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Breaking the passivation: Sodium borohydride synthesis by reacting hydrated borax with aluminium

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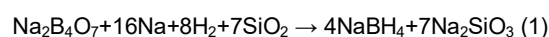
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Abstract: A significant obstacle in the large-scale applications of sodium borohydride (NaBH₄) for hydrogen storage is its high cost. Herein, we report a new method to synthesize NaBH₄ by ball milling hydrated sodium tetraborate (Na₂B₄O₇·10H₂O) with 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. MgH_2 was used as the reducing agent to react with NaBO_2 [5e-g] or $\text{Na}_2\text{B}_4\text{O}_7$ [6c, 6d] facilitated by high-energy ball milling with the

maximum NaBH_4 yield of 76% and 78%, respectively. The low temperature is certainly an operational

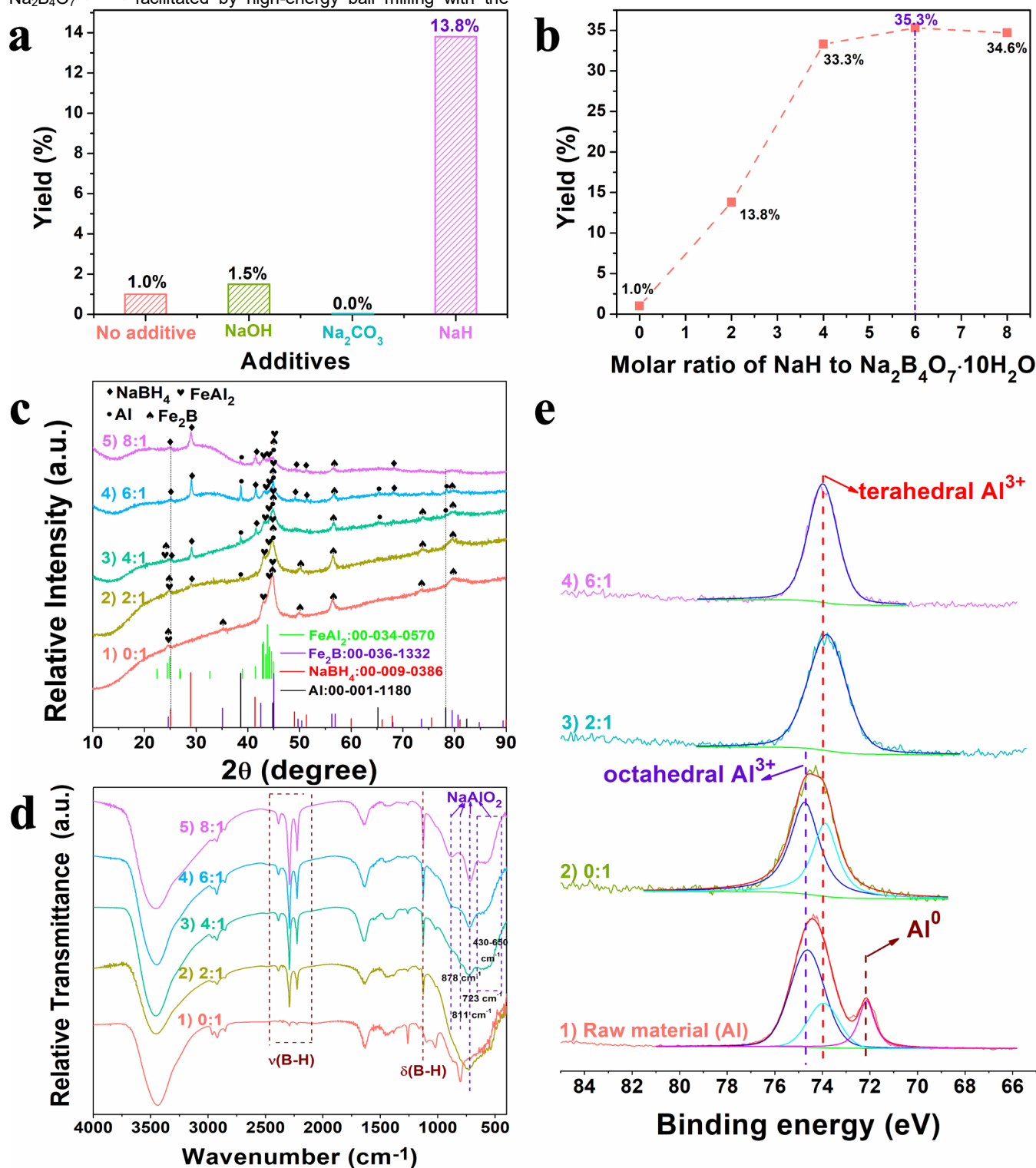


Figure 1. (a) Yields of NaBH_4 obtained via ball milling $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and Al with and without additives for 20 h. (b) Yields of NaBH_4 , (c) XRD patterns and (d) FTIR spectra of products obtained via ball milling NaH and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in different molar ratios ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and 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 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in different molar ratios for 20 h.

