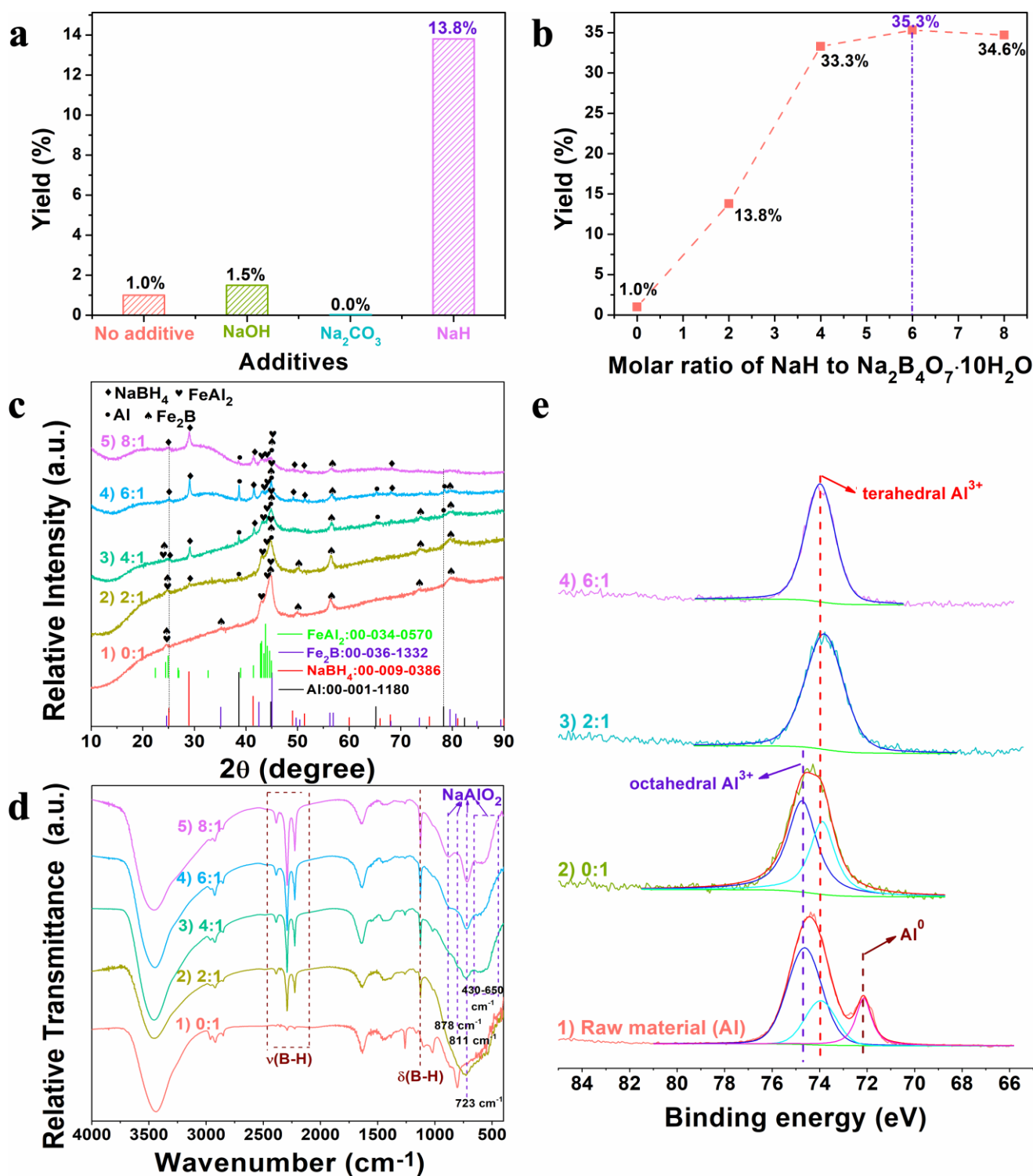


Figure 1. (a) Yields of NaBH₄ obtained via ball milling Na₂B₄O₇·10H₂O and Al with and without additives for 20 h (not including the pauses). (b) Yields of NaBH₄, (c) XRD patterns and (d) FTIR spectra of products obtained via ball milling NaH and Na₂B₄O₇·10H₂O in different molar ratios (Na₂B₄O₇·10H₂O and Al were fixed at a 1:14.16 molar ratio) for 20 h. (e) XPS Al 2p spectra of commercial Al and the products obtained via milling NaH and Na₂B₄O₇·10H₂O in different molar ratios for 20 h.

advantage but MgH₂ is still expensive. In addition, the approaches mentioned above rely on anhydrous NaBO₂ and Na₂B₄O₇, which requires dehydration of NaBO₂·xH₂O (real spent

fuel) at over 350°C [7] or Na₂B₄O₇·10H₂O (borax mineral) at approximately 600°C [8]. Dehydration causes additional energy consumption and therefore raises up the price of NaBH₄.

