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Synthesis, structural characterization, and hydrogen desorption properties of Na[Al(NH₂BH₃)₄]

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ABSTRACT: Na[Al(NH₂BH₃)₄], a mixed-metal amidoborane, was synthesized by ball-milling (solid method) and the chemical reaction in THF (solution method). Solid method has a tendency to remain unreacted NaAlH₄ and AB. In the solution method, the partial decomposition of Na[Al(NH₂BH₃)₄] would proceed during mixing in THF. The local structural characterization of as-synthesized material was performed by MAS NMR and FT-IR. While Na[Al(NH₂BH₃)₄] desorbed hydrogen in two steps as reported, the results of structural characterization suggested that the hydrogen desorption in the 2nd step would originate from the Al-N-B-H phase. Effect of hydrogen pressure during ball-milling was also investigated for *n*NH₃BH₃-NaAlH₄ (*n* = 1, 4) composites. In the case of *n* = 4, Na[Al(NH₂BH₃)₄] was formed under both Ar and H₂ atmosphere. However, in the case of *n* = 1, Na[Al(NH₂BH₃)₄] was only formed under H₂ atmosphere, whereas most of H₂ was desorbed during ball-milling under Ar atmosphere. Thus,

the hydrogen pressure is necessary for the synthesis in the case of $n = 1$. Potential energy diagram of AB-NaAlH₄ system was described.

Keywords: Amidoborane; Ammonia borane; Sodium alanate; Gas eruption

Introduction

Materials based on a boron-nitrogen (B-N) bond (structure) are promising hydrogen storage materials. In particular, ammonia borane (NH₃BH₃, AB),^{1,2} metal amidoborane ($M(\text{NH}_2\text{BH}_3)_n$),³ hydrazine borane (N₂H₄BH₃),^{4,5} and metal borohydride ammoniates ($M(\text{BH}_4)_n \cdot m\text{NH}_3$)⁶ are attractive materials because of their high gravimetric hydrogen densities. In general, they desorb hydrogen in exothermic reactions between H^{δ+} and H^{δ-}, indicating that the hydrogen absorption of the spent material is thermodynamically impossible.^{7,8} The slow desorption kinetics and by-product gases emission (e.g., ammonia (NH₃), diborane (B₂H₆), and borazine (B₃H₆N₃)) are also drawbacks for applications.^{7,8} Among various kinds of B-N based materials, Al-B-N-H phases have shown excellent hydrogen storage properties.⁹ For instance, Al(BH₄)₃·6NH₃ releases more than 10 mass% of hydrogen below 140 °C with favorable kinetics by a weak exothermic reaction.¹⁰ In another instance, Al(BH₄)₃·NH₃BH₃ can desorb 2 equiv. of hydrogen at 70 °C with an endothermic reaction, suggesting that direct rehydrogenation is possible.¹¹ AB-MAIH₄ ($M = \text{Na, Li}$) system consists of Na(Li), Al, N, B and H, which is similar composition as Al-B-N-H system. By-product gases emitted from AB-MAIH₄ ($M = \text{Na, Li}$) composites were effectively suppressed during the hydrogen desorption compared with those from AB.¹² In the case of 4AB-NaAlH₄ system, the crystal structure and hydrogen desorption

properties of Na[Al(NH₂BH₃)₄] have been reported.¹³ This Al-based amidoborane was synthesized by ball-milling with the following reaction:

Na[Al(NH₂BH₃)₄] showed a large amount of hydrogen desorption (9 mass%) and a partial reversibility by pressurising hydrogen.¹³ Therefore, this material has attracted much attention as a promising hydrogen storage material. The formation of the Al-based amidoborane was also suggested in *n*AB-Li₃AlH₆ (*n* = 4-6) system, which can desorb around 10 mass% H₂ below 200 °C and can be partially regenerable by chemical treatments.¹⁴