advantage but MgH_2 is still expensive. In addition, the approaches mentioned above rely on anhydrous NaBO_2 and $\text{Na}_2\text{B}_4\text{O}_7$, which requires dehydration of $\text{NaBO}_2 \cdot x\text{H}_2\text{O}$ (real spent fuel) at over 350°C ^[7] or $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (borax mineral) at approximately 600°C ^[8]. Dehydration causes additional energy consumption and therefore raises up the price of NaBH_4 . Recently, we reported that NaBH_4 could be synthesized by ball-milling $\text{NaBO}_2 \cdot x\text{H}_2\text{O}$ ($x=2, 4$) or CO_2 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 $\text{Na}_2\text{B}_4\text{O}_7$).

As the 3rd 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 valence state (Al^{3+}) and would convert more $\text{Na}_2\text{B}_4\text{O}_7$ or NaBO_2 into NaBH_4 . 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 NaBH_4 production using low-cost Al as a reducing agent is highly desired. In this study, efforts have been devoted to NaBH_4 synthesis by ball milling Al or $\text{Al}_{88}\text{Si}_{12}$ with $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ 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 NaBH_4 . There are a few advantages associated with hydrated borax. First, H^+ in the crystal water in $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ acts as a hydrogen source during the reaction, which reduces the demand for an external H_2 sources and therefore lowers the cost. Moreover, dehydration of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ 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

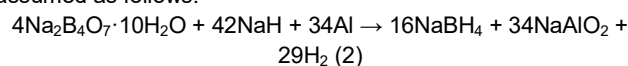
Na-containing compounds were used to compensate the Na insufficiency because the atomic ratio of Na:B in $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ is 1:2, while it is 1:1 in NaBH_4 . Attempts were first made to synthesize NaBH_4 by reacting Al with $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and different Na-containing compounds (Figure S1). In experiments with NaOH, Na_2CO_3 and no additives, FTIR peaks corresponding to typical IR bands ($1125, 2200\text{--}2400\text{ cm}^{-1}$) of NaBH_4 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 NaBH_4 . The vibration and deformation IR bands of B-H at $2200\text{--}2400\text{ cm}^{-1}$ 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 $\text{NaH}:\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, from 33.3% for 4:1 to 35.3% for 6:1 (Figure 1b). The intensities of the XRD peaks of NaBH_4 increase when more NaH was used, while those of Fe_2B and FeAl_2 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 Fe_2B is a reaction product between Fe and NaBH_4 , these results indicate less NaBH_4 decomposition with the presence of NaH.^[9b] As a result, NaH addition is favorable for the formation of NaBH_4 .

The yield is still lower than those using Mg as the reducing agent. According to our previous studies,^[9b, 9c] ball milling $\text{Mg-Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Mg-NaOH-Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, and $\text{Mg-Na}_2\text{CO}_3\text{-Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ systems leads to the formation of NaBH_4 and MgO . We speculate that Al_2O_3 film forms on the surface of Al during ball milling. Unlike relatively loose MgO , dense Al_2O_3 blocks hydrogen from reaching Al underneath the oxide film,^[11] thus restricting the formation of NaBH_4 . The other reason could be that hydrogen dissociation on Al has high dissociation barrier ($>1\text{ eV}$) than that on Mg (0.92 eV).^[12]

