

Hydrogen Releasing of Lithium Amidoborane-LiNH₂BH₃

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This paper reports on the preparation and hydrogen releasing of lithium amidoborane (LiNH₂BH₃, LiAB). LiAB is synthesized by a wet-chemical route through the direct interaction of LiH with NH₃BH₃ in tetrahydrofuran (THF) at room temperature. The structure of the as-prepared sample is investigated using X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy. The thermal decomposition process is determined by temperature programmed desorption/mass spectrometer (TPD/MS). The results show that the as-prepared LiAB starts to release H₂ at the temperature of 70.9°C, which is much lower than that of pure AB, while detectable NH₃ releasing should be controlled.
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1. Introduction

Great efforts have been devoted to hydrogen storage materials in terms of gravimetric and volumetric hydrogen densities.¹⁻³⁾ Ammonia-borane (AB), which is a white crystalline solid synthesized in 1955,⁴⁾ has recently attracted a great interest as an efficient hydrogen storage material for its low molecular weight (30.87 g mol⁻¹) and high gravimetric hydrogen capacity (19.6 mass%).⁵⁻⁷⁾ However, AB's thermal decomposition occurs at temperatures around 110, 150, and 1400°C, respectively. Furthermore, AB has shown a slow thermal kinetics below 100°C and the volatile byproducts such as borazine (HNBH₃).^{8,9)} To solve these problems, recent studies have focused on the alkali and alkaline earth metal amidoboranes (MABs), which are synthesized by the interaction of metal hydride and ammonia borane. MABs can be formed in the solid state reaction of AB with metal hydrides by ball milling¹⁰⁻¹³⁾ or through a wet-chemical route using tetrahydrofuran (THF) as a solvent.¹⁴⁾ Xiong *et al.* reported that LiAB and NaAB release 10.9 mass% and 7.5 mass% hydrogen, respectively, at the temperatures of 90°C with no borazine emission.¹⁰⁾ Kang *et al.* showed that LiAB with a H-capacity of around 10 mass% can rapidly release over 7 mass% (on a material basis) hydrogen at around 100°C.¹¹⁾ Fijalkowskia and Grochala displayed that a substantial amount of ammonia is released during early stages of the thermal decomposition of NaAB.¹³⁾ Autrey's group synthesized a series of alkali metal amidoboranes by solution phase methods, and found that non-volatile products released from MABs are significantly different from that formed after hydrogen releasing of AB.¹⁴⁾ The emission of ammonia not only impacts the application of MABs in fuel cells, but also results in the decrease of hydrogen capacity from AB. Therefore, the study on the hydrogen releasing with controlled NH₃ emission from the thermal decomposition of LiAB should be important. In this paper, we report on the preparation of LiAB through a simple wet-chemical route and its hydrogen releasing by temperature programmed desorption/mass

spectrometer (TPD/MS). It is found that the H₂-release temperature of LiAB is efficiently lowered in comparison with that from pure AB; While detectable ammonia is releasing in accompany with H₂.

2. Experimental

2.1 Synthesis of LiNH₂BH₃

LiH (98%, Alfa-Aesar) and NH₃BH₃ (90%, Sigma-Aldrich) were commercial products and used as received. Tetrahydrofuran (THF) was purified by distilling with sodium-potassium alloy under an inert Ar atmosphere. AB (154.4 mg, 5 mmol) was dissolved in THF (5 mL) under magnetic stirring for 3 min. LiH (79.5 mg, 10 mmol) was added into 5 mL THF to form a suspension that was added into the stirring THF/AB solution and allowed the mixture to react for 90 min. At the end of the reaction, the solution was filtered. LiAB was obtained by vacuum drying the solution overnight at room temperature. All the samples were handled in a glove-box filled with Ar (99.9999%), which was equipped with a circulative purification system to control the H₂O/O₂ levels below 0.1 ppm. The reaction involved for the production of LiAB can be expressed in eq. (1).



