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Hydrogen Storage

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,[1] such as $M(NH_2BH_3)_m$, where M = Li, Na, Ca, $C(NH_2)_3BH_4$, $N_2H_4BH_3$, and $M(BH_4)_m{\cdot}n\,NH_3$ (M = Li, Mg).[2–6] 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.[1,2–4] Although indirect chemical routes to regenerate the composite from their decomposed products do provide a feasible solution,[5,7] 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[1–8] 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.[9–12] However, its hexamine compound, $Al(BH_4)_3{\cdot}6\,NH_3$, which has a theoretical hydrogen capacity of 17.4 wt %, will not sublime in a vacuum, even up to its decomposition temperature.[9–11] 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[9] and later confirmed in 1961.[10] 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 °C) is utilized to react with ammonia to produce $Al(BH_4)_3{\cdot}6\,NH_3$.[11] 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.[9,11]

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 $Al(BH_4)_3{\cdot}6\,NH_3$, in which the

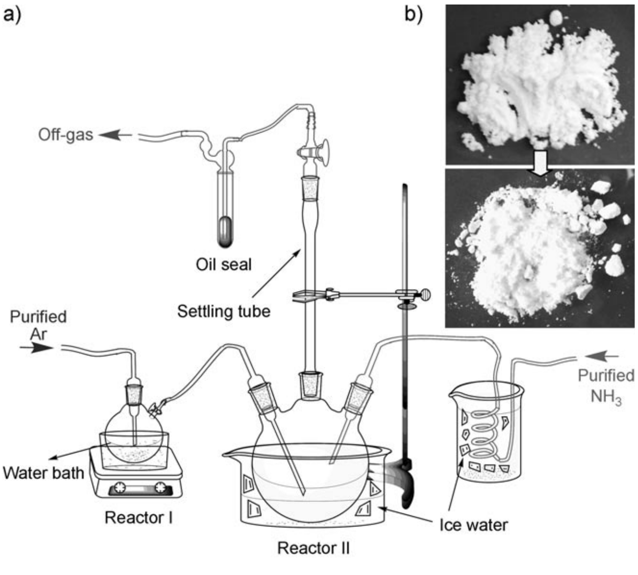

Figure 1. a) Preparation of $Al(BH_4)_3{\cdot}6\,NH_3$. Reactor I and Reactor II correspond to the reactions of Equation (1) and Equation (2), respectively. b) Photographs of $Al(BH_4)_3{\cdot}6\,NH_3$ powder before (top) and after exposure to dry air for 9 days (bottom).

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direct separation and purification of $Al(BH_4)_3$, obtained by the reaction of either sodium borohydride or lithium borohydride with aluminum chloride [Eq. (1)] are not required. The $Al(BH_4)_3{\cdot}6NH_3$ is synthesized by passing a stream of $Al(BH_4)_3$, diluted in argon and purified by aluminum powder, into dry ammonia at around 0 °C [Eq. (2)] for more than 6 h.

$$AlCl_3(s) + 3\,Li(Na)BH_4\ (s) \rightarrow 3\,LiCl(s) + Al(BH_4)_3(g) \tag{1}$$

$$Al(BH_4)_3(g) + 6\,NH_3(g) \rightarrow Al(BH_4)_3 \cdot 6\,NH_3\ (s) \tag{2}$$

The product, a white powdery solid with controllable morphology and particle size in the range of 50 nm–1 μm (Figure 1 b; Supporting Information, Figure S3), depending on the velocity and concentration of the flowing $Al(BH_4)_3$ gas, was confirmed to be $Al(BH_4)_3{\cdot}6NH_3$ 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 $Al(BH_4)_3{\cdot}6NH_3$ by prolonging the exposure time. As much as 10 g of $Al(BH_4)_3{\cdot}6NH_3$ can be prepared at one time in our laboratory, with a yield of more than 80 %. The synthesized $Al(BH_4)_3{\cdot}6NH_3$ 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 1 b), which is an important advantage for a hydrogen storage system.

