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Low temperature hydrogen generation from ammonia combined with Lithium borohydride

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Experimental Section

The source materials, namely, anhydrous magnesium chloride ($MgCl_2$) and lithium boron hydride ($LiBH_4$) were obtained commercially. To prevent materials weight gaining due to moisture, a series of operation during sample preparation was performed under anhydrous condition. Mg $(NH_3)_n$ Cl_2 (here n=1, 2 and 6) was prepared according to previous literatures. In order to understand what kind of role the anion BH_4 plays in dehydrogenation process, the mixture of $Mg(NH_3)_nCl_2$–$nLiBH_4$ (here n=1, 2 and 6) were loaded into different milling vessels under argon atmosphere. The typical weight is 1.5g-2g.The balling is conducted at 580 rpm for 6 min.

The phrases of all these samples as milled for 6 min and ones after heat treatment at different typical temperatures were shown by XRD patterns. All samples were mounted in a glove box and amorphous polymer tapes were used to cover the surface of samples to avoid oxidation during the XRD measurement. Hydrogen and ammonia release measurement was performed by TG-MS with a heating rate of 10℃ min^{-1} under 1 bar argon and a carrier of flow 200 cm^3 min^{-1}. The typical sample quantities were 5-15 mg. Heat treatments of $Mg(NH_3)Cl_2-LiBH_4$ mixtures were carried out in a close test tube under an argon atmosphere, and hydrogen was released into a carrier stream of argon through a T-joint with a thin connection tube to maintain the argon atmosphere over the samples. The products after heat treatment were also characterized at RT by the ^{11}B NMR performed (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 argon atmosphere glove boxes. A 0.55 u s single-pulse excitation was employed, with repetition times of 1.5 s. Sample I and those after heat treatments at different temperature were characterized by infrared absorption spectroscopy using a Nicolet Nexus 470 FT-IR spectrometer and KBr pellets. Due to the high reactivity of these compounds with moisture and oxygen, all of the samples are loaded into one tube with CaF_2 windows. The temperature-programmed desorption (TPD) was performed on a semi-automatic Sievert's apparatus, connected with a reactor filled with sample under hydrogen atmosphere (1bar). The reactor connected with a chamber of known volume was heated from RT to 480℃ at a 10 ℃ min^{-1} heating rate.

Table S1. Summary of H_2 and NH_3 content and NH_3 conversion ratio in the samples of $Mg(NH_3)_n Cl_2$ -$nLiBH_4$ (n=1, 2, and 6).

Sample	Gravimetric NH_3, wt.%	Gravimetric H wt.%	The results of TG wt.%	n(H_3)/sample, mole·[c]	n(NH_3)/sample, mole·[c]	Converted NH_3, wt.%
$Mg(NH_3)_6Cl_2$-$6LiBH_4$	31.1	12.8	15.2[a]/20.1·[b]	10.5	1.6	72.4
$Mg(NH_3)_2Cl_2$-$2LiBH_4$	19.7	8.1	11[a]/12[b]	5.1	0.4	78.9
$Mg(NH_3)Cl_2$-$LiBH_4$	12.7	5.2	5.2[a]/6.2[b]	2.9	0.08	91.6

[a] after heating to 275 ℃; [b] after heating to 550 ℃; [c] calculated according to the TG results heating to 275 ℃ and the TPD results performed under hydrogen atmosphere(1 bar) from room temperature to 480 ℃.

Table S2. Absorption bands detected in IR spectra (wavenumber [cm^{-1}]) of sample I (milled for 6 min) and sample I after heat treatment at different temperatures as compared to the substrates($Mg(NH_3)Cl_2$ and $LiBH_4$).