To confirm the reaction of Al with $\text{NaH-Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ mixture, the products were characterized by FTIR (Figure 1d) and XPS (Figure 1e). In the raw Al powders, XPS spectrum reveals the coexistence of Al^0 (Al 2p at 72.1 eV) and Al^{3+} (Al 2p at 74.7 eV and 73.9 eV corresponding to the octahedral and tetrahedral coordination state of Al^{3+} , respectively),^[13] indicating the formation of Al_2O_3 due to slight oxidation of Al. With the increase in NaH loading, the XPS peaks of Al^0 and the octahedrally coordinated Al^{3+} disappears (Figure 1e(2-4)) and only tetrahedrally coordinated Al^{3+} remains,^[13] which indicate the conversion of Al^0 to Al^{3+} . Since Al^{3+} largely adopts tetrahedral coordination, the oxide is unlikely to be Al_2O_3 . 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 AlO_2^- . Based upon the XPS and IR results and the atomic ratio between Na and Al in the starting materials, it is hypothesized that NaAlO_2 is formed during ball milling. NaAlO_2 appears to be amorphous since related XRD peaks are absent from Figure 1c. The intensities of the characteristic FTIR bands of NaAlO_2 increase when more NaH is used, indicating that NaH facilitates the formation of NaAlO_2 . Different from Al_2O_3 , NaAlO_2 is relative loose and porous, which allows for efficient mass transfer required for the NaBH_4 formation during ball milling.^[11, 15]

Analysis of the NaBH_4 formation

To investigate the reaction mechanism, mixtures of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, NaH, and Al were milled for different periods. $\text{Na}_2[\text{BO}_2(\text{OH})]$ 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). H_2 can be detected during this period (Figure S2(2)). The formation of NaBH_4 is confirmed by the appearance of IR bands at 1125 and $2200\text{--}2400\text{ cm}^{-1}$ that are associated with B-H bond (Figure 2b(1)) and the NMR resonance of BH_4^- 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 NaAlO_2 became more visible. The XRD peaks of NaBH_4 were observed only after 7 h milling, which could be due to small crystallite size of NaBH_4 and also the lower quantities of NaBH_4 in 0.5-4 h milled products. With further ball milling, the characteristic FTIR bands and XRD peaks of NaBH_4 become stronger (Figure S3). Throughout the whole process, the diffraction peaks of NaAlO_2 are invisible. NaAlO_2 appears to be amorphous, as previously discussed in section 3.1. H_2 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 ($\Delta G^{\circ}_{298\text{K}} = -929.08 \text{ kJ mol}^{-1} \text{ NaBH}_4$).

