Stepwise combination of BH_4^- and NH_3 in metal ammine borohydride

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1. EXPERIMENTAL DETAILS

1.1. Synthesis. The starting materials ($LiBH_4$, $AlCl_3$, and Al) were purchased from Alfa Aesar Co. and used as received. NH_3 was purified by soda lime before use. All samples were handled in a nitrogen-filled glove box which kept both water and oxygen concentrations below 1ppm during operation.

To produce ammine aluminum chlorides (AAC) with various coordination number, $AlCl_3 \cdot 6NH_3$ was first prepared according to eq 1. Approximately 3 g $AlCl_3$ was loaded into a Schlenk flask in nitrogen glove box. Then, the flask was connected to a vacuum-ammonia manifold Schlenk line. After being evacuated, the flask was refilled with purified ammonia and stand for 24 h. Then, the flask was further evacuated for a certain time until it reached the desired weight. The yielded white fine powder was confirmed by XRD to be $AlCl_3 \cdot 6NH_3$. Other AAC with lower coordination numbers were prepared via the reaction of $AlCl_3 \cdot 6NH_3$ with $AlCl_3$ according to equation 2. To promote this reaction, two methods of ball-milling and heat-treatment were tried. For ball-milling method, around 2 g mixture of $AlCl_3/AlCl_3 \cdot 6NH_3$ (in stoichiometric ratio) were ball milled using Planetary QCM-2 with a ball-to-sample ratio of 30:1, agitation frequency of 500 rpm. For heat-treatment method, around 2 g mixture of $AlCl_3/AlCl_3\cdot 6NH_3$ (in stoichiometric ratio) was loaded in a sealed steel vessel and sintered at 170 °C for 3 h to produce $AlCl_3\cdot nNH_3$ (n=5, 4, 3).

$AlCl_3+6NH_3 \rightarrow AlCl_3\cdot 6NH_3$ (1)

$AlCl_3\cdot 6NH_3+xAlCl_3 \rightarrow AlCl_3\cdot nNH_3$ (n=5, 4, 3) (2)

The formation of metallic borohydrides adducted with ammonia successfully proceeds according to the metathesis reaction between $AlCl_3\cdot nNH_3$ (n=6, 5, 4, 3) and $LiBH_4$. During the preparation, mixtures of $AlCl_3\cdot nNH_3-LiBH_4$ were ball milled for 2 h using Planetary QCM-2 with a ball-to-sample ratio of 30:1, agitation frequency of 450 rpm. To avoid the temperature increasing of the powder in the vessel, the milling process was carried out by alternating 6 min of milling and 6 min of rest.

1.2. Instrument and Analysis. Temperature-programmed desorption (TPD) and volumetric-release measurements were carried out using a semiautomatic Sievert's apparatus, connected with a reactor filled with a sample (typical weight ~50m g) under nitrogen atmosphere (~1 bar) with a heating rate of 5 °C/min. The H_2 and NH_3 contents within the emission gas were determined using gravimetric and volumetric results. First, the mass percent (Wp) and mole per gram (Mp) of gas released from the sample were calculated from the weights of the samples and volumetric results, then the mole proportion of H_2 ($C(H_2)$) and NH_3 ($C(NH_3)$) can be calculated from the follow two equations,

$C(H_2)+C(NH_3)=1$ (5)

$((C(H2)\times 2.02)+(C(NH3)\times 17.03))\times Mp=Wp$ (6)

Simultaneous thermo-gravimetric analysis and mass spectrometry (TGA-MS) were conducted under 1 atm argon in the temperature range of room temperature to 400 ^{o}C at a heating rate of 5 $^{o}C\ min^{-1}$ using a netzsch STA 409 C analyzer equipped with a quadrupole mass spectrometer for the analysis of the evolved gas. The targeted evolving gases monitored by MS were NH_3 (16), H_2 (2), B_2H_6 (26) and borazine (80).

Powder X-ray diffraction (XRD) patterns were obtained with a Bruke X'PERT diffractometer (Cu Ka radiation, 16Kw). During the XRD measurement, samples were mounted in a glove box, and an amorphous polymer tape was used to cover the surface of the powder to avoid oxidation.