In the present study, the structural characterizations of Na[Al(NH₂BH₃)₄] by using XRD, MAS NMR, and FT-IR were performed to obtain the insights about hydrogen desorption process of Na[Al(NH₂BH₃)₄]. NMR is a useful technique to characterize the local structure of metal amidoborane because their dehydrogenated states are amorphous(-like) structure.¹⁵⁻¹⁷ The single-phase synthesis of Na[Al(NH₂BH₃)₄] is also important to characterize the material. Although the synthesis of mixed-metal amidoboranes such as Na[Al(NH₂BH₃)₄] and Na[Li(NH₂BH₃)₂] were performed by ball-milling method,^{13,14,18,19} the reported Na[Al(NH₂BH₃)₄] was not single-phase. On the other hand, there are some reports which focus on the liquid state synthesis of mixed-metal amidoborane²⁰ and solution synthesis of mono-metal amidoborane.^{21,22} In this study, both the ball-milling (solid method) and the chemical reaction in THF (solution method) were employed as the synthesis methods in order to obtain the single-phase of Na[Al(NH₂BH₃)₄]. Since the synthesis of metal amidoborane causes the exothermic dehydrogenation reaction, the

solution method would be effective for unstable material to minimize unfavourable decomposition during the synthesis. We also studied the dependency of milling atmosphere (Ar or H₂) for *n*AB-NaAlH₄ (*n* = 1, 4) composites because hand-mixing of AB and MAlH₄ (*M* = Na, Li) in an agate mortar in an Ar-purified glovebox often causes the gas eruption.¹²

Experimental Section

Sample Synthesis

The starting materials, NH₃BH₃ and NaAlH₄ (purity 97 % and 90 %, respectively), were purchased from Sigma Aldrich Co. Ltd. All samples were handled in a glovebox filled with purified Ar or N₂. Na[Al(NH₂BH₃)₄] was synthesized by ball-milling (solid method) and the chemical reaction in THF (solution method). The solid method was performed by using a planetary ball-milling apparatus (Fritsch Pulverisette 7) with 20 stainless steel balls (7 mm in diameter) and 300 mg samples (NH₃BH₃ : NaAlH₄ molar ratio = 4 : 1, ball : powder weight ratio = 70 : 1). The milling was executed under 1.0 MPa H₂ atmosphere with 300 rpm for 3 hours with six cycles of 30/30 min operation/interval per each cycle in order to avoid an excess heating of sample. This composite was labelled as BM composite. For the solution synthesis method, NaAlH₄ and NH₃BH₃ were mixed by using magnetic stirrer for 3 h in anhydrous THF (Kanto Chemical Co. Inc.) and then solvent was removed by evacuation. Since the product was still sticky paste just after simple evacuation and AB was used more than 4 equivalents of NaAlH₄, the sample was flushed and AB was removed with anhydrous diethyl ether for three times by the following procedure: ether was introduced and stirred for 30 minutes; filtration was operated in order to remove the excess AB from the sample and then; residual substance was evacuated. Finally, we obtained white solvent-free powder. This composite was labelled as SL composite.

We also tried solution method using other solvents and finally we optimized that THF is the best solvent for this reaction. In this case, the ratio of NaAlH₄/THF was about 17 mmol/L. The ratio of NaAlH₄/THF is important for the synthesis of Na[Al(NH₂BH₃)₄] because Na[Al(NH₂BH₃)₄] was not formed when small amount of THF was used.

Characterization

Powder X-ray diffraction (XRD, PANalytical, X'Pert Pro with Cu K α radiation) measurements were performed to investigate the crystalline phases of mixtures. The samples for XRD were placed on a greased glass plate in a glovebox and then covered with a polyimide sheet (Kapton, The Nilaco Co. Ltd.) and sealed by grease in order to avoid the oxidation during measurement. Hydrogen desorption properties were examined by a thermogravimetry and differential thermal analysis equipment (TG-DTA, Bruker, 2000SA) connected to a mass spectrometer (MS, ULVAC, BGM-102). The desorbed gases were carried from TG-DTA to MS through a capillary by 300 mL min⁻¹ stream of high purity He as a carrier gas. The samples were heated from room temperature to 260 °C with a heating rate of 5 °C min⁻¹. Solid-state magic angle spinning - nuclear magnetic resonance (MAS-NMR) spectra were recorded on a JNM-ECA600 spectrometer (JEOL) at a magnetic field of 14.1 T with the ¹¹B, ²³Na and ²⁷Al resonant frequency of 192.6, 159.1 and 156.7 MHz, respectively. All the samples were spun at 15 kHz, using 4 mm ZrO₂ rotors filled in argon atmosphere. Chemical shifts were calibrated by saturated aqueous solutions of H₃BO₃ for ¹¹B, NaCl for ²³Na, and AlCl₃ for ²⁷Al at 19.49, 0.00, and -0.10 ppm, respectively. Fourier transform infrared spectrometer (FT-IR, JASCO Co., FT/IR-6100) was operated in order to observe their vibration modes of the synthesized materials. Each sample was diluted with KBr (mass ratio of sample/KBr = 1:10) and then pelletized for the measurement.