Assignment	Substrates(RT)	Milled and after heat treatment				
		RT	50□	150□	200□	250□
ν(NH)	3349	3347	3347	3350	-------	-------
	3275	3277	3274	3274	-------	--------
ν(BH)	2378	2378	2378	2360	2360	2360
	------	-------	------	2344	2344	------
	2286	2286	2286	2289	2292	2292
	2219	2219	2219	2225	2228	2225
δ(NH)	1277	1277	1277	1277	------	------
	1259	1259	1259	1259	-------	--------
	1402	1406	1406	1405	1405	1400
ν(BN)	--------	------	-----	-------	1457	1457
					------	1366
					------	1354

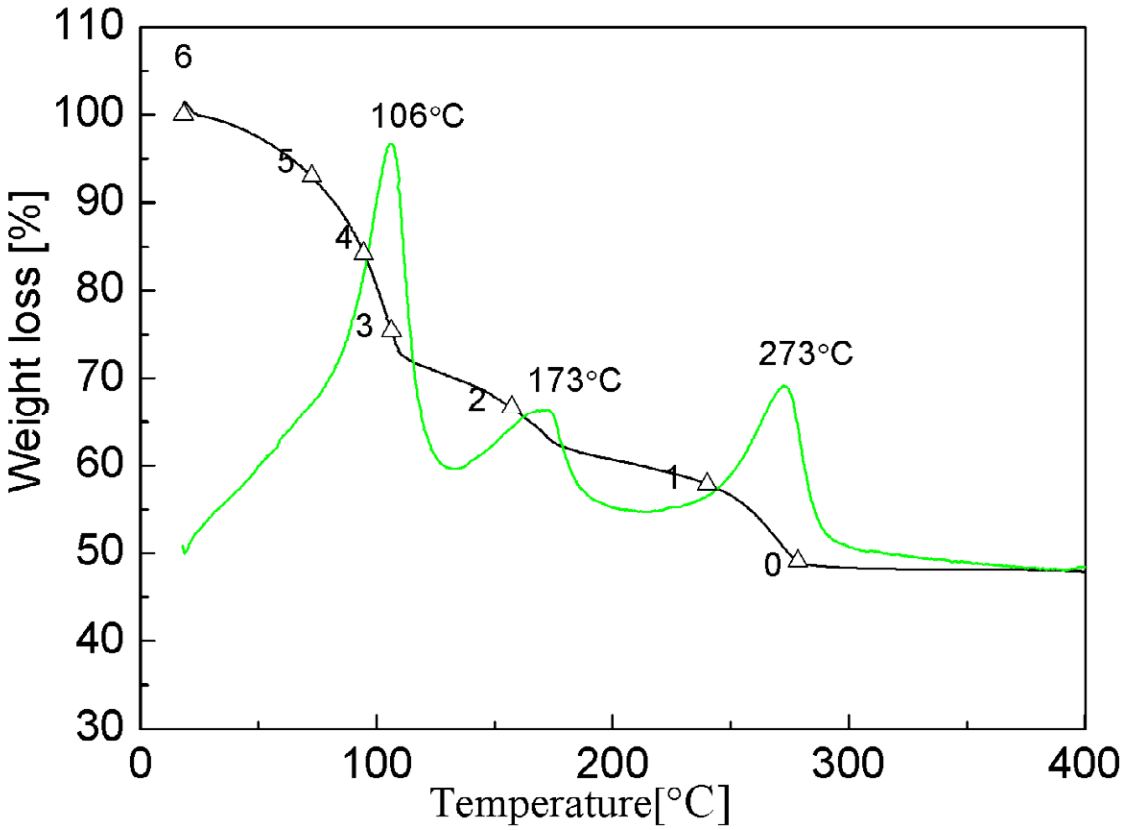

Figure S1. The TG (in black line) and DTA (in green line) of $Mg(NH_3)_6Cl_2$. The quantity of remaining ammonia is marked with △.