The solid-state ^{11}B NMR was recorded (DSX 300) using a Doty CP-MAS probe with no probe background. All of those solid samples were spun at 12 kHz, using 4mm ZrO_2 rotors filled up in purified nitrogen atmosphere glove box. A 0.55μs single-pulse excitation was employed, with repetition times of 1.5 s.

To further reveal the evolution of chemical bonding during the decomposition, in-situ FT-IR spectra of the samples were recorded in the range of 1000 cm^{-1} to 2500 cm^{-1} on Nicolet iS50 with a sealed reaction cell. The specimens for measurements were a mixture of $AlCl_3(NH_3)_5/5LiBH_4$ and dried KBr with a weight ratio of 1:100 and was filled into a sample holder in the sealed reaction cell. The reaction cell was purged by Ar and then spectra were collected when the sample was heated from room temperature to 400 ^{o}C at a heating rate of 5 ^{o}C/min.

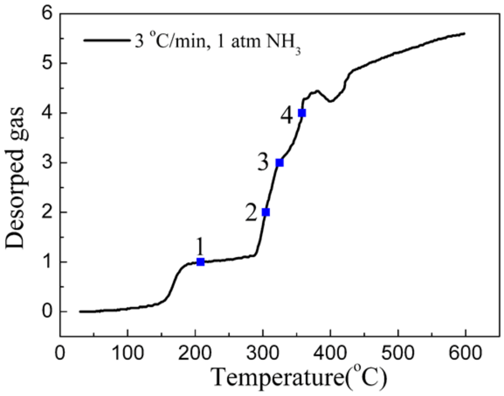
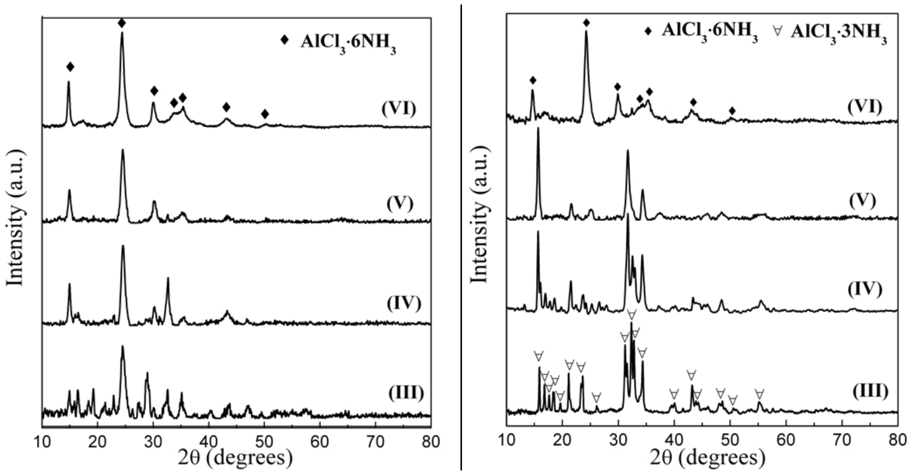


Figure S1 Thermal decomposition of $AlCl_3 \cdot 6NH_3$ in ammonia, the number of ammonia released from $AlCl_3 \cdot 6NH_3$ were marked on the line.



(a)

(b)

Figure S2. XRD patterns for the $AlCl_3 \cdot 6NH_3$ (VI) and $AlCl_3 \cdot 6NH_3/AlCl_3$ mixtures with NH_3:$AlCl_3$ ratio of 5 (V), 4(IV) and 3(III) after ball milling (a) and heat treatment at 180 °C for 3h (b).