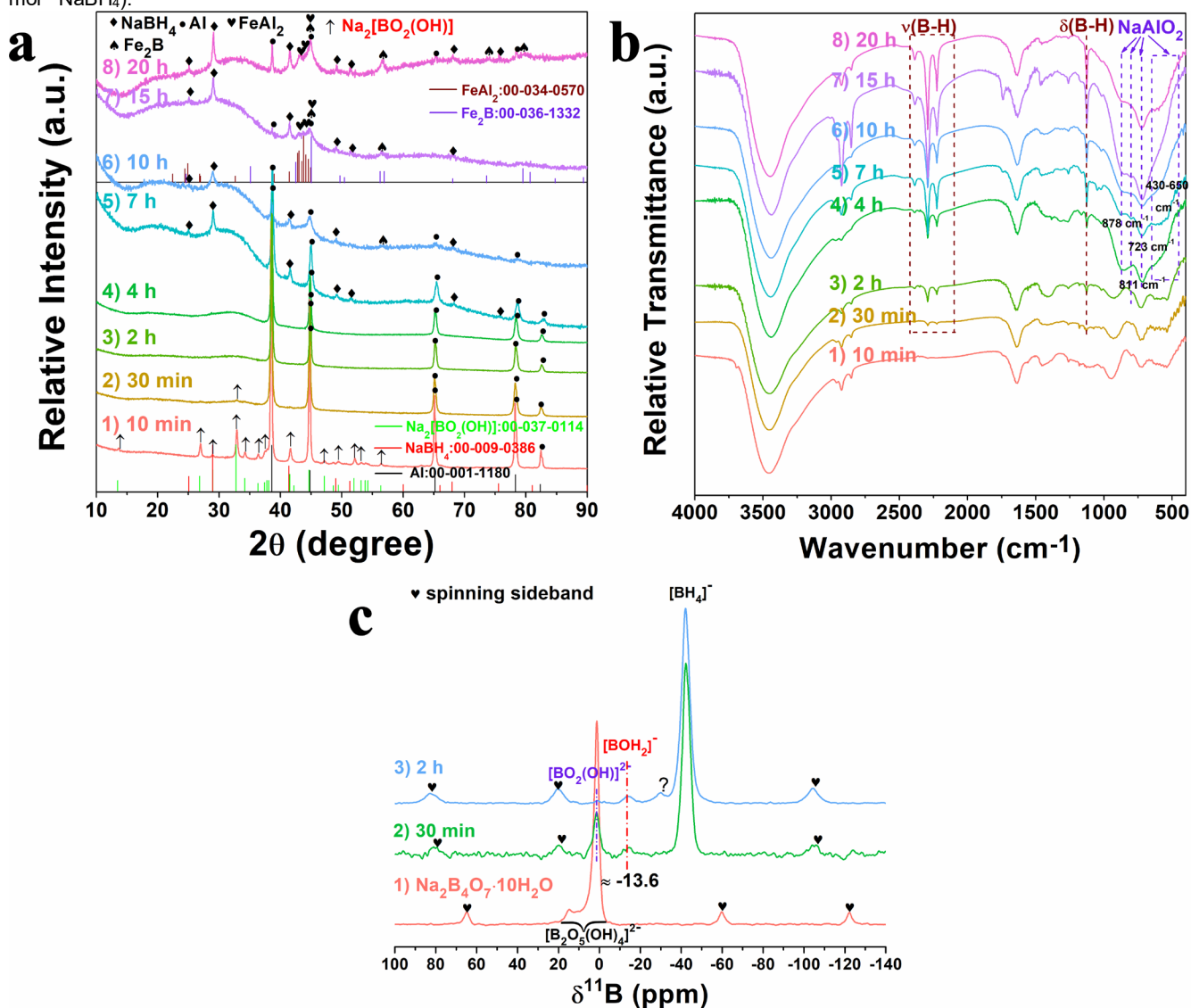


Figure 2. (a) XRD patterns and (b) FTIR spectra of the products obtained after milling $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, NaH , and Al mixtures (in a 1:6:14.16 molar ratio) for different durations; (c) Solid-state ^{11}B NMR spectra of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and products obtained after milling for different durations.

To further understand the process, the as-milled mixtures were also characterized using solid-state ^{11}B NMR. The resonance at around -13.6 ppm is assigned to the special intermediate $[\text{BOH}_2]^-$ 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 NaBH_4 takes place according to the following steps. First, crystal water in $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ firstly reacts with NaH forming NaOH and H_2 . The hydrogen gas molecules are absorbed on Al surfaces and dissociate into H . NaOH then reacts with borax to form $\text{Na}_2[\text{BO}_2(\text{OH})]$ which plays an important role in NaAlO_2 formation. This is in agreement with a previous study where $\text{Na}_2[\text{BO}_2(\text{OH})]$ was obtained from by heating $\text{Na}_2\text{B}_4\text{O}_7$ and NaOH .^[17] Second, since B-O bond with bond length of 1.35 \AA in $\text{Na}_2[\text{BO}_2(\text{OH})]$ are stronger than B-OH (1.439 \AA), B-OH preferentially breaks and combines with H^-

(from the dissociation of H_2 on Al surface) to form $\text{Na}_2[\text{BO}_2\text{H}]$ which was not observed in experiments owing to its high activity and short lifetimes.^[18] Third, O^{2-} in $\text{Na}_2[\text{BO}_2\text{H}]$ bonds with Al releasing electrons to the absorbed H , generating Al-O and H^- . H^- combines with B to form NaBOH_2 , and another Na^+ in $\text{Na}_2[\text{BO}_2\text{H}]$ combines with AlO_2^- forming NaAlO_2 . Finally, B in NaBOH_2 , as a Lewis acid, accepts H^- to replace O^{2-} forming NaBH_4 . This process is similar to what happens during the synthesis of NaBH_4 by reacting sodium borate with Mg and H_2 .^[5h]

Using $\text{Al}_{88}\text{Si}_{12}$ for the synthesis

Based on the report that the yield of NaBH_4 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

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efficiency and therefore facilitate the reaction. Al-rich $\text{Al}_{88}\text{Si}_{12}$ eutectic alloy was chosen to react with NaH and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. In comparison, a mixture of Al and Si powders