Recently, we reported that NaBH₄ could be synthesized by ball-milling NaBO₂·xH₂O (x=2, 4) or CO₂ treated hydrolytic product with Mg with high yields (above 68.55%).^[9] It should be noted that little attention has been paid to naturally abundant borax (hydrated Na₂B₄O₇).

As the 3th most abundant elements in the earth crust, Al is more abundant and readily available than Mg (8th), Ca (5th) and Na (6th). Al is more stable than Mg, Ca and Na in air, rendering it convenient for transport and storage. More importantly, Al can be oxidized into a higher valance state (Al³⁺) and would convert more Na₂B₄O₇ or NaBO₂ into NaBH₄. Besides, Al has higher Moh's hardness (MH) of 2.75 than Na (MH:0.4), Ca (MH: 1.75), and Mg (MH: 2.5), which could result in better ball-milling efficiency. Based upon all these reasons, a large-scale NaBH₄ production using low-cost Al as a reducing agent is highly desired. In this study, efforts have been devoted to NaBH₄ synthesis by ball milling Al or Al₈₈Si₁₂ with Na₂B₄O₇·10H₂O in the presence of a sodium-containing compound as a Na supplement to achieve an atomic ratio of 1:1 for Na:B, as in NaBH₄. There are a few advantages associated with hydrated borax. First, H⁺ in the crystal water in Na₂B₄O₇·10H₂O acts as a hydrogen source during the reaction, which reduces the demand for an external H₂ sources and therefore lowers the cost. Moreover, dehydration of Na₂B₄O₇·10H₂O is avoided, which improves the overall energy efficiency and decreases the cost. Based on experimental results, the reaction mechanism was also discussed.

Results and Discussion

Choice of Na-containing compounds as a Na supplement

Na-containing compounds were used to compensate the Na insufficiency because the atomic ratio of Na:B in Na₂B₄O₇·10H₂O is 1:2, while it is 1:1 in NaBH₄. Attempts were first made to synthesize NaBH₄ by reacting Al with Na₂B₄O₇·10H₂O and different Na-containing compounds (Figure S1). In experiments with NaOH, Na₂CO₃ and no additives, FTIR peaks corresponding to typical IR bands (1125, 2200-2400 cm⁻¹) of NaBH₄ are almost invisible (Figure S1),^[9a, 9b, 10] indicative of low yields (below 1.5%) (Figure 1a). In contrast, NaH effectively facilitates the formation of NaBH₄. The vibration and deformation IR bands of B-H at 2200-2400 cm⁻¹ and 1125 cm⁻¹, respectively, are highly visible in the FTIR spectra (Figure S1).^[9a, 9b, 10] To improve the yield, different amounts of NaH were added. For 20 h milling, the yield increases with increasing molar ratio of NaH:Na₂B₄O₇·10H₂O, from 33.3% for 4:1 to 35.3% for 6:1 (Figure 1b). The intensities of the XRD peaks of NaBH₄ increase when more NaH was used, while those of Fe₂B and FeAl₂ decreases significantly (Figure 1c). These indicate that NaH can reduce Fe peeling off the ball mill reactor and improve the synthesis. This is supported by EDS results (Table S1) which reveal decreasing amounts of Fe in the ball milled powders when more NaH was used. Since Fe₂B is a reaction product between Fe and NaBH₄, these results indicate less NaBH₄ decomposition with the presence of NaH.^[9b] As a result, NaH addition is favorable for the formation of NaBH₄.

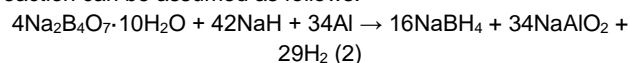
The yield is still lower than those using Mg as the reducing agent. According to our previous studies,^[9b, 9c] ball milling Mg-Na₂B₄O₇·10H₂O, Mg-NaOH-Na₂B₄O₇·10H₂O, and Mg-Na₂CO₃-

Na₂B₄O₇·10H₂O systems leads to the formation of NaBH₄ and MgO. We speculate that Al₂O₃ film forms on the surface of Al during ball milling. Unlike relatively loose MgO, dense Al₂O₃ blocks hydrogen from reaching Al underneath the oxide film,^[11] thus restricting the formation of NaBH₄. The other reason could be that hydrogen dissociation on Al has high dissociation barrier (>1 eV) than that on Mg (0.92 eV).^[12]