Results and discussion

Structural characterization of Na[Al(NH₂BH₃)₄]

Fig. 1 XRD profiles of SL and BM composites synthesized from AB and NaAlH₄; (a) as-synthesized, and (b) after heating up to 260 °C. Broad diffraction peaks around 20° and 27° originate from the polyimide film and grease to prevent the sample oxidation.

Fig. 1 shows the XRD profiles of composites prepared by both solid (BM composite) and solution methods (SL composite) before and after dehydrogenation. Although their sample amounts were the same, the peak intensity of Na[Al(NH₂BH₃)₄] in BM composite was higher than that in SL composite, suggesting that the crystallinity of Na[Al(NH₂BH₃)₄] in BM composite was higher than that in SL composite. In the case of the SL composite, some unidentified peaks corresponding to impurities were observed in the range of 10-20°. In both composites, the peaks corresponding to AB and/or NaNH₂BH₃ were observed. Although it is difficult to distinguish NaNH₂BH₃ from AB due to close diffraction pattern to each other,²³ we suggested the existence of NaNH₂BH₃

Fig. 2 TG-DTA-MS profiles of SL and BM composites synthesized from AB and NaAlH₄. Heating rate was 5 °Cmin⁻¹.

in these composites by ²³Na NMR, which is discussed later. The peak intensity of NaAlH₄ in BM composite was stronger than that in SL composite, indicating the solid synthesis have a tendency to remain unreacted NaAlH₄. After heating up to 260 °C, NaBH₄ was observed in both SL and BM composites. There is no peak except NaBH₄, but the existence of amorphous phases was suggested in the previous study.¹³

Fig. 2 shows TG-DTA-MS profiles of SL and BM composites. The hydrogen desorption process of Na[Al(NH₂BH₃)₄] was similar to that of AB²⁴ and Na[Li(NH₂BH₃)₂].¹⁸ In the DTA profile of SL composite, an endothermic reaction followed by two exothermic reactions were observed. The endothermic reaction would correspond to the melting/amorphization of the mixture. Two exothermic H₂ desorption reactions in both MS profiles indicate that these reactions are irreversible. Theoretically, 9.5 mass% of hydrogen can be released from Na[Al(NH₂BH₃)₄] in the total decomposition step considering the formation of NaBH₄. The weight losses in the 1st step (RT-140 °C) and the 2nd step (140-260 °C) from TG profile for SL

composite were 7.3 and 5.8 mass%, respectively, where including by-products (NH_3 , B_2H_6 and $\text{B}_3\text{H}_6\text{N}_3$) emission only in the 1st step. Although the profile of BM composite is similar to that of SL composite, there are some minor different features. First, the minor exothermic hydrogen desorption peak at 77 °C appears only in BM composite. This peak would come from the H_2 desorption reaction between unreacted NaAlH_4 and AB as described in the previous study.¹³ Second, the weight loss and H_2 desorption peak in the 1st step (11.1 mass% in Figure 2) were larger than those of SL composite. The total weight loss value (16.8 mass%) was also larger than that of ball-milled composite in ref.13 (-9 mass%). This result would come from a larger amount of by-product gases emission in BM composite probably from the residual AB, NaAB or other intermediates. According to the previous volumetric studies of ball-milled composite, a total hydrogen release amount from 1 eq. of $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ was 6.2 eq. up to 250 °C, which corresponds to 7.4 mass% hydrogen release.¹³

The local structural characterization of $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ was performed by using solid-state NMR. Fig. 3 shows the ^{11}B MAS NMR spectra of SL and BM composites. The peak at -42.4 ppm was observed in both SL and BM composites, which can be assigned to $[\text{BH}_4]$ species as in NaBH_4 .²⁵ This peak intensity in SL composite shows much larger than that in BM composite, suggesting that the partial decomposition of $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ proceed during the synthesis process. Since $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ is probably unstable in THF, synthesis procedure using solution method would be necessary to operate below room temperature in order to obtain single-phase of $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$. The peaks at -24.8 and -24.9 ppm were observed in both SL and BM composites, respectively, while the peak at -25.4 ppm is originated from a $[\text{NBH}_3]$ environment from neat AB.¹⁵ According to the first-principles calculations, the stability of metal amidoborane generally follows the behavior of the metal electronegativities.²⁶ In this context, the

Fig. 3 ^{11}B MAS NMR spectra of SL and BM composites synthesized from AB and NaAlH_4 and a reference material of AB.