2.2 Characterization

Powder X-ray diffraction (XRD) patterns were taken on a Rigaku-Dmax 2500 X-ray diffractometer using Cu K α radiation ($\lambda = 1.541\ 78\ \text{\AA}$). The patterns of LiH and LiAB were obtained by the samples mixed with a protective coating of pyrophyllite oil, smeared on a glass slide because pure LiH and LiAB are susceptible to the air. The X-ray intensity was measured over a diffraction angle from 10° to 80° with a velocity of 8° min⁻¹. FTIR spectra were collected at room temperature by using a FTIR-650 spectrometer (Tianjin Gangdong) at a resolution of 4 cm⁻¹ using KBr pellets. The thermal desorption properties of the samples were measured using a temperature programmed desorption/mass spectrometer (TPD/MS) Autosorb-1C with a PrismaPlus QME 220 MS detector (Quantachrome, USA).

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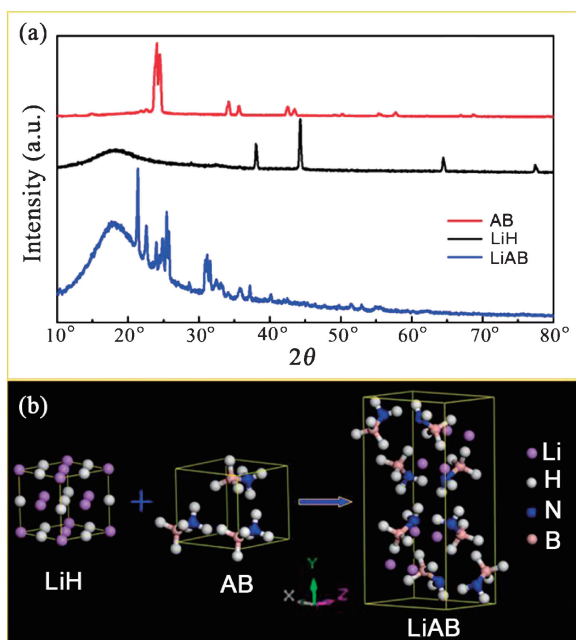


Fig. 1 (a) Powder XRD patterns of AB, LiH and LiAB, (b) structural model sketch of the phase AB, LiH and LiAB.

3. Results and Discussion

3.1 Structure analysis

Figure 1(a) shows the XRD patterns of the starting reactants and the as-prepared LiAB. It can be seen that the peaks of the starting reactants disappeared in the XRD pattern of LiAB, indicating that NH_3BH_3 is completely changed to LiAB. There is a Lewis base (the hydride anion H^-) in LiH, and there is a proton Lewis acid H^+ in NH_3 group in NH_3BH_3 . Thus, when NH_3BH_3 is mixed with LiH, Lewis base H^- will combine with the proton Lewis acid H^+ to form H_2 , and then Li^+ ions will combine with $[\text{NH}_2\text{BH}_3]^-$ ions to form ionic compounds LiAB. Figure 1(b) shows the structural model sketch of the phase transformation from LiH and NH_3BH_3 to LiAB, which is drawn according to the data of Inorganic Crystal Structure Database (ICSD) and the previous studies.^{10,12} It is noted that Xiong *et al.* have confirmed that LiAB is an ionic compound that has an orthorhombic structure with the space group $Pbca$ (No. 61) and lattice parameters of $a = 7.1051 \text{ \AA}$, $b = 13.9300 \text{ \AA}$, and $c = 5.1477 \text{ \AA}$.¹⁰ This structure is different from that of NH_3BH_3 (a tetragonal crystal structure with space group $Pmn21$ (No. 31) and lattice parameters of $a = 5.3950 \text{ \AA}$, $b = 4.8870 \text{ \AA}$, and $c = 4.986 \text{ \AA}$)¹⁵ and that of LiH (a cubic crystal structure with space group $Fm\bar{3}m$ (No. 225) and lattice parameters of $a = b = c = 4.0850 \text{ \AA}$).

