

# The Hydrogen-Enriched Al–B–N System as an Advanced Solid Hydrogen-Storage Candidate\*\*

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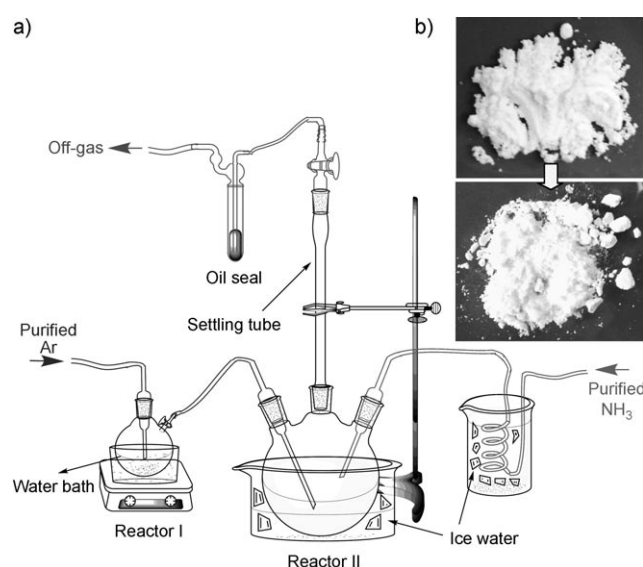
After decades of intensive exploration, dehydrogenation based on a simple combination mechanism between  $H^{\delta+}$  and  $H^{\delta-}$  was demonstrated to be a promising strategy to explore possible hydrogen-storage candidates, and in particular ammonia–borane (AB) and related B–N-based materials,<sup>[1]</sup> such as  $M(NH_2BH_3)_m$ , where  $M = Li, Na, Ca, C(NH_2)_3BH_4, N_2H_4BH_3$ , and  $M(BH_4)_m \cdot nNH_3$  ( $M = Li, Mg$ ).<sup>[2–6]</sup> In many cases, high gravimetric hydrogen densities and favorable dehydrogenation targets established for hydrogen storage could be easily satisfied based on the simple combination mechanism, but most such materials suffer from unfavorable thermodynamics, that is, a strong exothermic dehydrogenation reaction, which is theoretically infeasible for direct rehydrogenation.<sup>[1,2–4]</sup> Although indirect chemical routes to regenerate the composite from their decomposed products do provide a feasible solution,<sup>[5,7]</sup> the design and synthesis of new B–N-based materials with favorable thermodynamics may be a more promising route towards a satisfactory solution. Taking into account previous experience<sup>[1–8]</sup> on the main factors involved, that is, the forms and linking modes of B–H and N–H groups, that could affect the thermodynamics of B–N-based materials, we have developed a new hydrogen-enriched Al–B–N system (ammoniates of aluminum borohydride) that shows a weak exothermic dehydrogenation with high hydrogen capacity at mild temperatures, which is competitive with most of the current B–N-based candidates.

$Al(BH_4)_3$  is one of the borohydrides that is richest in hydrogen, but it is not feasible for hydrogen storage owing to its volatility at room temperature and instability, involving release of borane upon heating.<sup>[9–12]</sup> However, its hexamine compound,  $Al(BH_4)_3 \cdot 6NH_3$ , which has a theoretical hydrogen capacity of 17.4 wt %, will not sublime in a vacuum, even up to its decomposition temperature.<sup>[9–11]</sup> More importantly, this compound exhibits the potential for hydrogen storage based on a similar  $H^{\delta+}$  and  $H^{\delta-}$  combination mechanism to that

mentioned above. Unfortunately, its dehydrogenation properties have remained unknown until now, which may be due to the difficulty in its synthesis.

