Supporting Information

Aluminum borohydride-ethylenediamine as hydrogen storage candidate

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1. Experimental

General considerations:

The source materials, LiBH₄ 95% (Sigma–Aldrich, USA), AlCl3 99.99%, and ethylene diamine (EDA) (Alfa Aesar, China); hydrochloric acid, trans-1,2-Diaminocyclohexane-N,N,N',N'-tetraacetic acid monohydrate (DCTA), xylenol orange and NaOH (analytical pure, Aladdin, China) were obtained commercially. LiBH₄ and AlCl₃ were ball-milled for 1 h before used. EDA was distilled in calcium hydride for 12 hours under nitrogen protection before used. All handling, except for amine-related procedures, was conducted under anaerobic and anhydrous environment by Schlenk techniques.

Complexometric titration was used for the determination of Al content in the product. Around 0.0300g precisely weighted product and 20.0mL 0.02M DCTA solution were added into 250mL flask. Then diluted hydrochloric acid was dripped into the solution until it didn't bubble. After standing for 0.5h, 10mL hexamine-hydrochloric acid buffer solution was added to the flask. Then, the sample solution was back-titrated with standardized 0.02M lead solution with xylenol orange indicator. The titration was repeated twice. The Al content was calculated based on these results..

The active hydrogen was determined via hydrolysis of the adduct in 2Mhydrochloric acid within a sealed bulb. The amount of hydrogen released during the hydrolysis was calculated by the pressure variation of the system. Simultaneous thermo-gravimetric analysis and mass spectrometry (TGA-MS) were conducted under 1 atm argon in the temperature range of room temperature to 350 °C at a heating rate of 5 °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 EDA(30), H₂ (2) and B₂H₆ (26).

Meanwhile, desorption properties for some samples were also evaluated using Sievert's volumetric methods with heating rate of 5 °C/min under 1 atm argon. Differential scanning calorimetry (DSC) was performed simultaneously on a Netzsch STA 409 PC with pure argon as the purge gas.

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.

FT-IR (Magna-IR 550 II, Nicolet) analyses were conducted to determine the chemical bond. Samples were pressed with KBr then loaded in sealed chamber filled with argon for the measurement. 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 $Al(BH_4)_3 \cdot 2C_2H_8N_2$ 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 °C at a heating rate of 5 °C/min.

The H₂ and EDA gas contents within the emission gas were determined using gravimetric and volumetric results. Firstly, 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 H₂ (C_H) and EDA (C_{EDA}) can be calculated from the following two equations, C_H + C_{EDA} =1 ((C_H * 2.02) + (C_{EDA} *60.11*n)) *Mp = Wp *n*=1,2,3,4

Synthesis of amine metal borohydrides (Al(BH₄)₃· $nC_2H_8N_2$, n = 4, 3, 2, 1)

The experimental set-up for the preparation of amine metal borohydrides $(Al(BH_4)_3 \cdot nC_2H_8N_2, n=5, 4, 3, 2, 1)$ is schematically depicted in Fig. S1(a) and S1(b). Firstly, Al(BH₄)₃ $\cdot nC_2H_8N_2$ (n<6) with no identified coordination number is obtained by passing a stream of Al(BH₄)₃, diluted in argon, into dry EDA at room temperature for 6 h. Then coordination number of the product is confirmed by the complexometric titration and active hydrogen analysis. Then, by further reaction of the above product with $Al(BH_4)_3$, a series of $Al(BH_4)_3 \cdot nC_2H_8N_2$ with n=5, 4, 3, 2, 1 were produced within apparatus as shown in Fig. S1(b). During the reaction, the increasing weight of the product was monitored by weighting reactor B during the experiment for process control, which gave the formation of the targeted amine metal borohydrides with various EDA units. Amine metal borohydrides with different coordination numbers were synthesized by allowing $Al(BH_4)_3 \cdot nC_2H_8N_2$ to remain in contact with the $Al(BH_4)_3$ vapor until it reach the certain weight. Furthermore, the Al contents of the products determined through complexometric titration just confirmed their coordination numbers calculated based on the weighing method, suggesting the feasibility of our process to produce Al(BH₄)₃· $nC_2H_8N_2$. The Al(BH₄)₃· $nC_2H_8N_2$ (n=5, 4, 3, 2, 1) products were all white powdery solids.

It should be noticed that $Al(BH_4)_3$ is pyrophoric and toxic, EDA is corrosive and toxic. Therefore, they should be handled in fume hood with ventilation.



Fig S1 (a) Preparation of Al(BH₄)₃·nC₂H₈N₂. Reactor I and Reactor II correspond to the reactions of Equation (1) and Equation (2), respectively.
(b) Apparatus for the preparation of EDA aluminum borohydrides: A, Al(BH₄)₃ source produced by a reaction of AlCl₃ with LiBH₄, B, solid Al(BH₄)₃·nC₂H₈N₂ prepared by (a).

$$AlCl_{3}(s)+3Li(Na)BH_{4}(s)\rightarrow 3Li(Na)Cl(s)+Al(BH_{4})_{3}(g)$$
(1)
$$Al(BH_{4})_{3}(g)+nC_{2}H_{8}N_{2}(g)\rightarrow Al(BH_{4})_{3}\cdot nC_{2}H_{8}N_{2}(s) n<6$$
(2)



Fig S2. XRD results of Al(BH₄)₃·*n*C₂H₈N₂, n=5,4,3,2,1

XRD patterns with unknown phases were observed for all these products, suggesting the formation of new compounds. However, as a bridging ligand, EDA is suggested to take a gauche (δ and γ) or a trans conformation in the complex. [S2] Thus, these compounds may be a mixture of different conformations with a definite coordination number, which may be responsible for the unsuccessful index of their XRD results.