The thermogravimetry/mass spectroscopy (TG/MS) results (Figure 2 a) revealed that the dehydrogenation of $Al(BH_4)_3{\cdot}6NH_3$ occurred in the temperature range of 60–180 °C, and was accompanied by a trace of ammonia release in the same temperature range. No B_2H_6 and/or $[NHBH]_n$ byproducts 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 °C (Table 1). The isothermal volumetric temperature-programmed desorption (TPD) results for $Al(BH_4)_3{\cdot}6NH_3$ (Figure 2 b) revealed that its dehydrogenation could proceed slowly at 139 °C, releasing 11.6 wt % hydrogen within 7 h. Higher operating temperatures resulted in faster dehydrogenation: for example, at 160 °C, 11.9 wt % hydrogen, corresponding to 10.3 equiv of 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 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 $Al(BH_4)_3{\cdot}6NH_3$ in air was further confirmed by the decomposition studies, from which less than 20 % dehydrogenation degradation was observed after exposure of $Al(BH_4)_3{\cdot}6NH_3$ to dry air for 9 days (Supporting Information, Figure S9). The results above clearly demonstrates the advantages and potential of $Al(BH_4)_3{\cdot}6NH_3$ as an advanced hydrogen-storage candidate.

Table 1: Calculated capacity and purity of H_2 released from $Al(BH_4)_3{\cdot}6NH_3$ and its composites.

Samples[a]	Wt % H_2 capacity[b]	Mol % H_2[b]	Equiv H_2[c]
$Al(BH_4)_3{\cdot}6NH_3$	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
$Al(BH_4)_3{\cdot}6NH_3$ at 139 °C	11.1	96.8	9.6
Composite I at 140 °C	10.1	99.6	10.7
Composite II at 120 °C	7.7	97.3	10.2
Composite IV at 120 °C	7.8	98.0	10.2
Composite IV at 100 °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 H_2 emission gas were determined using gravimetric and volumetric results, with the assumption that the impurity was only NH_3 to facilitate calculations. [c] Mol of H_2 released per mol of $Al(BH_4)_3{\cdot}6NH_3$.

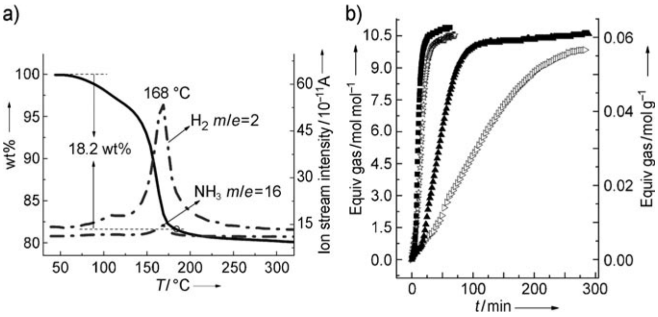

Figure 2. a) TG (——) and MS (–•–•) profiles for $Al(BH_4)_3{\cdot}6NH_3$ at a heating rate of 10 °C min^{-1} in argon. b) Isothermal TPD curves for the decomposition of $Al(BH_4)_3{\cdot}6NH_3$. ▷ 139 °C, ▲ 149 °C, ☆ 160 °C, ■ 174 °C.