To confirm the reaction of Al with NaH-Na₂B₄O₇·10H₂O mixture, the products were characterized by FTIR (Figure 1d) and XPS (Figure 1e). In the raw Al powders, XPS spectrum reveals the coexistence of Al⁰ (Al 2p at 72.1 eV) and Al³⁺ (Al 2p at 74.7 eV and 73.9 eV corresponding to the octahedral and tetrahedral coordination state of Al³⁺, respectively),^[13] indicating the formation of Al₂O₃ due to slight oxidation of Al. With the increase in NaH loading, the XPS peaks of Al⁰ and the octahedrally coordinated Al³⁺ disappears (Figure 1e(2-4)) and only tetrahedrally coordinated Al³⁺ remains,^[13] which indicate the conversion of Al⁰ to Al³⁺. Since Al³⁺ largely adopts tetrahedral coordination, the oxide is unlikely to be Al₂O₃. From Figure 1d, IR band at 811 cm⁻¹ is associated with O-O triangular species and the bands at 617 and 558 cm⁻¹ can be assigned to the vibrations of Al-O bond^[14] in AlO₂⁻. Based upon the XPS and IR results and the atomic ratio between Na and Al in the starting materials, it is hypothesized that NaAlO₂ is formed during ball milling. NaAlO₂ appears to be amorphous since related XRD peaks are absent from Figure 1c. The intensities of the characteristic FTIR bands of NaAlO₂ increase when more NaH is used, indicating that NaH facilitates the formation of NaAlO₂. Different from Al₂O₃, NaAlO₂ is relative loose and porous, which allows for efficient mass transfer required for the NaBH₄ formation during ball milling.^[11, 15]

Analysis of the NaBH₄ formation

To investigate the reaction mechanism, mixtures of Na₂B₄O₇·10H₂O, NaH, and Al were milled for different periods. Na₂[BO₂(OH)] appeared after milling for 10 min and then rapidly disappeared upon further milling, which may result from the combination of reaction and amorphization during ball milling (Figure 2a). H₂ can be detected during this period (Figure S2(2)). The formation of NaBH₄ is confirmed by the appearance of IR bands at 1125 and 2200-2400 cm⁻¹ that are associated with B-H bond (Figure 2b(1)) and the NMR resonance of BH₄⁻ at -42.1 ppm (Figure 2c(2)) after milling for 30 min.^[9a, 9b, 10, 16] The intensity of the XRD peaks of Al decreases with milling time. As the ball milling time increased to 4 h, the FTIR bands of NaAlO₂ became more visible. The XRD peaks of NaBH₄ were observed only after 7 h milling, which could be due to small crystallite size of NaBH₄ and also the lower quantities of NaBH₄ in 0.5-4 h milled products. With further ball milling, the characteristic FTIR bands and XRD peaks of NaBH₄ become stronger (Figure S3). Throughout the whole process, the diffraction peaks of NaAlO₂ are invisible. NaAlO₂ appears to be amorphous, as previously discussed in section 3.1. H₂ was detected as one of the by-products of the ball-milling reaction (Figure S2 (5)). The overall reaction can be assumed as follows:



Reaction (2) is thermodynamically favorable ($\Delta G^\circ_{298\text{K}} = -929.08$ kJ mol⁻¹ NaBH₄).