The preparation of $AlCl_3 \cdot nNH_3$ was first tried via the traditional process of thermal decomposition of the ammine aluminum chloride with the highest coordination number-$AlCl_3 \cdot 6NH_3$ in ammonia. However, the lack of clear stabilized range and the formation of a great amount of by-product [1] (Figure S1) make this approach less feasible to produce ammine aluminum chloride with various coordination numbers. Therefore, the reaction of $AlCl_3 \cdot 6NH_3$ with $AlCl_3$ was tried to produce $AlCl_3 \cdot nNH_3$ (n=3, 4, 5), and two methods of ball milling and heat treatment were utilized to promote their reaction. Figure S2 shows XRD results for the as-prepared products. It is observed that there is still a large amount of $AlCl_3·6NH_3$ remains in the ball milled $AlCl_3·6NH_3/AlCl_3$ mixture, suggesting that ball milling is not an effective method. While, for the heat treatment mixtures the characteristic peaks of $AlCl_3·6NH_3$ and $AlCl_3$ were all disappeared. It is further confirmed that the disappearance of these characteristic peaks should result from the interaction of $AlCl_3·6NH_3$ with $AlCl_3$ rather than the decomposition of $AlCl_3·6NH_3$ as its XRD patterns remain unchanged after heat treatment (Figure S2 b). Meanwhile, the XRD pattern also indicates the success synthesis of pure $AlCl_3·3NH_3$. Thus, it is suggested that heat treatment of $AlCl_3·6NH_3/AlCl_3$ mixture might be an effective method to promote the reaction of $AlCl_3·6NH_3$ with $AlCl_3$. Regarding to $AlCl_3+5NH_3$ and $AlCl_3+4NH_3$, there has been no XRD reports on the ammine aluminum chloride with coordination number of 5 and 4 yet. Based on the fact that the XRD peaks of the starting materials of $AlCl_3·6NH_3$ and $AlCl_3$ disappeared and their XRD patterns were quite different with either $AlCl_3·6NH_3$ or $AlCl_3·3NH_3$, there might exists new ammine aluminum chloride. Combining the decomposition behavior of $AlCl_3·6NH_3$ in ammonia (Figure 1), it is highly possible that the new specie is $AlCl_3·5NH_3$. For $AlCl_3+4NH_3$, it is the mixture of $AlCl_3·5NH_3$ and $AlCl_3·3NH_3$. However, it is difficult to determine the structure based on current XRD results and further work is still awaited.

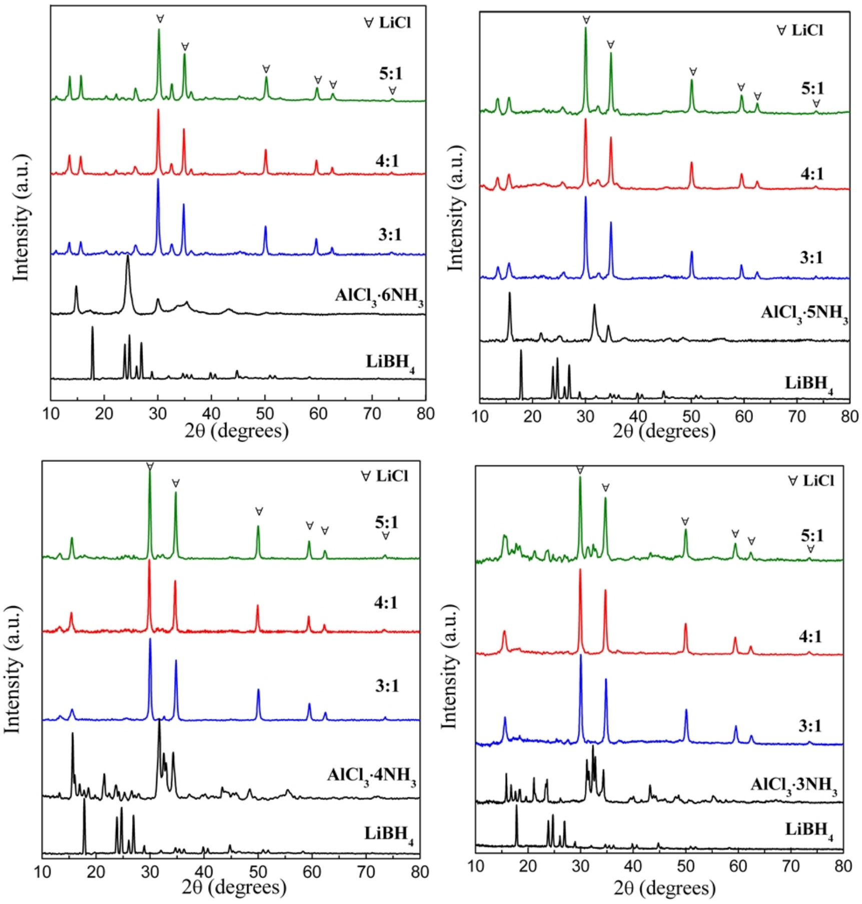


Figure S3. XRD patterns for the as-prepared $AlCl_3·nNH_3/LiBH_4$ composites. The $AlCl_3·nNH_3$: $LiBH_4$ ratio in these composites was 5, 4 and 3.