2. Results



Fig S3. DSC curves for Al(BH₄)₃· $nC_2H_8N_2$ (n=5, 4, 3, 2, 1) with a heating rate of 5 °C min⁻¹ in argon.

DSC profiles at the heating rating of 5 °C min⁻¹ for Al(BH₄)₃· $nC_2H_8N_2$ (n=5, 4, 3, 2, 1) are shown in Fig S3. For Al(BH₄)₃·5C₂H₈N₂ a large and sharp endothermic peak at 80 °C and two exothermic peaks at 159 °C and 201 °C were observed. The endothermic peak should be attributed to the release of EDA which resulted in a large amount of weight loss at relatively low temperature. While, the two exothermic peaks should be attributed to the two dehydrogenation of this compound indicated by the TG-MS results (Fig. 3). For Al(BH₄)₃·4C₂H₈N₂, a small endothermic peak at 80 °C and two exothermic peaks at 154 °C and 199 °C were observed. For Al(BH₄)₃· $nC_2H_8N_2$ (n=3, 2, 1) no endothermic peak at around 80 °C, but the exothermic peaks for their corresponding dehydrogenation (Fig. 3) were observed. The evolution of the endothermic peak at around 80 °C may demonstrate the affinity of Al(BH₄)₃ for EDA. The loss of EDA at low temperature from $Al(BH_4)_3 \cdot 5C_2H_8N_2$ indicated the weak affinity of a portion of EDA in this compound. While for Al(BH₄)₃·nC₂H₈N₂ (n=4, 3, 2, 1), much less EDA was released from $Al(BH_4)_3 \cdot 4C_2H_8N_2$, suggesting a stronger affinity of of $Al(BH_4)_3$ for EDA. Since the XRD patterns of Al(BH₄)₃·5C₂H₈N₂ and Al(BH₄)₃·4C₂H₈N₂ were quite similar (Fig. S2), it is supposed that $Al(BH_4)_3$ could combine no more than 4 equivalent EDA and the extra EDA in Al(BH₄)₃·5C₂H₈N₂ may be only physical absorbed by Al(BH₄)₃·4C₂H₈N₂.



Fig S4. FTIR results of Al(BH₄)₃·*n*C₂H₈N₂, *n*=4,3,2,1

Vibration	и мси				AI(BH).C
VIDIALIOII		$AI(DII_4)_3$ ·4C	$AI(DII_4)_3$ ·SC	$AI(DII_4)_3^{\cdot}2C$	$AI(DI14J3 \cdot C_2)$
mode	$CH_2NH_2^a$	$_2H_8N_2^{D}$	${}_{2}H_{8}N_{2}$	${}_{2}H_{8}N_{2}$	$H_8N_2^{b}$
NH_2	3360	3343	3230	3352	3344
Stretching	3280	3223	3114	3214	3220
	3196	3112		3114	3113
CH_2	2931	2967	2967	2967	2968
Stretching	2859	2909	2911	2875	2876
		2872			
B-H	-	2253	2252	2258	2317
Stretching					2293
-					2267
NH ₂ Bend	1602	1587	1582	1581	1589
		1557	1557	1557	1557
CH ₂ Bend	1461	1465	1468	1466	1460
N-H	1253	1338	1338	1338	1370
Deformatio	1170	1315	1315	1313	1337
n					1315
B-H Bend	-	1166	1168	1166	1166
C-C C-N	1099	1099	1098	1095	1094
Stretching	1055	1051	1051	1051	1050
Al-N	-	567	565	565	565
Stretching					
^a Data obtained from reported spectra figures, ref S2 and S3(with an uncertainty					

Table S1. FTIR results of Al(BH₄)₃·*n*C₂H₈N₂, *n*=4,3,2,1

^a Data obtained from reported spectra figures, ref S2 and S3(with an uncertainty of about 15 cm⁻¹); ^b Data obtained in this work.



Fig S5. XRD results of Al(BH₄)₃·2C₂H₈N₂ at 25 °C, 135 °C and 350 °C.



Fig S6. FTIR spectra for Al(BH₄)₃·2 $C_2H_8N_2$ composite before and after dehydrogenation at 350 °C.



Fig S7. FTIR spectra for Al(BH₄)₃·2 C₂H₈N₂ composite from 30 °C to 350 °C.

References:

[s1] A. de Sousa, Anal. Chim. Acta, 1960, **22**, 522.

[s2] K. Nakamoto, *Infrared and Raman spectra of inorganic and coordination compounds*, Wiley Online Library, 1986.

[s3] D. Powell and N. Sheppard, *Journal of the Chemical Society (Resumed)*, 1959, 791-795.

[s4] D. B. Powell and N. Sheppard, Journal of the Chemical Society, 1961, 1112-&.1.

K. Nakamoto, *Infrared and Raman spectra of inorganic and coordination compounds*, Wiley Online Library, 1986.