To understand the hydrogen release pathway, Fourier-transform infrared spectroscopy (FTIR) was employed to follow the decomposition of $Al(BH_4)_3{\cdot}6NH_3$ in the range of 25–210 °C (Supporting Information, Figure S10). The spectrum of the as-prepared $Al(BH_4)_3{\cdot}6NH_3$ was in agreement with a previous report, indicating a salt-like structure with $[Al(NH_3)_6]^{3+}$ and BH_4^- ions in this compound.[13] During the heat treatment, only an intensity decrease in the characteristic absorption bands for $Al(BH_4)_3{\cdot}6NH_3$ can be observed below 160 °C, which indicates its partial decomposition, resulting in a small amount of hydrogen and ammonia evolution. After dehydrogenation at 210 °C, all the absorption bands assigned to the NH_3 group and BH_4^- ion have disappeared, which strongly suggests that both the NH_3 group and the BH_4^- ion contribute to the hydrogen release. Meanwhile, the disappearance of all $Al{-}N_6$ bonds was also observed, indicating a total structural transformation of $Al(BH_4)_3{\cdot}6NH_3$. The ^{11}B NMR spectra of $Al(BH_4)_3{\cdot}6NH_3$ (Supporting Information, Figure S11) showed a single boron species ($\delta = -36.7$ ppm), which is similar to that for $Al(BH_4)_3$ ($\delta = -36.5$ ppm),[14] indicating the assignment of this boron to the boron nucleus in the tetrahedral BH_4^- unit, consistent with the results of FTIR. After heat treatment at 210 °C, two ^{11}B resonances appeared at $\delta = 17.7$ and -0.9 ppm, along with the disappearance of the peak ascribed to BH_4^-, suggesting the interaction of BH_4^- with the NH_3 group in $Al(BH_4)_3{\cdot}6NH_3$ and leading to the formation of tricoordinate ($\delta = 17.7$ ppm) and tetracoordinate ($\delta = -0.9$ ppm) boron atoms, respectively.[15] The ^{27}Al NMR spectrum of $Al(BH_4)_3{\cdot}6NH_3$ 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 °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,[16] suggesting breakage of the $N{:}\rightarrow Al^{3+}$ coordination bond, consistent with the results of FTIR.[13] XRD results indicate that some new intermediates appeared in the $Al(BH_4)_3{\cdot}6NH_3$ sample heated to 160 °C, and after dehydrogenation at 210 °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 $Al(BH_4)_3{\cdot}6NH_3$ (Supporting Information, Figure S5). This observation confirms its composition with lowered coordination of NH_3, which may result from the fractional ammonia dissociation of $Al(BH_4)_3{\cdot}6NH_3$, 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 °C, along with the $Al(BH_4)_3{\cdot}6NH_3$ phase, traces of the intermediate phase appeared. With increasing temperature, a gradual decrease in intensity for $Al(BH_4)_3{\cdot}6NH_3$ and an intensity increase for the intermediate phase are observed, and upon heating to 140 °C, only the intermediate phase is present in the diffraction pattern, indicating a trend in which $Al(BH_4)_3{\cdot}6NH_3$ 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 °C. Therefore, the main reactions of $Al(BH_4)_3{\cdot}6NH_3$ that proceed during heating can be summarized as a phase transformation of $Al(BH_4)_3{\cdot}6NH_3$ 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 H_2 from the decomposed $Al(BH_4)_3{\cdot}6NH_3$, it may be concluded that the dehydrogenation of $Al(BH_4)_3{\cdot}6NH_3$ is also based on the combination mechanism of $H^{\delta+}$ and $H^{\delta-}$.

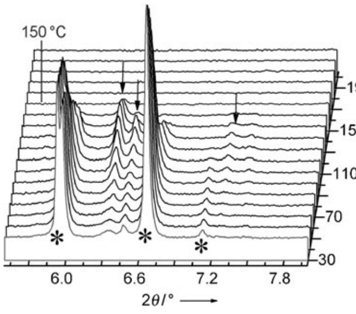

Figure 3. Selected parts of the in-situ XRD patterns for $Al(BH_4)_3{\cdot}6NH_3$. The sample was heated to a scheduled temperature at a heating rate of 6 °C min^{-1} and then held for 8 min to allow collection of the data. The stars indicate $Al(BH_4)_3{\cdot}6NH_3$, and arrows indicate an intermediate phase.

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.[6] However, the metal ion, depending on the element, has a varied influence on both $[BH_4]^-$ and NH_3, such as electronegativity and polarity of the $[BH_4]^-$ group and N–H bond, resulting in differing abilities to promote combination to achieve hydrogen release. In light of the decomposition properties of $LiBH_4{\cdot}NH_3$ and $Mg(BH_4)_2{\cdot}2NH_3$, 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 $[BH_4]^-$ and NH_3, which favors the combination and the formation of N–H–H–B dihydrogen bonds.[2] In the case of $Al(BH_4)_3{\cdot}6NH_3$, a stronger $N{:}\rightarrow Al^{3+}$ coordination bond is expected, which contributes positively to the combination of $H^{\delta+}$ and $H^{\delta-}$, achieving a maximum hydrogen release rate at around 163 °C, which is 42 °C lower than that of $Mg(BH_4)_2{\cdot}2NH_3$. However, the accompanying ammonia emission is fatal for practical applications. From the viewpoint of the $H^{\delta+}$ and $H^{\delta-}$ balance, as well as the XRD results (Figure 3; Supporting Information, Figure S5, S12), the excess N–H groups present in $Al(BH_4)_3{\cdot}6NH_3$ may account for evolution of the NH_3 impurity. Thus, a strategy aimed at balancing $H^{\delta+}$ and $H^{\delta-}$ and further reinforcing the $N{:}\rightarrow Al^{3+}$ 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 $[BH_4]^-$ by mixing $Al(BH_4)_3{\cdot}6NH_3$ with $AlCl_3/LiBH_4$ additive were performed (Figure 4). After mixing $Al(BH_4)_3{\cdot}6NH_3$ with $AlCl_3/LiBH_4$, the formation of new phases (Supporting Information, Figure S14) by the reaction