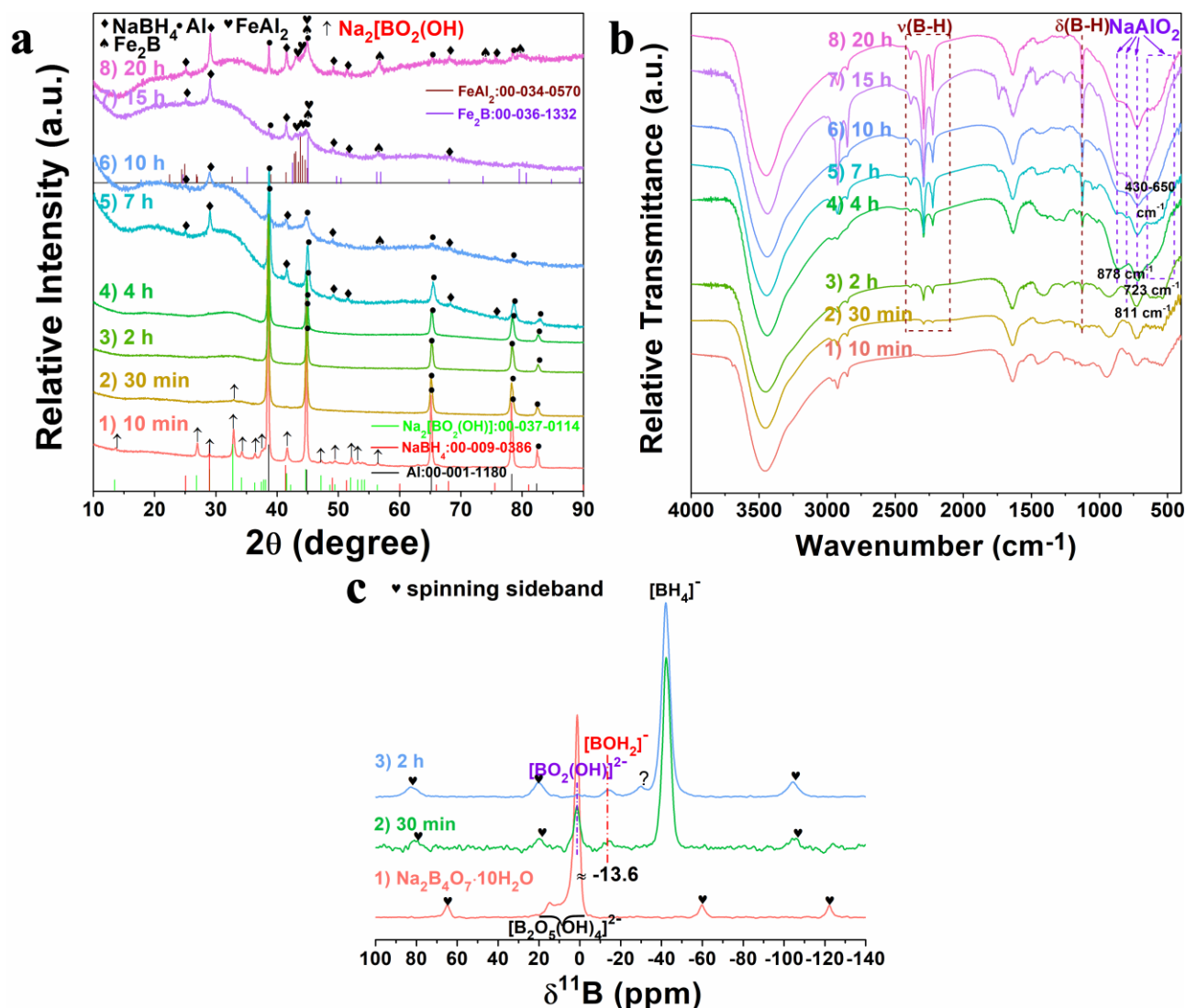


Figure 2. (a) XRD patterns and (b) FTIR spectra of the products obtained after milling Na₂B₄O₇·10H₂O, NaH, and Al mixtures (in a 1:6:14.16 molar ratio) for different durations; (c) Solid-state ¹¹B NMR spectra of Na₂B₄O₇·10H₂O and products obtained after milling for different durations.

To further understand the process, the as-milled mixtures were also characterized using solid-state ¹¹B NMR. The resonance at around -13.6 ppm is assigned to the special intermediate “[BOH₂]⁻” after ball milling of 30 min and 2 h (Figure 2c).^[9b, 16] Based upon the results, it can be inferred that the formation of NaBH₄ takes place according to the following steps. First, crystal water in Na₂B₄O₇·10H₂O firstly reacts with NaH forming NaOH and H₂. The hydrogen gas molecules are absorbed on Al surfaces and dissociate into H. NaOH then reacts with borax to form Na₂[BO₂(OH)] which plays an important role in NaAlO₂ formation. This is in agreement with a previous study where Na₂[BO₂(OH)] was obtained from by heating Na₂B₄O₇ and NaOH.^[17] Second, since B-O bond with bond length of 1.35 Å in Na₂[BO₂(OH)] are stronger than B-OH (1.439 Å), B-OH preferentially breaks and combines with H⁻ (from the dissociation of H₂ on Al surface) to form Na₂[BO₂H] which was not observed in experiments owing to its high activity

and short lifetimes.^[18] Third, O²⁻ in Na₂[BO₂H] bonds with Al releasing electrons to the absorbed H, generating Al-O and H⁻. H⁻ combines with B to form NaBOH₂, and another Na⁺ in Na₂[BO₂H] combines with AlO₂⁻ forming NaAlO₂. Finally, B in NaBOH₂, as a Lewis acid, accepts H⁻ to replace O²⁻ forming NaBH₄. This process is similar to what happens during the synthesis of NaBH₄ by reacting sodium borate with Mg and H₂.^[5h]

Using Al₈₈Si₁₂ for the synthesis

Based on the report that the yield of NaBH₄ can be improved through introducing Si as a milling aid,^[10b, 19] we tried an Al-Si alloy expecting that its hardness and brittleness can improve milling efficiency and therefore facilitate the reaction. Al-rich Al₈₈Si₁₂ eutectic alloy was chosen to react with NaH and Na₂B₄O₇·10H₂O. In comparison, a mixture of Al and Si powders