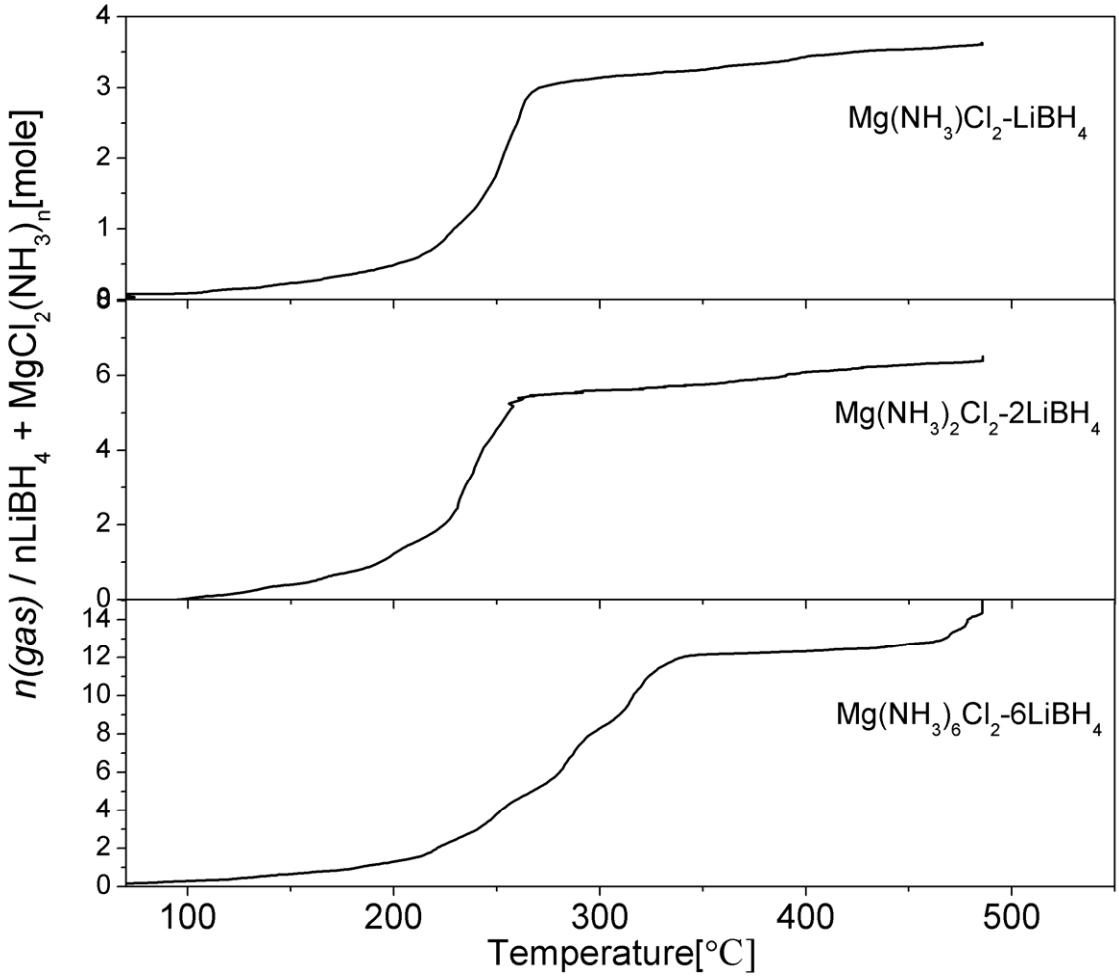

Figure S2. TPD results of hydrogen and ammonia release for $Mg(NH_3)Cl_2$—$LiBH_4$ $Mg(NH_3)_2Cl_2$—$2LiBH_4$. $Mg(NH_3)_6Cl_2$—$6LiBH_4$. The amount of gas released has been normalized as n(gas)/mol of $Mg(NH_3)_nCl_2$—$nLiBH_4$.