Synthesis of ammonia complexes of  $Al(BH_4)_3$  could be realized through a reaction of  $Al(BH_4)_3$  with ammonia, which was first reported in 1940<sup>[9]</sup> and later confirmed in 1961.<sup>[10]</sup> In the conventional synthesis, a two-step procedure is involved in which  $Al(BH_4)_3$  is first prepared and separated at low temperatures, and then liquid  $Al(BH_4)_3$  or its solution at low temperatures ( $-78^\circ C$ ) is utilized to react with ammonia to produce  $Al(BH_4)_3 \cdot 6NH_3$ .<sup>[11]</sup> However, there are two serious challenges for the above procedures: 1) Removing the volatile impurity (borane), which is always associated with the formation of  $Al(BH_4)_3$ ; and 2) storing the volatile  $Al(BH_4)_3$ , the vapor of which detonates spontaneously and violently on contact with air that contains even traces of moisture. To overcome these obstacles, employment of fractional distillation to remove the borane by-product and low-temperature conditions to store the purified  $Al(BH_4)_3$  have to be adopted. Thus, sophisticated apparatus (Supporting Information, Figure S1) and strict procedures are required during the preparation.<sup>[9,11]</sup>

With the aim of solving the above technical issues, we have developed a convenient one-step route with simple apparatus and operations (Figure 1 a; Supporting Information, Figure S2) for synthesis of  $Al(BH_4)_3 \cdot 6NH_3$ , in which the



**Figure 1.** a) Preparation of  $Al(BH_4)_3 \cdot 6NH_3$ . Reactor I and Reactor II correspond to the reactions of Equation (1) and Equation (2), respectively. b) Photographs of  $Al(BH_4)_3 \cdot 6NH_3$  powder before (top) and after exposure to dry air for 9 days (bottom).

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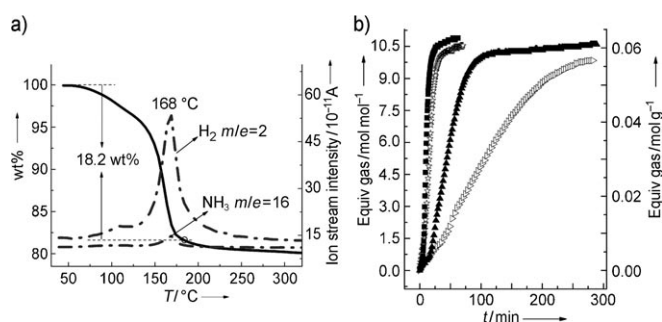
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direct separation and purification of  $\text{Al}(\text{BH}_4)_3$ , obtained by the reaction of either sodium borohydride or lithium borohydride with aluminum chloride [Eq. (1)] are not required. The  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  is synthesized by passing a stream of  $\text{Al}(\text{BH}_4)_3$ , diluted in argon and purified by aluminum powder, into dry ammonia at around  $0^\circ\text{C}$  [Eq. (2)] for more than 6 h.



The product, a white powdery solid with controllable morphology and particle size in the range of  $50\text{ nm} - 1\text{ }\mu\text{m}$  (Figure 1b; Supporting Information, Figure S3), depending on the velocity and concentration of the flowing  $\text{Al}(\text{BH}_4)_3$  gas, was confirmed to be  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  by high-resolution X-ray diffraction (XRD) measurements (Supporting Information, Figure S4 and Table S1) and with satisfactory purity. Eliminating the ammonia exposure stage or poor contact between product and ammonia will result in insufficient uptake of ammonia, producing some intermediates (Supporting Information, Figure S5). These intermediate phases can be transformed to  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  by prolonging the exposure time. As much as 10 g of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  can be prepared at one time in our laboratory, with a yield of more than 80%. The synthesized  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  was found to be relatively inert to air, and no apparent variation, just a slight agglomeration, was observed after exposure to dry air for 9 days (Figure 1b), which is an important advantage for a hydrogen storage system.