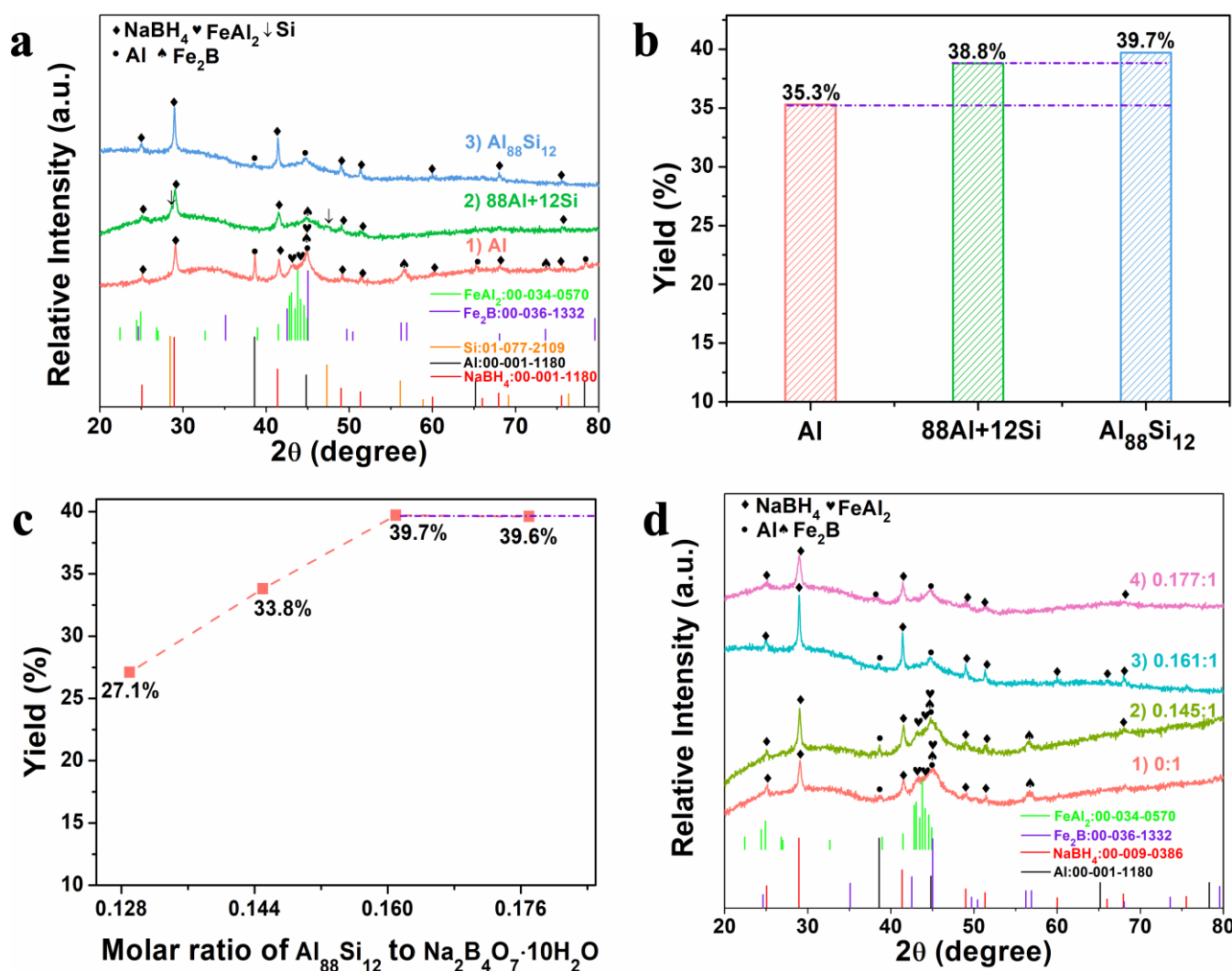


Figure 3. (a) XRD patterns and (b) Yields of NaBH₄ via ball milling the mixtures for 20 h at 1200 CPM: Na₂B₄O₇·10H₂O, NaH, and Al in a 1:6:14.16 molar ratio; Na₂B₄O₇·10H₂O, NaH, Al, and Si in a 1:6:14.16:1.92 molar ratio; Na₂B₄O₇·10H₂O, NaH, and Al₈₈Si₁₂ in a 1:6:0.161 molar ratio; (c) Impact of Al₈₈Si₁₂ loading on the yields of NaBH₄ and (d) XRD patterns of the products obtained after milling Al₈₈Si₁₂ and Na₂B₄O₇·10H₂O in different molar ratios (Na₂B₄O₇·10H₂O and NaH were fixed at a 1:6 molar ratio) for 20 h.

with a molar ratio of 88:12 was also tried. For both cases, the intensity of XRD peaks of FeAl₂ and FeB₂ decreases compared with the experiment without Si (Figure 3a), indicating reduced decomposition of NaBH₄. The yield increased and then plateaued when more Al₈₈Si₁₂ was used, and reached the maximum value of 39.7% for the ratio of 0.161:1 (Al₈₈Si₁₂: Na₂B₄O₇·10H₂O) (Figure 3b and 3c). The Al/Si mixture also displays similar high yield. The improvement is likely due to suppressed decomposition of NaBH₄ and also increased effective contact between the reactants.