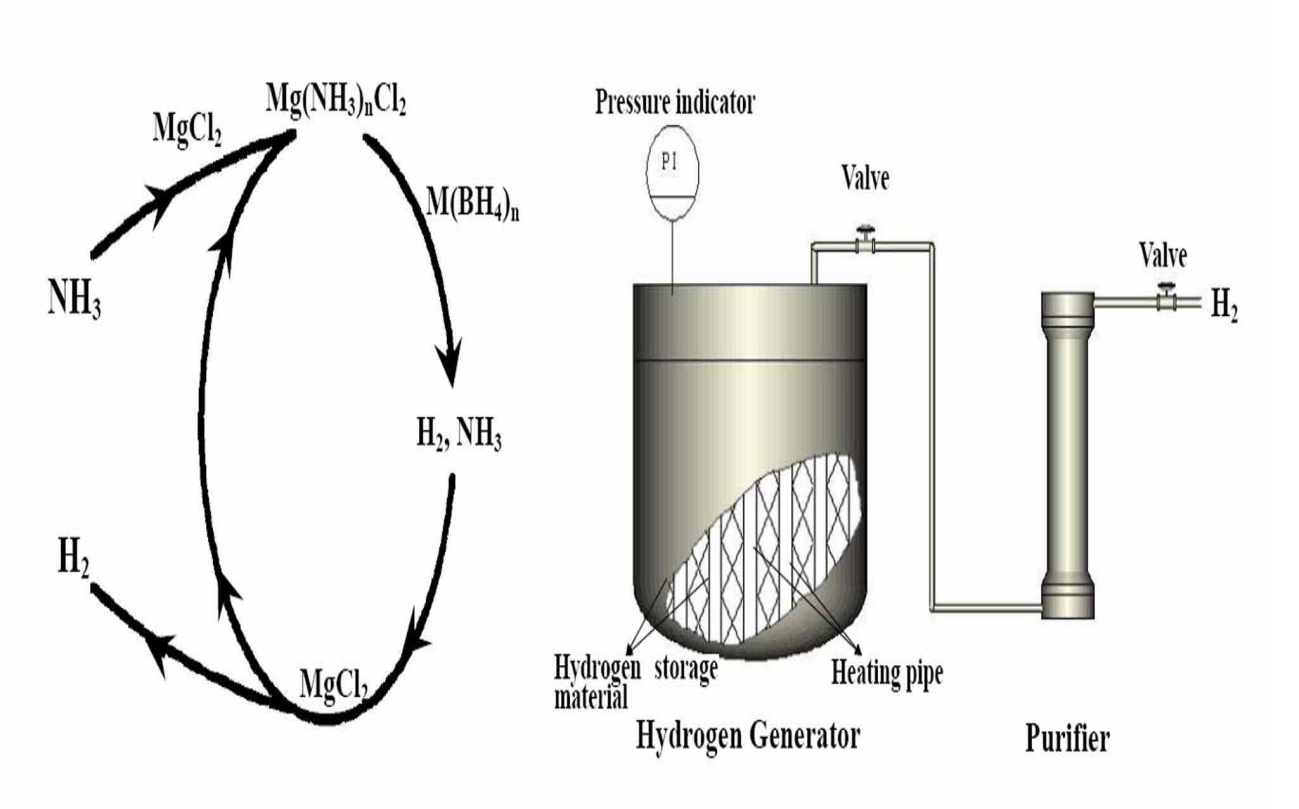

Figure S3. The conversion of NH_3 to H_2 (left) and one simple purifier to restrain ammonia release (right).