Figure 2 shows the FTIR spectrum of NH_3BH_3 and LiAB. We divided the spectrum into three regions: region I (above 3000 cm^{-1}), region II ($2000\text{--}3000 \text{ cm}^{-1}$), and region III (below 2000 cm^{-1}). Region I is the H-N stretching vibration area, in which the spectrum of LiAB has a board peak, and the H-N stretching at 3316 and 3255 cm^{-1} in LiAB is slightly different from that in NH_3BH_3 (3321 , 3258 cm^{-1}). Region II is the H-B stretching vibration area, where the peaks of NH_3BH_3 are boarder. Region III is mainly the H-B and H-N

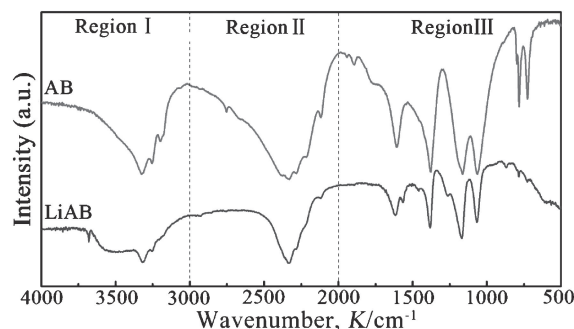


Fig. 2 FTIR spectra of AB and LiAB.

Table 1 The vibrational modes of AB and LiAB are obtained by FTIR measurements (all the frequencies are given in cm^{-1}).

Molecule	Experiment	Vibrational modes
AB	3321	H-N antisymmetric stretching
	3258	H-N symmetric stretching
	2337	H-B antisymmetric stretching
	2276	H-B symmetric stretching
	1602, 1384	H-N scissors
	1161	H-B scissors
	779	N-B stretching
LiAB	3316	H-N antisymmetric stretching
	3255	H-N symmetric stretching
	2333, 2287	H-B antisymmetric stretching
	2120	H-B symmetric stretching
	1563	H-N scissors
	1170, 1264	H-B scissors
	870	N-B stretching

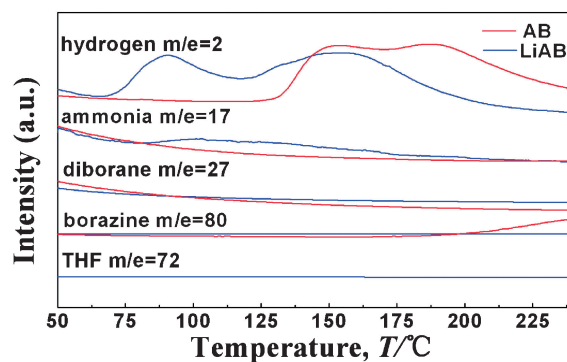


Fig. 3 TPD/MS profiles of AB and LiAB between 50°C and 240°C at a heating rate of $10^\circ\text{C min}^{-1}$.

bending vibration area, and the spectrum of LiAB has more spiky peaks than that of NH_3BH_3 . Vibrational modes and the corresponding identifications of NH_3BH_3 and LiAB are summarized in Table 1, which are consistent with the results reported by Lee *et al.*¹⁵

3.2 Thermal decomposition

Figure 3 shows a comparison of the thermolysis behaviors of AB and LiAB by employing synchronous temperature-

programmed desorption/mass spectrometry (TPD/MS). In the bottom line of Fig. 3, it can be seen that there is no detectable THF in the TPD/MS pattern. This information displays that the THF in the resulted LiAB sample has been removed after the vacuum drying. It is interesting to see that neat AB started to release hydrogen at about 120°C by a two-step process, with decomposition peaks at 153.3°C and 188.4°C, respectively. This trend to high-temperature side is mainly because the heating rate in this work is 10°C min⁻¹, while it is 2°C min⁻¹ in the work reported.¹⁶⁾ As seen in the MS profile of neat AB, borazine (NHBH)₃ was released during the second stage of the AB thermolysis. Interestingly, LiAB displays a starting hydrogen-release temperature at 70.9°C, and a two-step dehydrogenation with peaks centered at 90.5°C and 148.0°C, respectively. In the thermal decomposition process of LiAB, there was no signal of borazine or diborane observed. However, detectable NH₃ was released from 80 to 209°C during the desorption stage, which needs to be investigated in detail in further study.

4. Conclusions

In summary, we have synthesized LiNH₂BH₃ by the direct interaction of LiH with NH₃BH₃ in THF. The thermal decomposition results show that LiNH₂BH₃ exhibit dramatically improved dehydrogenation properties in comparison with that of neat NH₃BH₃. In particular, the as-prepared LiAB starts to release H₂ at a low temperature of 70.9°C, which is important for decreasing the hydrogen desorption temperature of LiAB. Certainly, the desorption of NH₃ from the as-prepared LiAB is to be controlled in future study.

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