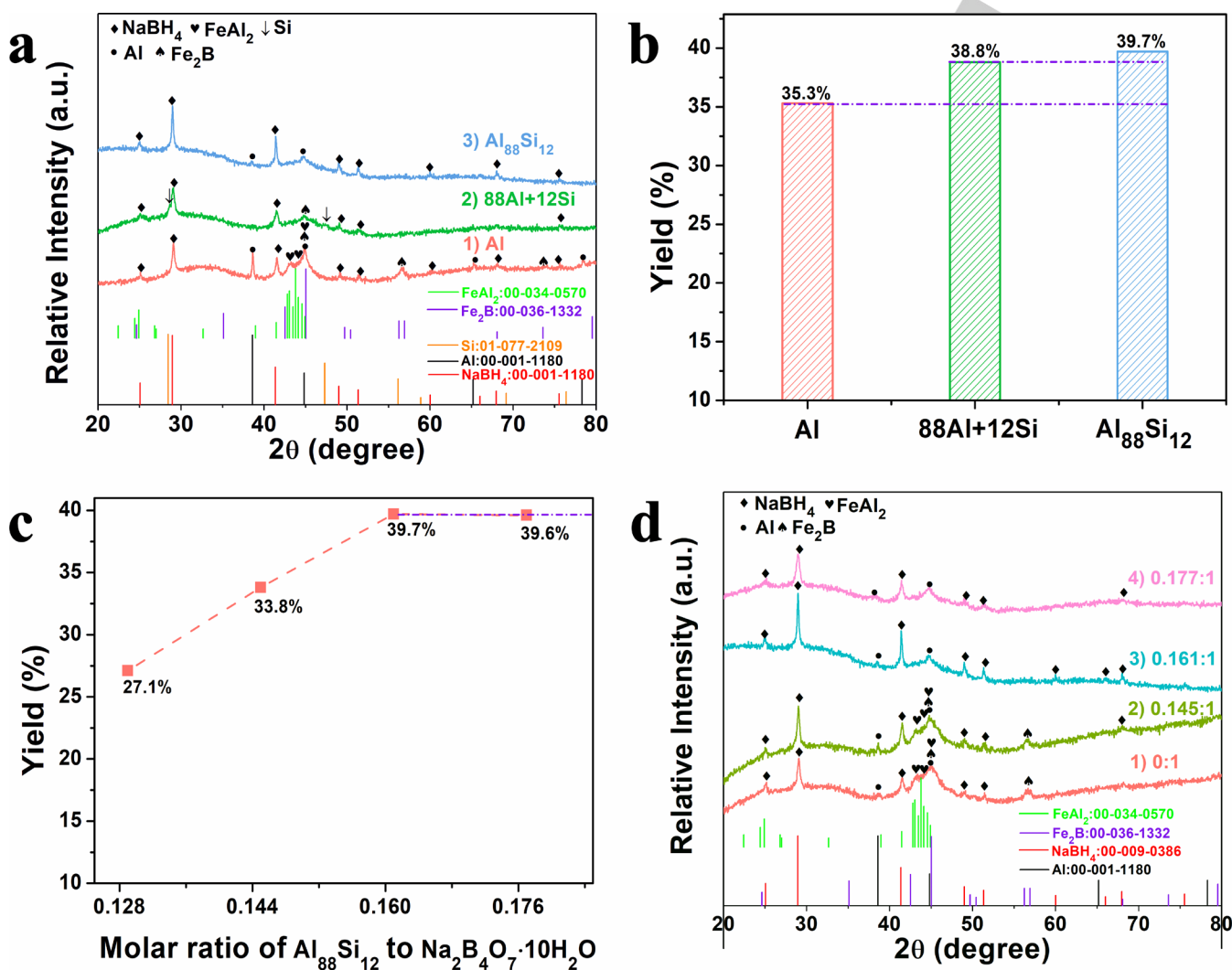


Figure 3. (a) XRD patterns and (b) Yields of NaBH_4 via ball milling the mixtures for 20 h at 1200 CPM: $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, NaH , and Al in a 1:6:14.16 molar ratio; $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, NaH , Al, and Si in a 1:6:14.16:1.92 molar ratio; $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, NaH , and $\text{Al}_{88}\text{Si}_{12}$ in a 1:6:0.161 molar ratio; (c) Impact of $\text{Al}_{88}\text{Si}_{12}$ loading on the yields of NaBH_4 and (d) XRD patterns of the products obtained after milling $\text{Al}_{88}\text{Si}_{12}$ 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 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 FeAl_2 and FeB_2 decreases compared with the experiment without Si (Figure 3a), indicating reduced decomposition of NaBH_4 . The yield increased and then plateaued when more $\text{Al}_{88}\text{Si}_{12}$ was used, and reached the maximum value of 39.7% for the ratio of 0.161:1 ($\text{Al}_{88}\text{Si}_{12}$: $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) (Figure 3b and 3c). The Al/Si mixture also displays similar high yield. The improvement is likely due to suppressed decomposition of NaBH_4 and also increased effective contact between the reactants.