The thermogravimetry/mass spectroscopy (TG/MS) results (Figure 2a) revealed that the dehydrogenation of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  occurred in the temperature range of  $60 -$



**Figure 2.** a) TG (—) and MS (---) profiles for  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  at a heating rate of  $10^\circ\text{C min}^{-1}$  in argon. b) Isothermal TPD curves for the decomposition of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$ .  $\triangleright$   $139^\circ\text{C}$ ,  $\blacktriangle$   $149^\circ\text{C}$ ,  $\star$   $160^\circ\text{C}$ ,  $\blacksquare$   $174^\circ\text{C}$ .

$180^\circ\text{C}$ , and was accompanied by a trace of ammonia release in the same temperature range. No  $\text{B}_2\text{H}_6$  and/or  $[\text{NHBH}]_n$  by-products were detected (Supporting Information, Figure S6), and the hydrogen evolution was calculated to be 11.8 wt% (with a purity of 94.6 mol%) from room temperature to  $300^\circ\text{C}$  (Table 1). The isothermal volumetric temperature-programmed desorption (TPD) results for  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  (Figure 2b) revealed that its dehydrogenation could proceed

**Table 1:** Calculated capacity and purity of  $\text{H}_2$  released from  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  and its composites.

| Samples <sup>[a]</sup>                                               | Wt% $\text{H}_2$ capacity <sup>[b]</sup> | Mol% $\text{H}_2$ <sup>[b]</sup> | Equiv $\text{H}_2$ <sup>[c]</sup> |
|----------------------------------------------------------------------|------------------------------------------|----------------------------------|-----------------------------------|
| $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$                        | 11.8                                     | 94.6                             | 10.2                              |
| Composite I                                                          | 11.7                                     | 97.8                             | 12.4                              |
| Composite II                                                         | 11.1                                     | 97.2                             | 15.1                              |
| Composite III                                                        | 7.8                                      | 91.8                             | 14.5                              |
| Composite IV                                                         | 12.2                                     | 97.7                             | 16.0                              |
| $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$ at $139^\circ\text{C}$ | 11.1                                     | 96.8                             | 9.6                               |
| Composite I at $140^\circ\text{C}$                                   | 10.1                                     | 99.6                             | 10.7                              |
| Composite II at $120^\circ\text{C}$                                  | 7.7                                      | 97.3                             | 10.2                              |
| Composite IV at $120^\circ\text{C}$                                  | 7.8                                      | 98.0                             | 10.2                              |
| Composite IV at $100^\circ\text{C}$                                  | 7.8                                      | 99.1                             | 10.2                              |

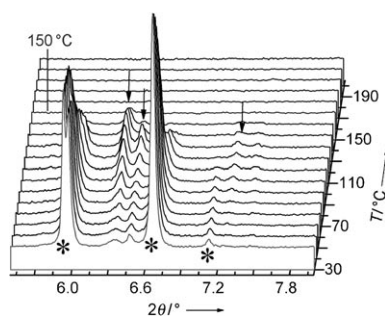
[a] Non-isothermal and isothermal heat treatment of the samples corresponding to Figure 2, Figure 4, and Supporting Information, Figure S15 and S18. [b] The capacity and purity of  $\text{H}_2$  emission gas were determined using gravimetric and volumetric results, with the assumption that the impurity was only  $\text{NH}_3$  to facilitate calculations. [c] Mol of  $\text{H}_2$  released per mol of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$ .

slowly at  $139^\circ\text{C}$ , releasing 11.6 wt% hydrogen within 7 h. Higher operating temperatures resulted in faster dehydrogenation: for example, at  $160^\circ\text{C}$ , 11.9 wt% hydrogen, corresponding to 10.3 equiv of  $\text{H}_2$  with a purity of 96.8 mol%, can be achieved within 1 h. Arrhenius treatment of the isothermal data yields an apparent activation energy  $E_a$  of  $105.5\text{ kJ mol}^{-1}$  (Supporting Information, Figure S7), indicating moderate kinetics. Moreover, it is noteworthy that no material foaming and expansion, a problem suffered by many other B–N–H systems was observed during its decomposition (Supporting Information, Figure S8). Meanwhile, the stability of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  in air was further confirmed by the decomposition studies, from which less than 20% dehydrogenation degradation was observed after exposure of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  to dry air for 9 days (Supporting Information, Figure S9). The results above clearly demonstrates the advantages and potential of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  as an advanced hydrogen-storage candidate.