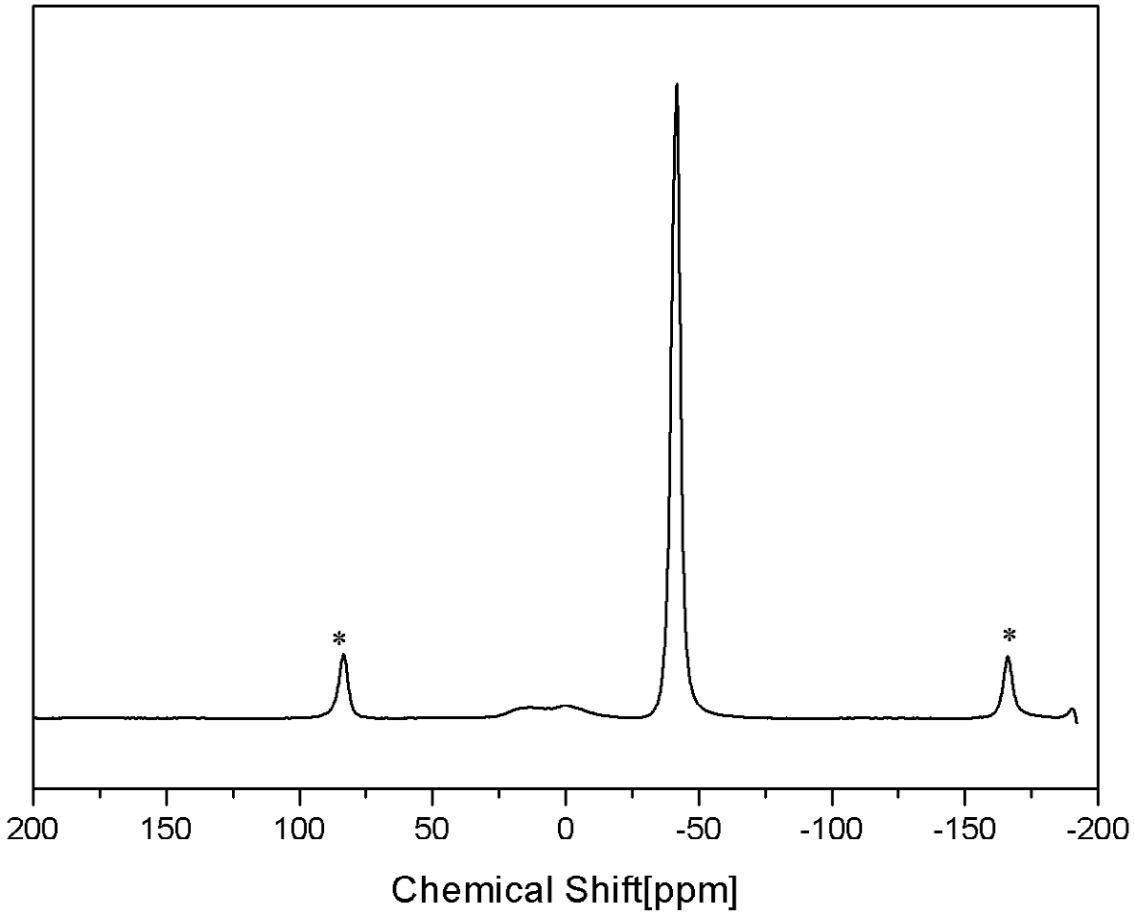

Figure S4. The ^{11}B NMR result of the product of $LiBH_4$ heating to 300℃ under pure ammonia atmosphere without $MgCl_2$ for 3 h.