Yield of NaBH₄

As known from previous studies the loadings of reducing agent has an important influence on the NaBH₄ yield.^[5b, 5e, 5g, 6c, 9a, 9b, 10] The yield was optimized by varying the molar ratio of Al:Na₂B₄O₇·10H₂O (Figure 4a). With the increase in the loading of Al, the yield of NaBH₄ increased to the highest value (35.3%)

and then decreased, a trend similar to previous studies.^[5e, 6c, 10a] Better contact among the reactants and more effective reaction are expected with the increase in Al loading. However, excessive amount of Al decreases effective contact and therefore lower the ball-milling efficiency. Na₂B₄O₇·10H₂O was replaced by Na₂B₄O₇·5H₂O to synthesize NaBH₄ in the same way, but the yields are much lower (Figure 4b). This is likely due to more crystal water available as the hydrogen source in Na₂B₄O₇·10H₂O than in Na₂B₄O₇·5H₂O.

To further improve the yield, a milling additive was introduced. Kojima et al.^[5a] found that the introduction of Si to NaBO₂-Mg-H₂ system significantly increased the yield of NaBH₄. As discussed in the previous section, Al₈₈Si₁₂ improves the yield to an extent similar to that of Al/Si mixture. Considering that Al₈₈Si₁₂ is slightly more expensive than Al, only Si was introduced as an additive. The yield increases with increasing the molar ratio of Si:Na₂B₄O₇·10H₂O, reaching the maximum of 61.9% for a ratio of 13.51:1 (Figure 4c), higher than