To understand the hydrogen release pathway, Fourier-transform infrared spectroscopy (FTIR) was employed to follow the decomposition of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  in the range of  $25 - 210^\circ\text{C}$  (Supporting Information, Figure S10). The spectrum of the as-prepared  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  was in agreement with a previous report, indicating a salt-like structure with  $[\text{Al}(\text{NH}_3)_6]^{3+}$  and  $\text{BH}_4^-$  ions in this compound.<sup>[13]</sup> During the heat treatment, only an intensity decrease in the characteristic absorption bands for  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  can be observed below  $160^\circ\text{C}$ , which indicates its partial decomposition, resulting in a small amount of hydrogen and ammonia evolution. After dehydrogenation at  $210^\circ\text{C}$ , all the absorption bands assigned to the  $\text{NH}_3$  group and  $\text{BH}_4^-$  ion have disappeared, which strongly suggests that both the  $\text{NH}_3$  group and the  $\text{BH}_4^-$  ion contribute to the hydrogen release. Meanwhile, the disappearance of all Al–N<sub>6</sub> bonds was also observed, indicating a total structural transformation of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$ . The  $^{11}\text{B}$  NMR spectra of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  (Supporting Information, Figure S11) showed a single boron species ( $\delta = -36.7\text{ ppm}$ ), which is similar to that for  $\text{Al}(\text{BH}_4)_3$  ( $\delta = -36.5\text{ ppm}$ ),<sup>[14]</sup> indicating the assignment of this boron to

the boron nucleus in the tetrahedral  $\text{BH}_4^-$  unit, consistent with the results of FTIR. After heat treatment at  $210^\circ\text{C}$ , two  $^{11}\text{B}$  resonances appeared at  $\delta = 17.7$  and  $-0.9$  ppm, along with the disappearance of the peak ascribed to  $\text{BH}_4^-$ , suggesting the interaction of  $\text{BH}_4^-$  with the  $\text{NH}_3$  group in  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  and leading to the formation of tricoordinate ( $\delta = 17.7$  ppm) and tetracoordinate ( $\delta = -0.9$  ppm) boron atoms, respectively.<sup>[15]</sup> The  $^{27}\text{Al}$  NMR spectrum of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  has a symmetric peak centered at  $\delta = 9.1$  ppm, which is assigned to the six-coordinated aluminum atom in the compound. After heat treatment at  $210^\circ\text{C}$ , a principal signal at around  $\delta = 106.0$  ppm, along with two signals at  $\delta = 32.1$  and  $9.1$  ppm, was observed, which may correspond to four-, five-, and six-coordinate aluminum, respectively,<sup>[16]</sup> suggesting breakage of the  $\text{N} \rightarrow \text{Al}^{3+}$  coordination bond, consistent with the results of FTIR.<sup>[13]</sup> XRD results indicate that some new intermediates appeared in the  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  sample heated to  $160^\circ\text{C}$ , and after dehydrogenation at  $210^\circ\text{C}$ , a poorly crystalline product was obtained (Supporting Information, Figure S12). These intermediates could not be identified in the database, but match well with the impure phase of insufficiently ammoniated  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  (Supporting Information, Figure S5). This observation confirms its composition with lowered coordination of  $\text{NH}_3$ , which may result from the fractional ammonia dissociation of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$ , as indicated by the MS results (Figure 2).