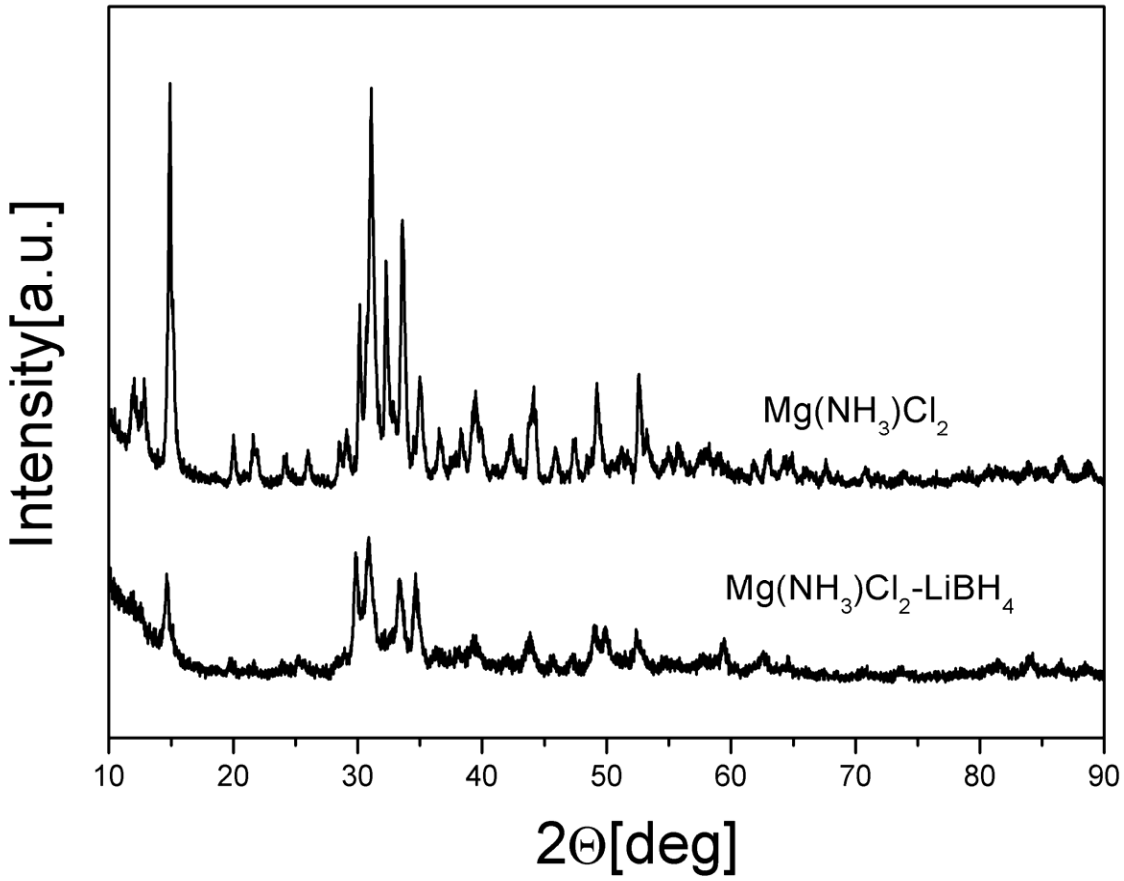

Figure S5. The XRD patterns of Mg (NH_3) Cl_2 and sample Ⅰ at room temperature . After ball milling, the peaks corresponding to $LiBH_4$ and $Mg(NH_3)Cl_2$ disappeared and new phase, the reflection of which is assigned to the mixture of $Mg(NH_3)Cl_2$—$LiBH_4$, appeared.