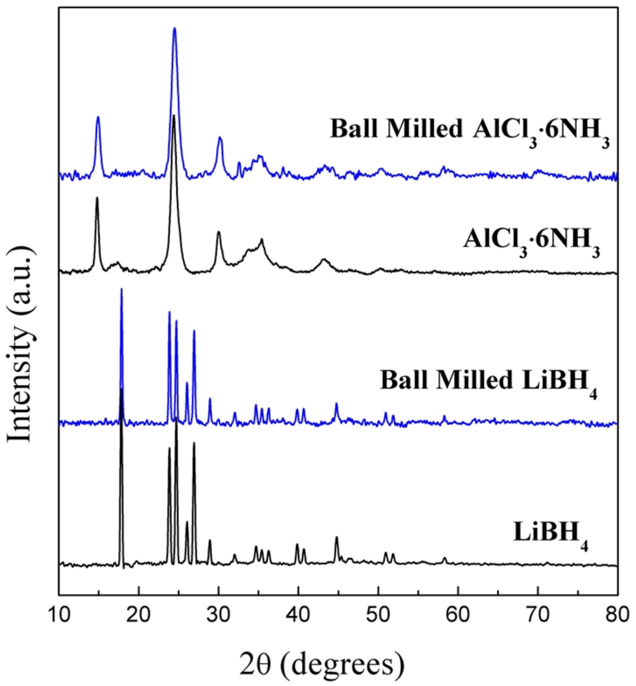


Figure S4. The XRD patterns for $AlCl_3 \cdot 6NH_3$ and $LiBH_4$ before and after ball milling at 450 rpm, respectively.

The XRD patterns of the $AlCl_3 \cdot 6NH_3$ and $LiBH_4$ were almost the same before and after ball milling, implying that ball milling does not affect their crystal structures.

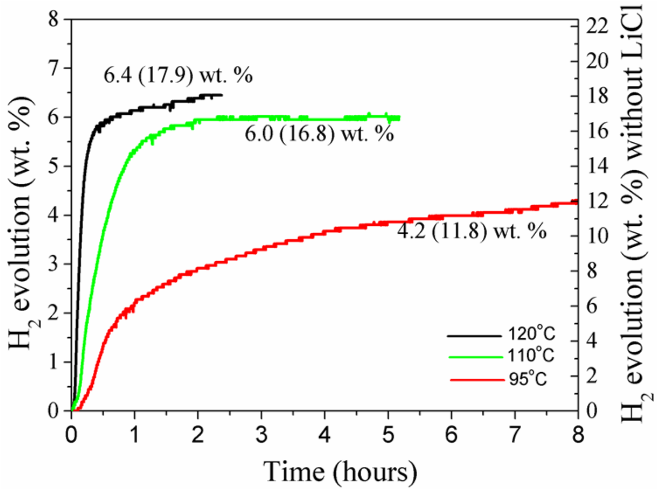


Figure S5. Isothermal curves of $AlCl_3(NH_3)_5/5LiBH_4$ at temperatures of 95, 110 and 120 °C, respectively.

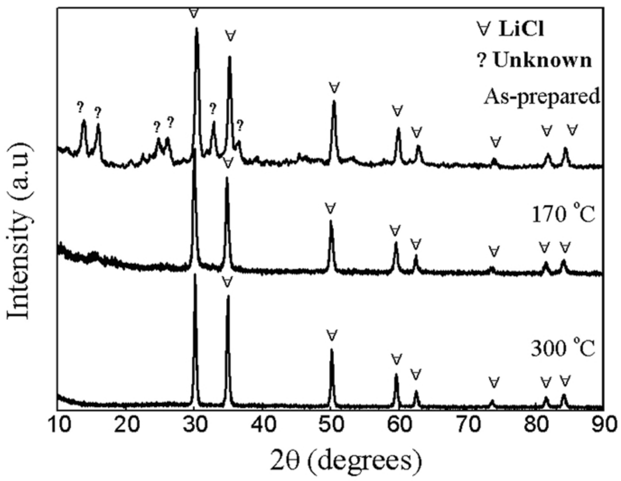


Figure S6. XRD patterns for the as prepared $AlCl_3(NH_3)_5/5LiBH_4$ with a mole ratio of 1:5 and its products after heated to 170 and 300 ^{o}C in argon.