High-resolution in-situ XRD results (Figure 3; Supporting Information, Figure S13) provide further information to help understand the decomposition process. At  $30^\circ\text{C}$ , along with



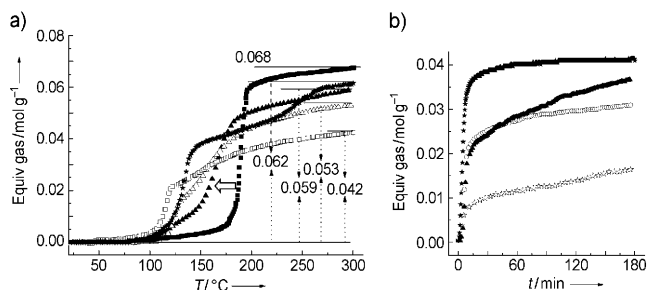
**Figure 3.** Selected parts of the in-situ XRD patterns for  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$ . The sample was heated to a scheduled temperature at a heating rate of  $6^\circ\text{C min}^{-1}$  and then held for 8 min to allow collection of the data. The stars indicate  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$ , and arrows indicate an intermediate phase.

the  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  phase, traces of the intermediate phase appeared. With increasing temperature, a gradual decrease in intensity for  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  and an intensity increase for the intermediate phase are observed, and upon heating to  $140^\circ\text{C}$ , only the intermediate phase is present in the diffraction pattern, indicating a trend in which  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  produces the intermediate phase during heating. Further heating leads to a decrease in intensity of the intermediate phase and finally yields the amorphous phase at about  $160^\circ\text{C}$ . Therefore, the main reactions of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  that proceed during heating can be summarized as a phase transformation of  $\text{Al}$ -

$(\text{BH}_4)_3 \cdot 6\text{NH}_3$  to produce an intermediate phase with lowered coordination of ammonia and dehydrogenation of the intermediate phase to form an amorphous B–N-related compound. Although the nature of the intermediate phase is not very clear, by combining the NMR, FTIR, and XRD results and the evolution of more than 10 equivalents of  $\text{H}_2$  from the decomposed  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$ , it may be concluded that the dehydrogenation of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  is also based on the combination mechanism of  $\text{H}^{\delta+}$  and  $\text{H}^{\delta-}$ .

In ammonia complexes of metal borohydrides, B–H and N–H groups are drawn together by the metal ion, achieving the basic requirement of their combination.<sup>[6]</sup> However, the metal ion, depending on the element, has a varied influence on both  $[\text{BH}_4]^-$  and  $\text{NH}_3$ , such as electronegativity and polarity of the  $[\text{BH}_4]^-$  group and N–H bond, resulting in differing abilities to promote combination to achieve hydrogen release. In light of the decomposition properties of  $\text{LiBH}_4 \cdot \text{NH}_3$  and  $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ , it seems that a stronger ability to promote coordination between the metal ion and ammonia may lead to more favorable dehydrogenation, probably resulting from more polarized N–H bonds, as the lone pair electrons of the nitrogen atom are more strongly attracted by the metal ions, and closer-packed  $[\text{BH}_4]^-$  and  $\text{NH}_3$ , which favors the combination and the formation of N–H–H–B dihydrogen bonds.<sup>[2]</sup> In the case of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$ , a stronger  $\text{N} \rightarrow \text{Al}^{3+}$  coordination bond is expected, which contributes positively to the combination of  $\text{H}^{\delta+}$  and  $\text{H}^{\delta-}$ , achieving a maximum hydrogen release rate at around  $163^\circ\text{C}$ , which is  $42^\circ\text{C}$  lower than that of  $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ . However, the accompanying ammonia emission is fatal for practical applications. From the viewpoint of the  $\text{H}^{\delta+}$  and  $\text{H}^{\delta-}$  balance, as well as the XRD results (Figure 3; Supporting Information, Figure S5, S12), the excess N–H groups present in  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  may account for evolution of the  $\text{NH}_3$  impurity. Thus, a strategy aimed at balancing  $\text{H}^{\delta+}$  and  $\text{H}^{\delta-}$  and further reinforcing the  $\text{N} \rightarrow \text{Al}^{3+}$  coordination bond is expected to further improve its dehydrogenation.