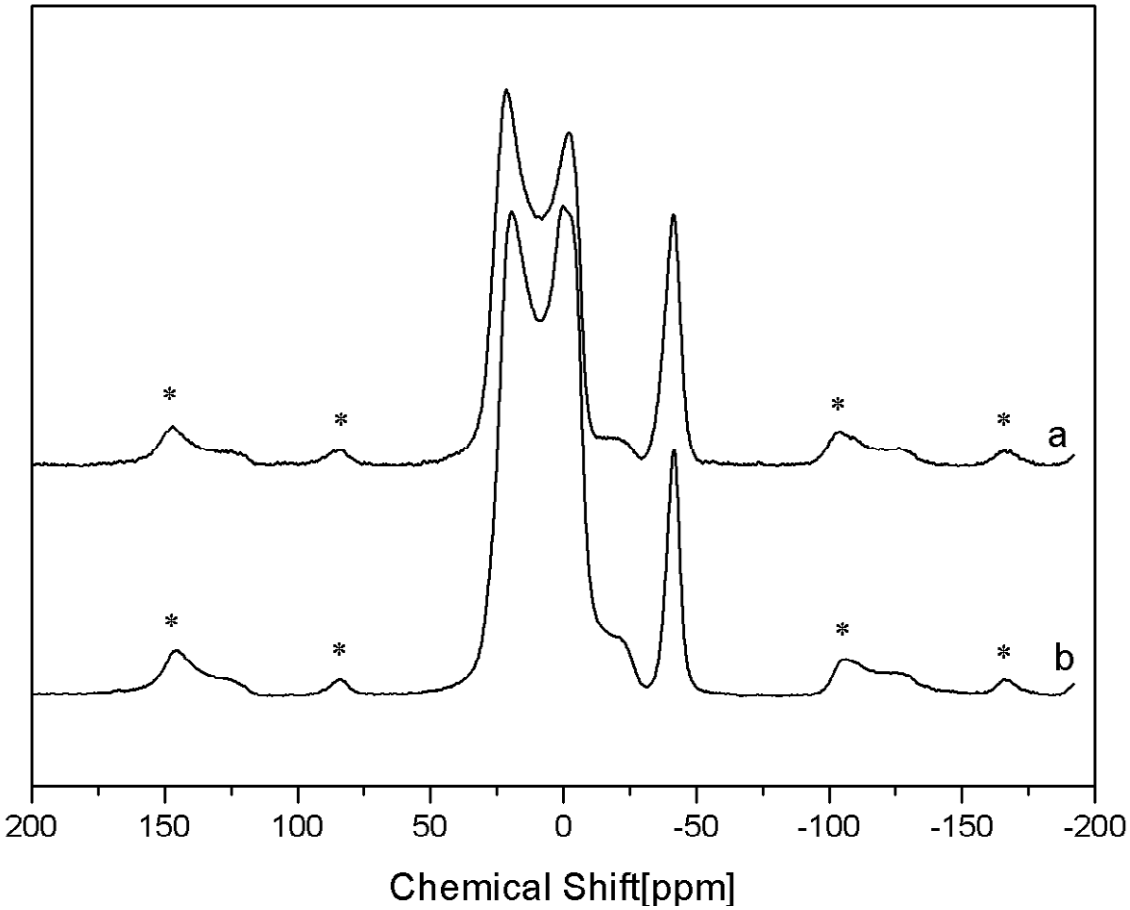

Figure S6. The ^{11}B NMR of a) $Mg(NH_3)Cl_2$—$LiBH_4$ dehydrogenated after heat treatment at 280℃ for 3 hours; b) Lithium amidoborane dehydrogenated after heat treatment at 250℃ for 3h. Spinning side bands are marked with ＊

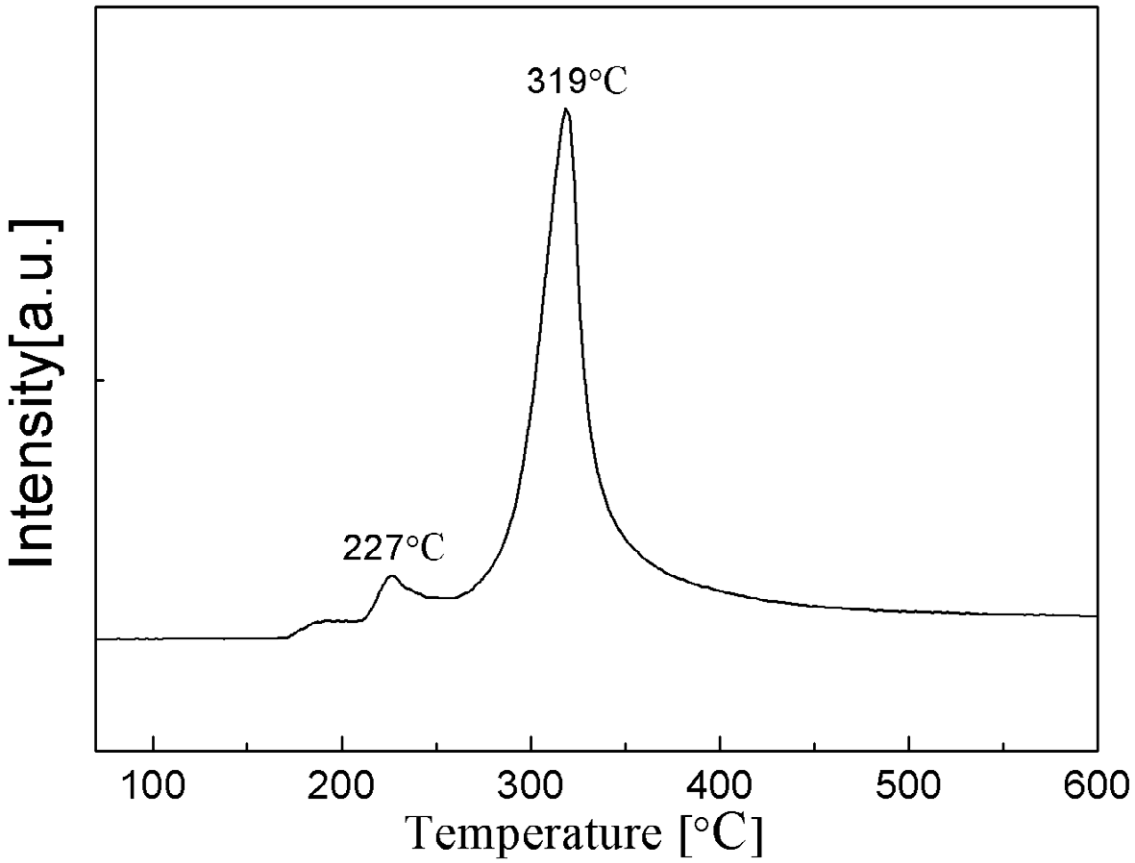

Figure S7. MS result of the home made $Mg(NH_3)Cl_2$.