Fig. 4 ^{23}Na MAS NMR spectra of SL and BM composites synthesized from AB and NaAlH_4 and a reference material of NaAlH_4 .

Fig. 5 ^{27}Al MAS NMR spectra of SL and BM composites synthesized from AB and NaAlH_4 and a reference material of NaAlH_4 . Spinning sidebands are indicated by asterisks.

small difference in chemical shift could be ascribed to the high electronegativity of Al, which coordinates with $[\text{NH}_2\text{BH}_3]^-$. There was a tendency between the Pauling electronegativity of metal (χ_p) and the ^{11}B chemical shift in alkali metal amidoborane as shown in the previous study.^{15,16} The reason of similar hydrogen desorption temperature of $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ to that of AB would lie on similar ^{11}B chemical shift of the amidoborane to that of AB. Fig. 4 shows the ^{23}Na MAS NMR spectra. Two strong peaks at -11.3 and -6.5 ppm were observed in SL composite, where the peak at -11.3 ppm is similar to the peak in BM composite (-11.2 ppm). Considering the results of XRD and TG-DTA-MS, this peak would be originated in $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ phase. The latter peak position was similar to the peak originating from partially decomposed NaNH_2BH_3 at 84°C (-6.3 ppm).¹⁶ Thus, it was suggested that NaNH_2BH_3 could be formed in SL composite. However, further studies need to be conducted to determine

Fig. 6 ^{23}Na MAS NMR spectra of SL and BM composites synthesized from AB and NaAlH_4 after heating up to 260 °C.

the products in SL composite. A broad and small sharp peak around -8.1 ppm was observed in both SL and BM composites, respectively. This peak corresponds to NaBH_4 .¹⁶ As a result, it was revealed that SL composite contained other Na species except $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$. As-received NaAlH_4 showed two peaks at 94.0 and 13.2 ppm in ^{27}Al MAS NMR spectra (Fig. 5). The peak at 94.0 ppm is ascribed to NaAlH_4 phase and the small peak at 13.2 ppm is consistent with an octahedral coordinated aluminum oxide which is formed on NaAlH_4 .²⁷ This oxide would be formed during sample transportation from the glovebox to NMR apparatus. The peak at 15.0 ppm in the spectrum of BM composite would be ascribed to the aluminum oxide likewise that in NaAlH_4 spectrum. The peak at 110.0 ppm was observed in both SL and BM composites, which is similar to a $[\text{AlN}_4]$ environment (115 ppm).²⁸ Therefore, this peak would be attributed to $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$. Substitution of $[\text{NH}_2\text{BH}_3]^-$ for H^- induced substantial changes of the electronic state of Al and, therefore, would result in weaker shielding of Al atom in the amidoborane than that in NaAlH_4 . There are two broad peaks around 46.1 and 11.3 ppm in the spectrum of SL composite, which is similar peak position to that in other Al-N-B-H phases.^{10,29}

Thus, these peaks could be corresponding to amorphous Al-N-B-H phase. As shown in Fig. 6, both SL and BM composites after the decomposition showed the only peak at -8.8 ppm in ^{23}Na MAS NMR spectra, which can be assigned to NaBH_4 (-8.4 ppm).²⁵ This result indicates that $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ would decompose to NaBH_4 and amorphous Al-N-B-H phase, which has been suggested in the previous study.¹³ However, our results verified that Na species after the decomposition was only NaBH_4 . The characterization of structure/composition of amorphous Al-N-B-H phase is currently in progress. As shown in Fig. 2, $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ has two decomposition steps. Fig. S1 shows the XRD profiles of BM composite after heating up to each temperature. Fig. S1 showed that NaBH_4 was formed after the 1st decomposition step and the XRD peak intensity of NaBH_4 after the 2nd step was almost the same as that after the 1st step. This result indicates that NaBH_4 would form only after the 1st decomposition step and the 2nd decomposition step would be ascribed to the decomposition of amorphous Al-N-B-H phase. In fact, the hydrogen desorption profile in the 2nd step is similar to that of $\text{Al}(\text{NH}_2\text{BH}_3)_3$.³⁰