To confirm our assumption above, experiments on decreasing the coordination number of ammonia and supplying more  $[\text{BH}_4]^-$  by mixing  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  with  $\text{AlCl}_3/\text{LiBH}_4$  additive were performed (Figure 4). After mixing  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  with  $\text{AlCl}_3/\text{LiBH}_4$ , the formation of new phases (Supporting Information, Figure S14) by the reaction



**Figure 4.** TPD results for  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  and its composites: I:  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3/0.2 \text{ AlCl}_3/0.6 \text{ LiBH}_4$ ; II:  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3/0.5 \text{ AlCl}_3/1.5 \text{ LiBH}_4$ ; III:  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3/\text{AlCl}_3/3 \text{ LiBH}_4$ ; IV:  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3/0.2 \text{ AlCl}_3/3 \text{ LiBH}_4$ . a) Non-isothermal plot ( $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  ■, I ▲, II △, III □, IV ☆) and b) isothermal plots at  $120^\circ\text{C}$  (I ☆, II ▲, III □, IV ☆).

of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  with the supplementary  $\text{Al}(\text{BH}_4)_3$  produced from the  $\text{LiBH}_4/\text{AlCl}_3$  mixture was observed. Given that the new phase of composite I is similar to the intermediate phase discussed above (Supporting Information, Figure S5), it is suggested that the newly formed phases may consist of  $\text{Al}(\text{BH}_4)_3$  with a lower  $\text{NH}_3$  coordination number,  $\text{Al}(\text{BH}_4)_3 \cdot n\text{NH}_3$  ( $n < 6$ ). The dehydrogenation results show that the hydrogen release purity could be enhanced to above 99 mol % without apparent reduction of practical dehydrogenation capacity (composite I at 140 °C; Table 1; Supporting Information, Figure S15). Meanwhile, isothermal differential scanning calorimetry (DSC) result shows that the enthalpy of hydrogen release from composite I at 140 °C is weakly exothermic ( $-2.7 \text{ kJ mol}^{-1} \text{ H}_2$ ; Supporting Information, Figure S16), which is much less than that of AB ( $-21 \text{ kJ mol}^{-1}$ ),<sup>[1]</sup> indicating a favorable thermodynamics for Al–B–N–H system. Furthermore, it was found that excess  $\text{LiBH}_4$ , which will react with the  $\text{Al}(\text{BH}_4)_3 \cdot n\text{NH}_3$  to produce unidentified new phases (Supporting Information, Figure S17), may lead to a further improvement of dehydrogenation. In the case of composite IV, hydrogen capacities of 7.8 wt % were released at 100 °C and 120 °C within 3 h and 1.5 h, respectively. (Table 1; Supporting Information, Figure S18), which are quite close to the criteria of an ideal hydrogen storage material. The above experiments have demonstrated the likelihood of our assumption, providing a possible solution for the Al–B–N–H system to achieve more favorable hydrogen storage properties. More detailed research is still in progress.

In summary,  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  was synthesized by a facile and novel gas-phase reaction. It has been demonstrated that  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  is a promising solid hydrogen storage material and presents significant advantages over most other current candidates, which offers us a prospect and a strategy to achieve a practical product that might meet the criteria for an ideal solid-state hydrogen storage material, if the problems relating to reversibility and impurity, which appear to have feasible solutions, are overcome by further efforts.

## Experimental Section

The source materials,  $\text{LiBH}_4$  95 % (Sigma–Aldrich, USA),  $\text{AlCl}_3$  99.99 %, Al powder (345 mesh), and  $\text{NH}_3$  (Alfa Aesar, China), were obtained commercially.  $\text{LiBH}_4$  and  $\text{AlCl}_3$  were ball-milled for 1 h before use. Aluminum powder was used as received.  $\text{NH}_3$  was purified by soda lime when used. All handling, except for ammonia-related procedures, was conducted under anaerobic and anhydrous conditions by Schlenk techniques and in a glove box filled with argon.