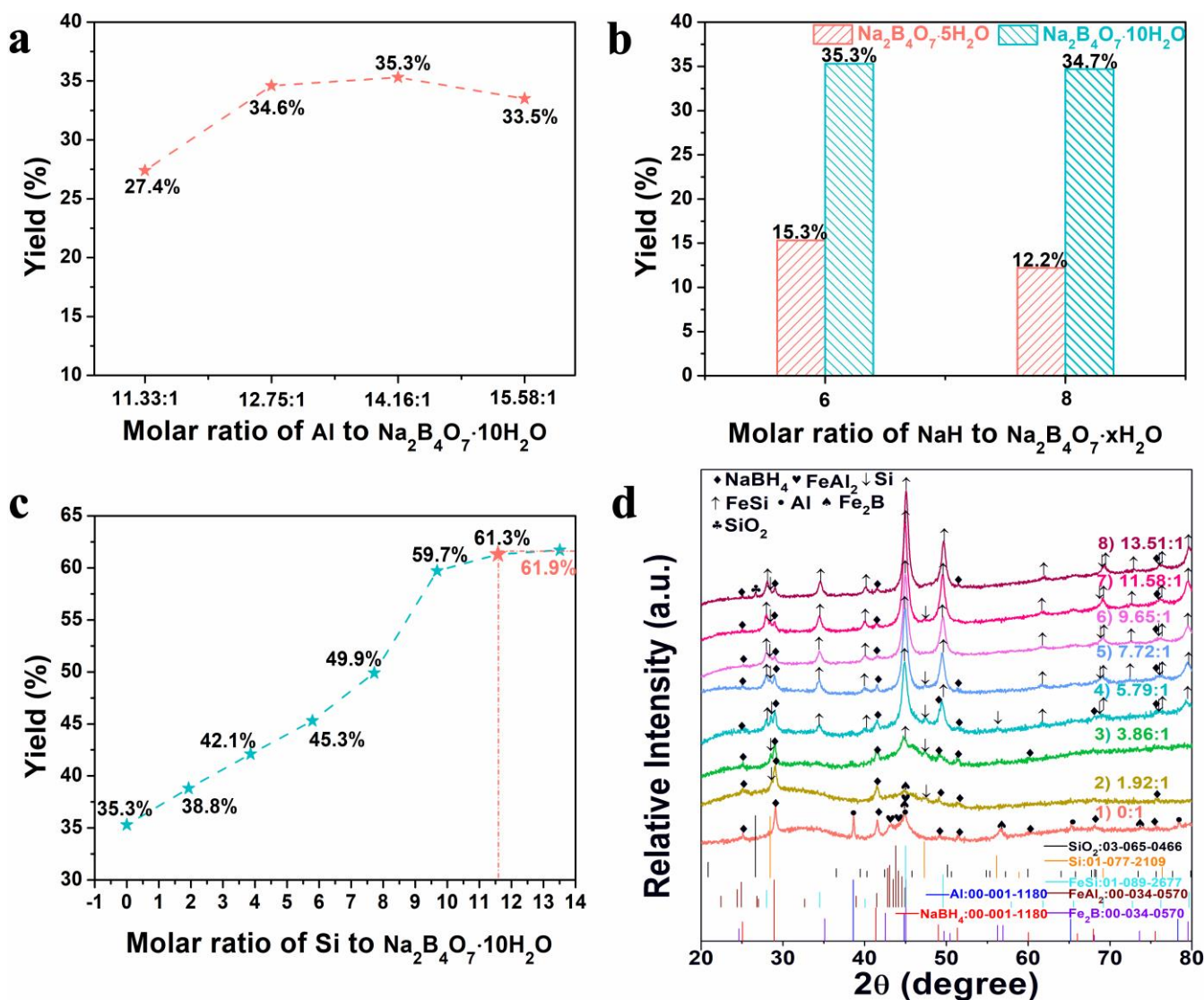


Figure 4. (a) Yields of NaBH_4 obtained after ball milling Al and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in different molar ratios ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}:\text{NaH}$ was fixed at a 1:6 molar ratio) for 20 h; (b) Yields of NaBH_4 obtained after ball milling NaH and $\text{Na}_2\text{B}_4\text{O}_7 \cdot x\text{H}_2\text{O}$ ($x=5, 10$) in different molar ratios for 20 h ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}:\text{Al}$ in a 1:10 molar ratio; $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}:\text{Al}$ in a 1:14.16 molar ratio); (c) Yields of NaBH_4 and (d) XRD patterns of the products obtained after milling Si and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in different molar ratios ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}:\text{NaH}:\text{Al}$ was fixed at a 1:6:14.16 molar ratio) for 20 h.

$\text{NaBO}_2\text{-Mg-H}_2$, $\text{NaBO}_2 \cdot 2\text{H}_2\text{O-Mg-H}_2$, $\text{Na}_2\text{B}_4\text{O}_7\text{-Mg-H}_2$, and $\text{Na}_2\text{B}_4\text{O}_7\text{-MgH}_2$ systems reported previously (10%, 12.3%, 45.6%, and 43% respectively).^[5a, 6b, 6c, 20] For 20 h ball-milling, the yield of 61.3% with Si is much higher than 35.3% without Si additive (Figure 4c). The enhancement can be attributed to the brittle and hard feature of Si that can help to break up passivation layers. The formation of FeAl_2 and Fe_2B decreases with increasing loading of Si, which indicates suppressed decomposition of NaBH_4 (Figure 4d). We note that the highest yield of this system is still lower than those of $\text{Na}_2\text{B}_4\text{O}_7\text{-NaOH-MgH}_2$ (64%)^[6c], $\text{Na}_2\text{B}_4\text{O}_7\text{-Na}_2\text{O}_2\text{-MgH}_2$ (67%)^[6c], and $\text{NaBO}_2\text{-MgH}_2$ (70/71%)^[5f, 5g] where expensive MgH_2 is used. This could be primarily attributed to the higher reactivity of MgH_2 than Al.

Conclusion

Herein, we report a low-cost method to produce NaBH_4 via ball milling mixtures of Al (or Al+Si, or $\text{Al}_{88}\text{Si}_{12}$)- $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ -NaH. Commercially available $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ serves as the source of B and also provides certain amount of Na and H. NaH plays a crucial role in improving the reaction by favoring the formation of loose NaAlO_2 instead of dense Al_2O_3 which restricts mass transfer. The yield of NaBH_4 increased from 35.5% to 61.9% after introducing Si, which acts as a grinding aid creating fresh surfaces. Si in the by-product can be extracted and reused. Compared with the commercial process, this mechanochemical method has several advantages such as requiring no external heat and no H_2 supply, and employing low-cost $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and Al. With further improvement in yield, this method can be an alternative to the existing commercial NaBH_4 synthesis process.