Yield of NaBH_4

As known from previous studies the loadings of reducing agent has an important influence on the NaBH_4 yield.^[5b, 5e, 5g, 6c, 9a, 9b, 10] The yield was optimized by varying the molar ratio of $\text{Al}:\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (Figure 4a). With the increase in the loading of Al, the yield of NaBH_4 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. $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ was replaced by $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ to synthesize NaBH_4 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 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ than in $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$.

To further improve the yield, a milling additive was introduced. Kojima et al. [5a] found that the introduction of Si to $\text{NaBO}_2\text{-Mg-H}_2$ system significantly increased the yield of NaBH_4 . As discussed in the previous section, $\text{Al}_{88}\text{Si}_{12}$ improves the yield to an extent similar to that of Al/Si mixture. Considering that $\text{Al}_{88}\text{Si}_{12}$ is slightly

more expensive than Al, only Si was introduced as an additive. The yield increases with increasing the molar ratio of Si: $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$, reaching the maximum of 61.9% for a ratio of 13.51:1 (Figure 4c), higher than

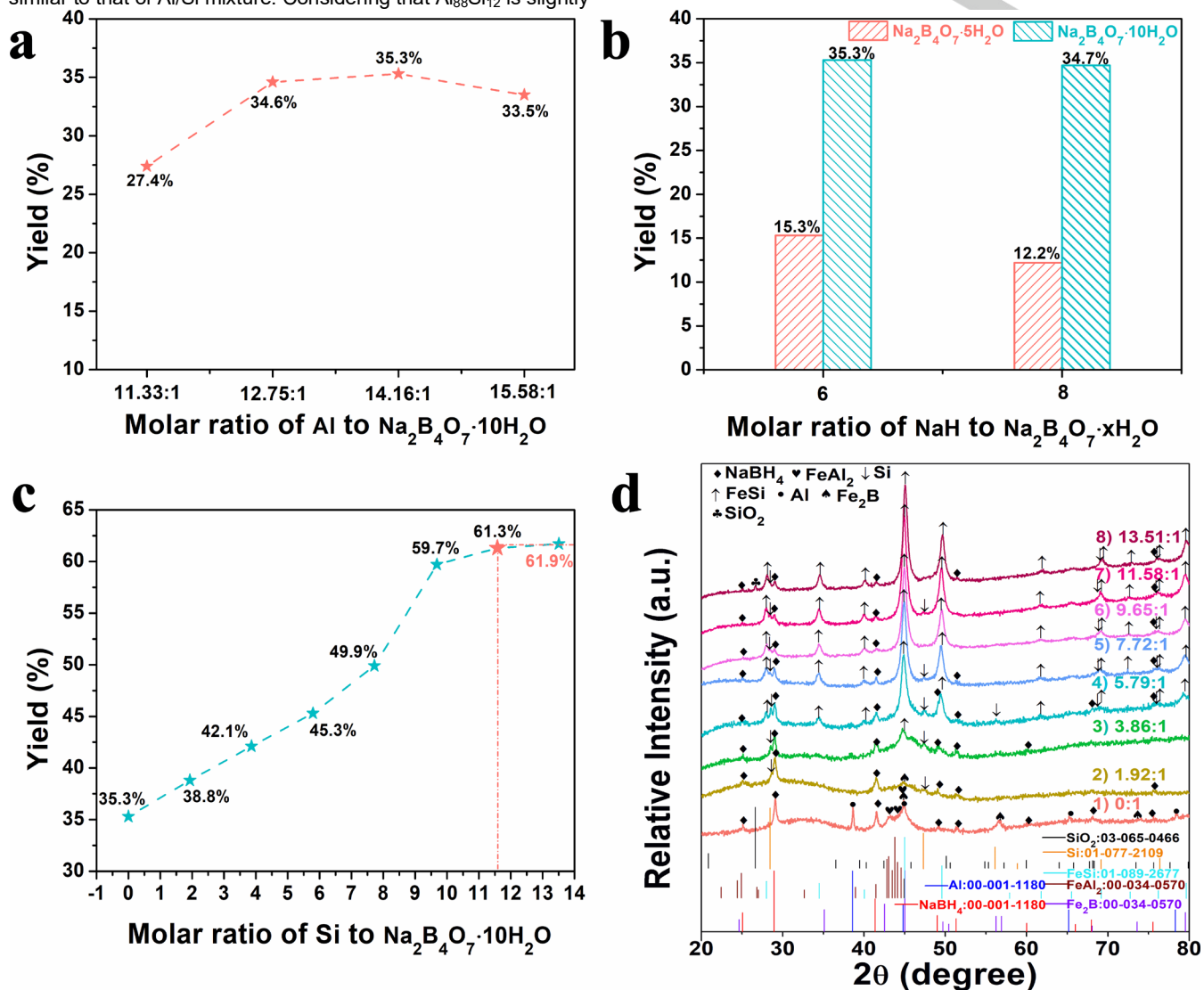


Figure 4. (a) Yields of NaBH_4 obtained after ball milling Al and $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$ in different molar ratios ($\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}:\text{NaH}$ was fixed at a 1:6 molar ratio) for 20 h; (b) Yields of NaBH_4 obtained after 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 FeB_2 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 NaBH_4

$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (ACS-grade, Aladdin), $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ (purity: $\geq 99.5\%$, Chron Chemicals), Al (purity: $\geq 99\%$, Aladdin), $\text{Al}_{88}\text{Si}_{12}$ alloy (purity: 99%, Aike Reagent), Si (powder, 1 μm , Desheng Alloy Materials Co., Ltd), NaOH (purity: $\geq 99\%$, Aladdin), Na_2CO_3 (purity: $\geq 99.8\%$, General-Reagent), and NaH (purity: 90%, Sigma-Aldrich) were used as received for the mechanochemical synthesis of NaBH_4 . All the raw materials except $\text{Na}_2\text{B}_4\text{O}_7 \cdot x\text{H}_2\text{O}$ ($x=5, 10$) are stored in an argon glove box (MIKROUNA, China) with <0.1 ppm H_2O and O_2 . 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. 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.