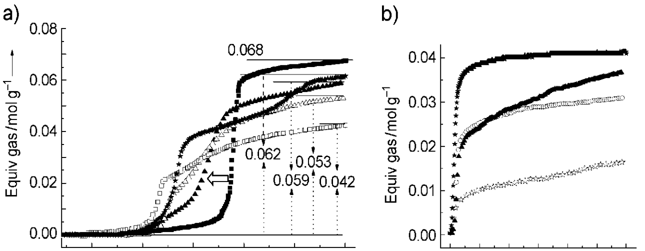

Figure 4. TPD results for $Al(BH_4)_3{\cdot}6NH_3$ and its composites: I: $Al(BH_4)_3{\cdot}6NH_3/0.2AlCl_3/0.6LiBH_4$; II: $Al(BH_4)_3{\cdot}6NH_3/0.5AlCl_3/1.5LiBH_4$; III; $Al(BH_4)_3{\cdot}6NH_3/AlCl_3/3LiBH_4$; IV: $Al(BH_4)_3{\cdot}6NH_3/0.2AlCl_3/3LiBH_4$. a) Non-isothermal plot ($Al(BH_4)_3{\cdot}6NH_3$ ■, I ▲, II △, III □, IV ★) and b) isothermal plots at 120 °C (I ☆, II ▲, III ○, IV ★).

of $Al(BH_4)_3{\cdot}6NH_3$ with the supplementary $Al(BH_4)_3$ produced from the $LiBH_4/AlCl_3$ 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 $Al(BH_4)_3$ with a lower NH_3 coordination number, $Al(BH_4)_3{\cdot}n\,NH_3$ ($n < 6$). 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 ($-2.7\,kJ\,mol^{-1}\,H_2$; Supporting Information, Figure S16), which is much less than that of AB ($-21\,kJ\,mol^{-1}$),[1] indicating a favorable thermodynamics for Al–B–N–H system. Furthermore, it was found that excess $LiBH_4$, which will react with the $Al(BH_4)_3{\cdot}n\,NH_3$ 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, $Al(BH_4)_3{\cdot}6NH_3$ was synthesized by a facile and novel gas-phase reaction. It has been demonstrated that $Al(BH_4)_3{\cdot}6NH_3$ 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, $LiBH_4$ 95% (Sigma–Aldrich, USA), $AlCl_3$ 99.99%, Al powder (345 mesh), and NH_3 (Alfa Aesar, China), were obtained commercially. $LiBH_4$ and $AlCl_3$ were ball-milled for 1 h before use. Aluminum powder was used as received. 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 $Al(BH_4)_3{\cdot}6NH_3$, the entire system (see, Figure 1a; Supporting Information, Figure S2) was dried by thorough evacuation and then refilled with dry argon three times. After the $AlCl_3$ and $LiBH_4$ 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 $Al(BH_4)_3{\cdot}6NH_3$.

Approximately 0.5 g mixtures of $Al(BH_4)_3{\cdot}6NH_3/LiBH_4/AlCl_3$ 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 $Al(BH_4)_3{\cdot}6NH_3$ 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 $10\,°C\,min^{-1}$ under 1 atm argon atmosphere. Desorption properties for some samples were also evaluated using Sieverts volumetric methods with a heating rate of $5\,°C\,min^{-1}$ 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 $Al(BH_4)_3{\cdot}6NH_3$ 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 $Al(BH_4)_3{\cdot}6NH_3$ 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 $Cu_{K\alpha}$ 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}B and ^{11}Al NMR experiments were performed on a Bruker DSX 300 spectrometer operating at 12 kHz, using 4 mm ZrO_2 rotors filled up in a purified argon atmosphere glove box. A 0.55 μs single-pulse excitation was employed, with repetition times of 1.5 s.

The stability studies on $Al(BH_4)_3{\cdot}6NH_3$ 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 $Al(BH_4)_3{\cdot}6NH_3$ 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 $5\,°C\,min^{-1}$ in argon atmosphere. Attempts to recharge the dehydrogenated sample carried out under 6.5 MPa of H_2 at 220 °C for 10 h were unsuccessful.

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