Experimental Section

Mechano-chemical synthesis of NaBH₄

Na₂B₄O₇·10H₂O (ACS-grade, Aladdin), Na₂B₄O₇·5H₂O (purity: ≥99.5%, Chron Chemicals), Al (purity: ≥99%, Aladdin), Al₈₈Si₁₂ alloy (purity: 99%, Aike Reagent), Si (powder, 1 μm, Desheng Alloy Materials Co., Ltd), NaOH (purity: ≥99%, Aladdin), Na₂CO₃ (purity: ≥99.8%, General-Reagent), and NaH (purity: 90%, Sigma-Aldrich) were used as received for the mechano-chemical synthesis of NaBH₄. All the raw materials except Na₂B₄O₇·xH₂O (x=5, 10) are stored in an argon glove box (MIKROUNA, China) with <0.1 ppm H₂O and O₂. 1 g of reactants were put in an 80 mL jar with 50 g of two different sized steel balls. Effects of ball milling duration and atomic ratios among the start materials on the yield were studied. In a shaker mill, impact is the most dominant force, which benefits the mechanochemical reactions. This is in contrast to a planetary mill which generates friction, shear, and impacts.^[21] Besides, shaker mills are generally capable of operating with higher rotation speeds. As a result, the shaker ball mill could supply higher energy to efficiently pulverize particles to allow better mechanochemical reactions. Shaker mills have been found to be more effective in promoting the NaBH₄ formation, as compared with planetary mills.^[5e] All reactions were conducted in a shaker mill (QM-3C, Nanjing, China) at 1200 cycles per min (CPM) at room temperature. To prevent overheating, the ball milling process was conducted by alternating 30 min of milling and 30 min of rest. Note that the ball-milling times mentioned in articles do not include the pauses.

Quantification of NaBH₄

Anhydrous ethylenediamine (C₂H₈N₂, Sigma-Aldrich, purity: 99%) was used to extract NaBH₄ from the milled products under an Ar atmosphere. The filtrate was collected after passing through polytetrafluoroethylene membrane (0.45 μm) and then dried in a freeze dryer, where the solvent vapor (C₂H₈N₂) was captured by a cold trap (-54°C). The amount of resultant NaBH₄ was determined by iodimetric analysis [15]. H₂SO₄ (GR), sodium thiosulfate solution (Na₂S₂O₃, 0.1000 mol L⁻¹), potassium iodide (KI, purity: ≥99%), potassium iodate (KIO₃, AR-grade), and starch indicator (≥99%) were used for iodimetric analysis. All these chemicals were purchased from Aladdin and used without further purification. The yield of NaBH₄ was calculated according to formula:^[5g]

Yield = [(obtained mass NaBH₄)/(theoretical mass NaBH₄)] × 100% (3)
where the theoretical mass NaBH₄ is calculated based upon the assumption that 1 mole Na₂B₄O₇·xH₂O (x=5,10) can produce 4 moles NaBH₄.

Characterization

The obtained powders were subjected to qualitative analyses using powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and solid-state ¹¹B nuclear magnetic resonance (NMR) spectroscopy. The crystal phase composition of the samples was characterized by XRD using a PANalytical Empyrean with a Cu Kα radiation (λ = 0.15418 nm, step size = 0.262°, integration time 300 s/step) at 40 mA and 45 kV. During the test, the sample was covered with Scotch tape to prevent exposure to air. To characterize chemical bonds in the samples, FTIR (Nicolet IS50) spectra were collected in the transmission mode. The sample was mixed with KBr powders (weight ratio of 1:99) and then pressed into pellets under 20 MPa. The spectra were recorded in the range of 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹. The NMR spectra were collected on a Bruker AVANCE III HD 400 NMR spectrometer using a 4 mm CP-MAS probe and a spinning speed of ν_R = 8.0 kHz. X-ray photoelectron spectroscopy (XPS) measurements were performed on Thermo Fisher Scientific K-Alpha using an Al Kα monochromatic source, and the XPS spectra were analyzed by XPSPEAK Fit 4.1 software. The gaseous components in the ball mill reactor were analyzed using Hiden-Qic 20 mass spectrometer (MS).

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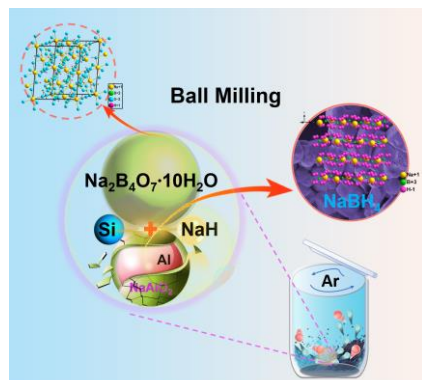
Keywords: aluminum • borax • borohydride • hydrogen • hydrogen storage

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Entry for the Table of Contents

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We present a cost-effective way to produce NaBH₄ with high yield by ball milling hydrated borax (Na₂B₄O₇·10H₂O) with cheap Al or Al₈₈Si₁₂ at ambient condition. An effective strategy was developed to facilitate mass transfer during the reaction by introducing NaH to enable the formation of loose NaAlO₂ instead of dense Al₂O₃ on Al surface, and by using Si as a milling additive that prevents agglomeration and also breaks up passivation layers.

Yongyang Zhu, Hao Zhong, Hui Wang, Liuzhang Ouyang*, Jiangwen Liu, Zhenguo Huang*, and Min Zhu