Quantification of NaBH_4

Anhydrous ethylenediamine ($\text{C}_2\text{H}_8\text{N}_2$, Sigma-Aldrich, purity: 99%) was used to extract NaBH_4 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 ($\text{C}_2\text{H}_8\text{N}_2$) was captured by a cold trap (-54°C). The amount of resultant NaBH_4 was determined by iodimetric analysis [15]. H_2SO_4 (GR), sodium thiosulfate solution ($\text{Na}_2\text{S}_2\text{O}_3$, 0.1000 mol L^{-1}), potassium iodide (KI, purity: $\geq 99\%$), potassium iodate (KIO_3 , AR-grade), and starch indicator ($\geq 99\%$) were used for iodimetric analysis. All these chemicals were purchased from Aladdin and used without further purification. The yield of NaBH_4 was calculated according to formula: ^[9]

$$\text{Yield} = \frac{[(\text{obtained mass NaBH}_4)/(\text{theoretical mass NaBH}_4)] \times 100\%}{3}$$

where the theoretical mass NaBH_4 is calculated based upon the assumption that 1 mole $\text{Na}_2\text{B}_4\text{O}_7 \cdot x\text{H}_2\text{O}$ ($x=5,10$) can produce 4 moles NaBH_4 .

Characterization

The obtained powders were subjected to qualitative analyses using powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and solid-state ^{11}B nuclear magnetic resonance (NMR) spectroscopy. The crystal phase composition of the samples was characterized by XRD using a PANalytical Empyrean with a Cu K α radiation ($\lambda = 0.15418$ nm, step size = 0.262 $^\circ$, 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 $\nu_{\text{R}} = 8.0$ kHz. X-ray photoelectron spectroscopy (XPS) measurements were performed on Thermo Fisher Scientific K-Alpha using an Al K α 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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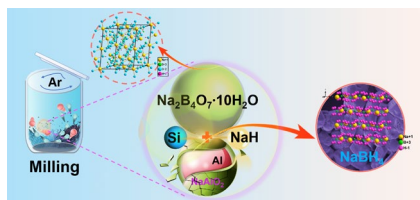
Keywords: aluminum • borax • borohydride • hydrogen • hydrogen storage

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Entry for the Table of Contents

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We report a highly efficient synthesis of NaBH₄ by introducing NaH and Si during the reaction of Na₂B₄O₇·10H₂O with Al.

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