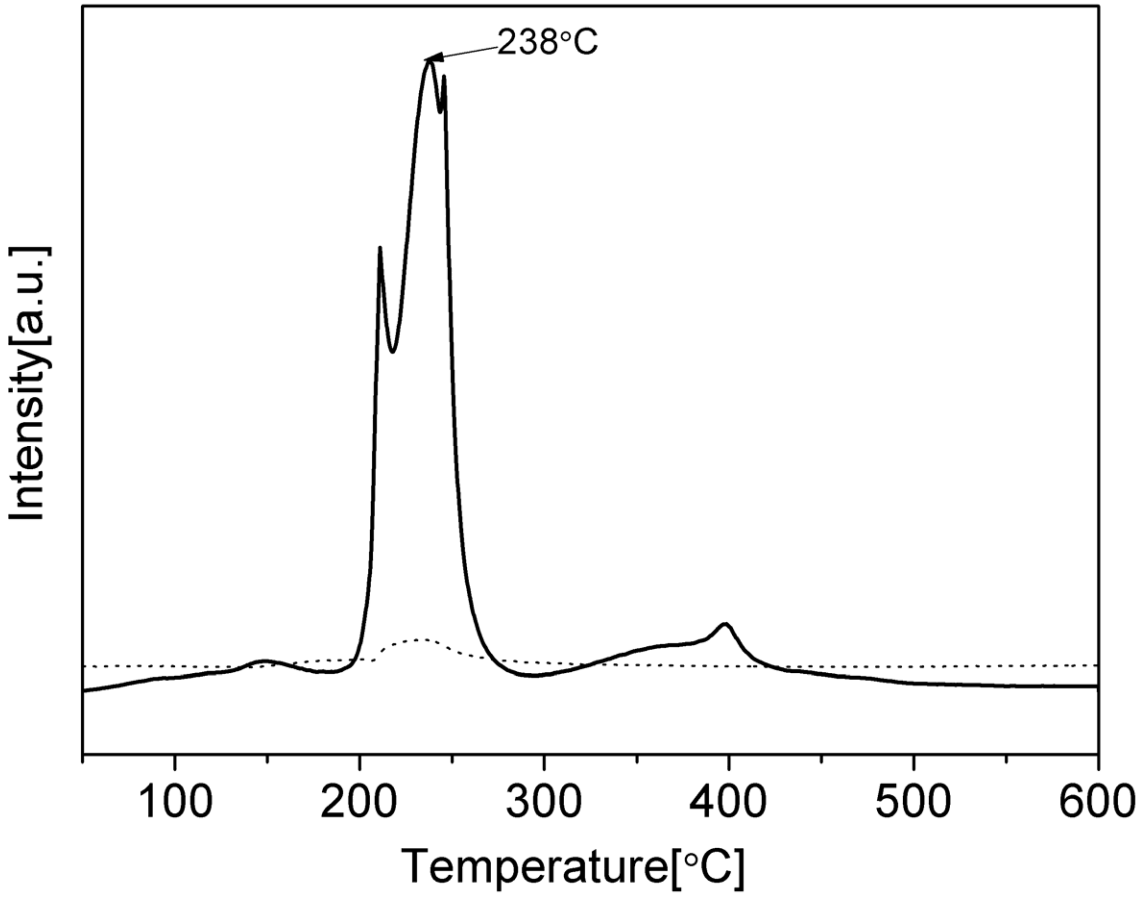

Figure S8. The H_2 (—) and NH_3(– – –) MS signal of $NaBH_4$---$Mg(NH_3)Cl_2$.