Before preparing  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$ , the entire system (see, Figure 1 a; Supporting Information, Figure S2) was dried by thorough evacuation and then refilled with dry argon three times. After the  $\text{AlCl}_3$  and  $\text{LiBH}_4$  mixture (suggested weight ratio of 2.2:1) was loaded into the Schlenk bulk of reactor I, the cock of the Schlenk bulk of reactor I was turned on to let in argon and ammonia gas. Reactor I was shaken to mix the reagents thoroughly, and then the mixture was gradually heated to 65 °C and held for a period of time until no more white smoke could be observed in Reactor II. The argon flow was then stopped, but the product was kept in an ammonia atmosphere for more than 6 h to yield  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$ .

Approximately 0.5 g mixtures of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3/\text{LiBH}_4/\text{AlCl}_3$  at various mol ratios were mechanically milled for 60 min (planetary QM-1SP2) in argon using stainless steel spheres with a ball-to-powder

ratio (BPR) of 30:1 to produce  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  composites. The milling process was carried out by alternating 6 min of milling and 6 min of rest to avoid increasing the temperature of the powders in the vial. All the powder handling procedures before and after milling were carried out in a glove box with argon atmosphere.

Thermal property measurements were performed by thermogravimetry (TG, STA 409C)/mass spectroscopy (MS, QMS 403), with a heating rate of  $10^\circ\text{C min}^{-1}$  under 1 atm argon atmosphere. Desorption properties for some samples were also evaluated using Sieverts volumetric methods with a heating rate of  $5^\circ\text{C min}^{-1}$  and at varied isothermal temperatures under argon atmosphere. Differential scanning calorimetry (DSC) was performed simultaneously on a Netzsch STA 409 PC, Germany, with highly pure Ar as the purge gas. The morphology and structure of the particles were observed using field emission scanning electron microscopy (FESEM, FEI SIRION).

High-resolution X-ray powder diffraction data was collected on an  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  sample on the Powder Diffraction Beamline, Australian Synchrotron by using a Mythen detector. For phase identification, samples were loaded into pre-dried 0.5 mm glass capillary tubes inside the argon atmosphere glove box and sealed with vacuum grease for X-ray diffraction measurements. Decomposition behavior of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  was also studied through in situ XRD by heating the sample with a Cybostar hot gas blower. For in-situ high temperature measurements, the sample was loaded into a 0.7 mm quartz capillary and kept in argon atmosphere. Then, the sample was heated from 30 °C to 200 °C at temperature intervals of 10 °C. The wavelength for all these measurements was 0.688702 Å. Powder X-ray diffraction (XRD, Rigaku D/max 2400) measurements with  $\text{Cu}_{\text{K}\alpha}$  radiation at 50 kV and 150 mA were also conducted to confirm the phase structure. During the XRD measurements, amorphous polymer tape was used to cover the surface of the powder to avoid oxidation.

FTIR (Magna-IR 550 II, Nicolet) analysis was conducted to determine the chemical bonding. During the IR measurements (KBr pellets), samples were loaded into a closed tube with KBr. Solid-state  $^{11}\text{B}$  and  $^{27}\text{Al}$  NMR experiments were performed on a Bruker DSX 300 spectrometer operating at 12 kHz, using 4 mm  $\text{ZrO}_2$  rotors filled up in a purified argon atmosphere glove box. A 0.55  $\mu\text{s}$  single-pulse excitation was employed, with repetition times of 1.5 s.

The stability studies on  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  in dry air were performed by monitoring the decomposition behavior variation during exposure of the samples to dry air. To conduct the tests, a small bottle of  $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$  was placed in a desiccator filled with silica gel at room temperature (ca. 30 °C) for a period of time, and then its decomposition behavior was measured using Sieverts volumetric methods with a heating rate of  $5^\circ\text{C min}^{-1}$  in argon atmosphere. Attempts to recharge the dehydrogenated sample carried out under 6.5 MPa of  $\text{H}_2$  at 220 °C for 10 h were unsuccessful.

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