Fig. S2 shows FT-IR spectra of SL and BM composites and references. The IR spectra of SL and BM composites showed the similar spectra to AB and previously reported $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$.¹³ As shown in Fig. S2(a), both spectra exhibit several distinct bands for the N-H ($1500\text{-}1650$ and $3200\text{-}3430\text{ cm}^{-1}$) and B-H ($1100\text{-}1150$ and $2340\text{-}2420\text{ cm}^{-1}$) vibration modes. The absence of Al-H vibration mode is consistent with ^{27}Al MAS NMR results (Fig. 5). After heating up to 260°C , the intensities of N-H stretching modes were markedly decreased in both composites as shown in Fig. S2(b). This phenomenon is often observed in metal amidoborane system.^{14,31,32} The vibration mode for $1300\text{-}1600\text{ cm}^{-1}$ was observed in both composites, which was assigned to in-plane B-N transverse optical modes of h-BN.³³ The B-H vibration modes in both composites would be originated from NaBH_4 . In the IR spectra of

AlN/BN mixture materials, the band for Al-N stretching mode ($600\text{--}800\text{ cm}^{-1}$) was observed.³⁴ These spectra after heating also showed the similar band positions, suggesting the presence of Al-N group in the decomposition product. In the SL composite, C-H bond ($2800\text{--}3000\text{ cm}^{-1}$) was observed after heating, which is probably originated from solvent (THF or ether) contaminated by vapor in glovebox during sample preparation. As the short summary of above results, the existence of Al-N, B-N, B-H and N-H groups in Fig. S2(b) suggests the formation of Al-N-B-H phase after the decomposition.

Effect of hydrogen pressure during ball-milling

Fig. 7 XRD profiles of as-synthesized AB-NaAlH₄ composites prepared by ball-milling (300 rpm, 20 min) with different milling atmospheres; (a) 0.1 MPa Ar, and (b) 0.1 MPa H₂.

Hand-mixing of AB and $M\text{AlH}_4$ ($M = \text{Na}, \text{Li}$) in an agate mortar in an Ar-purified glovebox often causes the gas eruption as shown in Fig. S3. After the gas eruption, $M\text{BH}_4$ ($M = \text{Na}, \text{Li}$) and Al phases were formed.¹² In order to suppress the gas eruption, milling under H₂ atmosphere was conducted in $n\text{AB-NaAlH}_4$ composites ($n = 1, 4$). In the case of $n = 1$, the results were different with Ar and H₂ atmospheres. Fig. 7 shows the XRD profiles of AB-NaAlH₄ composites

Fig. 8 XRD profile of AB-NaAlH₄ composite prepared by ball-milling (200 rpm, 5 min, 1.0 MPa H₂ atmosphere) followed by heating up to 75 °C for 2 hrs under 1.0 MPa H₂ atmosphere.

prepared by ball-milling under Ar and H₂ atmosphere. In the case of Ar atmosphere, the reaction was similar to hand-mixed mixture. The decomposition during milling would occur to form NaBH₄ and Al. In the case of H₂ atmosphere, NaAlH₄ was remained and unknown phases were generated. Thus, the hydrogen pressure is necessary for suppressing the gas eruption in AB-NaAlH₄ composite. In the case of 4AB-NaAlH₄ composite, Na[Al(NH₂BH₃)₄] was formed under both Ar and H₂ atmospheres. AB could melt during ball-milling because of its low melting temperature at 104 °C.³⁵ If AB melts and NaAlH₄ does not melt during milling by the reaction heat, sample temperature would not rise over 104 °C because of the large heat capacity. Therefore, the larger heat capacity of 4AB-NaAlH₄ composite than that of AB-NaAlH₄ composite could suppress the gas eruption reaction. In order to clarify the detailed mechanism of gas eruption reaction, the heat capacity and thermal conductivity of samples should be considered.