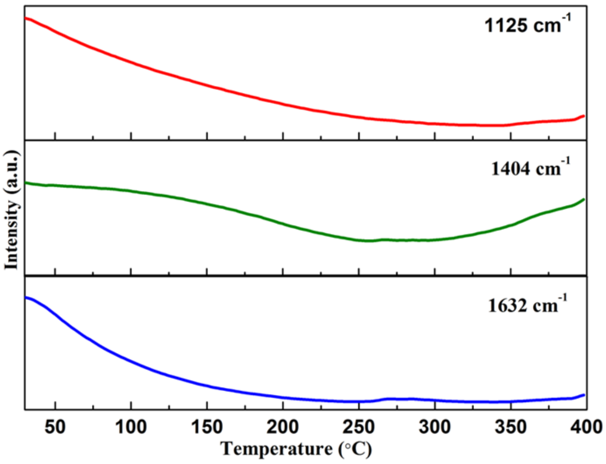


Figure S7 The integrated intensities of the peaks in *in situ* FTIR profiles of $AlCl_3(NH_3)_5/5LiBH_4$ composites. These intensities have been normalized to 100% at the maximum intensity of each peak.

Table S1. Decomposition properties and calculated H_2 capacities for $AlCl_3 \cdot nNH_3/mLiBH_4$ composites.

Sample[a]	Released gas (mol per unit / mol g^{-1})	Weight loss (wt. %)	Peak T [b] (°C)	Released H_2 [c] (mol per unit)	H_2 capacity (mol g^{-1} / wt. %)
$AlCl_3 \cdot 6NH_3$ -3$LiBH_4$	12.0 / 0.040	15.0	169	10.6	0.050 / 10.0
$AlCl_3 \cdot 6NH_3$ -4$LiBH_4$	15.0 / 0.047	13.3	164	14.1	0.053 / 10.6
$AlCl_3 \cdot 6NH_3$ -5$LiBH_4$	17.6 / 0.051	12.5	151	17.1	0.055 / 11.0
$AlCl_3 \cdot 5NH_3$ -3$LiBH_4$	10.3 / 0.038	9.9	159	9.9	0.048 / 9.6
$AlCl_3 \cdot 5NH_3$ -4$LiBH_4$	13.7 / 0.046	10.7	150	13.4	0.051 / 10.2
$AlCl_3 \cdot 5NH_3$ - 5$LiBH_4$	**15.7 / 0.048**	**10.7**	**141**	**15.4**	**0.054 / 10.8**
$AlCl_3$-4NH_3 -3$LiBH_4$	9.5 / 0.036	9.5	109	9.1	0.045 / 9.1
$AlCl_3$-4NH_3 -4$LiBH_4$	12.4 / 0.043	11.4	135	11.9	0.049 / 9.8
$AlCl_3$-4NH_3 -5$LiBH_4$	13.1 / 0.043	11.4	129	12.5	0.052 / 10.4
$AlCl_3 \cdot 3NH_3$ -3$LiBH_4$	8.2 / 0.033	10.1	130	7.7	0.042 / 8.5
$AlCl_3 \cdot 3NH_3$ -4$LiBH_4$	10.5 / 0.039	12.0	123	9.7	0.046 / 9.3
$AlCl_3 \cdot 3NH_3$ -5$LiBH_4$	11.0 / 0.037	foam	123	--	

[a] Non-isothermal heat treatment of the samples corresponding to Figure 1. [b] Peak temperature for the first step. [c] The released H_2 determined using gravimetric and volumetric results, with the assumption that the impurity was NH_3 to facilitate calculation.

Reference:

(1) Pouget, M.; Lecompte, J. P. *Journal of the European Ceramic Society* **1996**, *16*, 521.