Na[Al(NH₂BH₃)₄] was also formed in AB-NaAlH₄ composite prepared by milling (5 min) under 1.0 MPa H₂ atmosphere followed by heating under 1.0 MPa H₂ atmosphere (Fig. 8). This

Fig. 9 Potential energy diagram of AB-NaAlH₄ system under Ar and H₂ atmospheres.

composite released 6.2 mass% H₂ with no by-product gases emission (Fig. S4). Thus, NaAlH₄ was effective to decrease the by-product gases emission. Similar results were obtained in the composite milled for 3 hours under H₂ atmosphere in terms of by-product gases emission. By-product gases emission was effectively suppressed and the desorbed hydrogen amount was 5.0 mass% (Fig. S5). Only NaAlH₄ was observed in the XRD profile of as-milled sample (Fig. S6(a)). The disappearance of Na[Al(NH₂BH₃)₄] in the profile suggests that new amorphous compound would form in AB-NaAlH₄ composite milled for 3 hours. Although 4AB-NaAlH₄ composite (Na[Al(NH₂BH₃)₄]) was soluble in THF, AB-NaAlH₄ composite synthesized in THF was not soluble in THF. This phenomenon also suggests the formation of new compound. After heating up to 260 °C, NaBH₄ and Al were observed (Fig. S6(b)). These phases were also observed in the decomposition products of hand-mixed mixture.¹²

As the summary of above results, the energy diagram in AB-NaAlH₄ system is shown in Fig. 9. In the case of hand-mixing or ball-milling under Ar atmosphere, an exothermic gas eruption occurs to form NaBH₄, Al and Al-N-B-H phase. Most of the H₂ would be desorbed during the procedure. However, when the milling and heating are performed under H₂ atmosphere, the gas eruption reaction is suppressed. Instead of the reaction, Na[Al(NH₂BH₃)₄] is formed. Thus, the hydrogen pressure is necessary for the solid synthesis in AB-NaAlH₄ composite. This composite released 6.2 mass% H₂ up to 200 °C and by-product gases emission was effectively suppressed due to the existence of NaAlH₄. The suppression of NH₃ could be explained by the reaction between NaAlH₄ and NH₃. It is known that LiAlH₄ can react with NH₃ to form H₂ gas.³⁶ Therefore, the similar reaction could occur in the AB-NaAlH₄ composite. The suppression of B₂H₆ would be explained by the preferential formation of NaBH₄, which is thermodynamically stable than NaAlH₄.³⁷ Thus, NaAlH₄ is an effective additive to decrease by-product gases emission from AB. Although the present study focuses on AB-NaAlH₄ system, we expect to apply the hydrogen pressure to AB-LiAlH₄ system because this system also causes a gas eruption reaction during milling under Ar atmosphere.¹²⁻¹⁴

Conclusion

Na[Al(NH₂BH₃)₄] was synthesized by solid and solution methods. In case of the solution method, the partial decomposition of Na[Al(NH₂BH₃)₄] would proceed during mixing in THF. The synthesis below room temperature would be necessary in order to obtain single-phase of Na[Al(NH₂BH₃)₄] by solution method. Considering unreacted NaAlH₄ and AB tend to remain in the solid method, the solution method would become the better way to synthesize single-phase of Na[Al(NH₂BH₃)₄] if the synthesis procedure is

appropriately controlled. The synthesized $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ showed two hydrogen desorption steps up to 260 °C. By-product gases (NH_3 , B_2H_6 and $\text{B}_3\text{H}_6\text{N}_3$) were emitted in the 1st step, whereas only hydrogen gas was emitted in the 2nd step. The desorbed hydrogen amount in the 2nd step was around 6 mass%. The results of structural characterization suggested that the hydrogen desorption in the 2nd step would originate from decomposition of amorphous Al-N-B-H phase. Effect of hydrogen pressure during ball-milling was also investigated for $n\text{AB-NaAlH}_4$ ($n = 1, 4$) composites. In the case of $n = 4$, $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ was successfully synthesized under both Ar and H_2 atmosphere. However, in the case of $n = 1$, $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ was only formed under H_2 atmosphere. On the other hand, gas eruption reaction occurs during ball-milling under Ar atmosphere. Thus, the hydrogen pressure is necessary for suppressing the gas eruption in the case of $n = 1$. By-product gases emission was suppressed in AB-NaAlH_4 composite. This result indicates that NaAlH_4 is an effective additive to decrease by-product gases emission from AB. From these results, potential energy diagram of AB-NaAlH_4 system was described.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/>.

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