

**Electronic Supplementary Information for Dalton Transactions**

**Combined Formation and Decomposition of  
Dual-Metal Amidoborane  $\text{NaMg}(\text{NH}_2\text{BH}_3)_3$  for  
High-Performance Hydrogen Storage**

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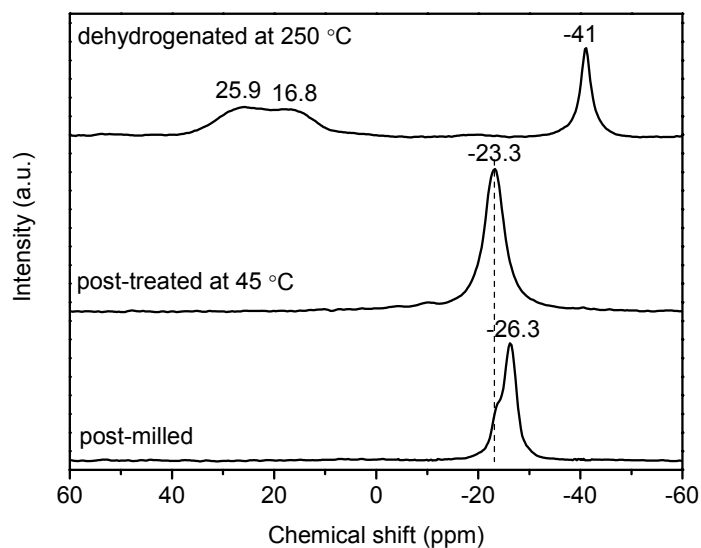
## Experimental

The starting material AB (97% purity) was purchased from Sigma-Aldrich Corp. and used as received. NaMgH<sub>3</sub> was synthesized by solid-phase reaction between NaH (Sigma-Aldrich, 95%) and MgH<sub>2</sub> (Alfa Aesar, 97%). The 1:1 NaH/MgH<sub>2</sub> mixture was firstly milled under argon (99.999% purity) atmosphere for 1 h using a Fritsch 7 Planetary mill at 400 rpm, followed by isothermal treatment at 350 °C under 7 MPa hydrogen pressure for overnight. The purity of NaMgH<sub>3</sub> was verified by XRD and IR analyses. The xAB/NaMgH<sub>3</sub> powder mixtures in varied molar ratio, x=1~3, were mechanically milled under argon atmosphere for 1 h, followed by isothermal treatment at 45 °C for overnight. All the sample handlings were carried out in an argon-filled glovebox, in which the H<sub>2</sub>O/O<sub>2</sub> levels were typically below 0.1 ppm.

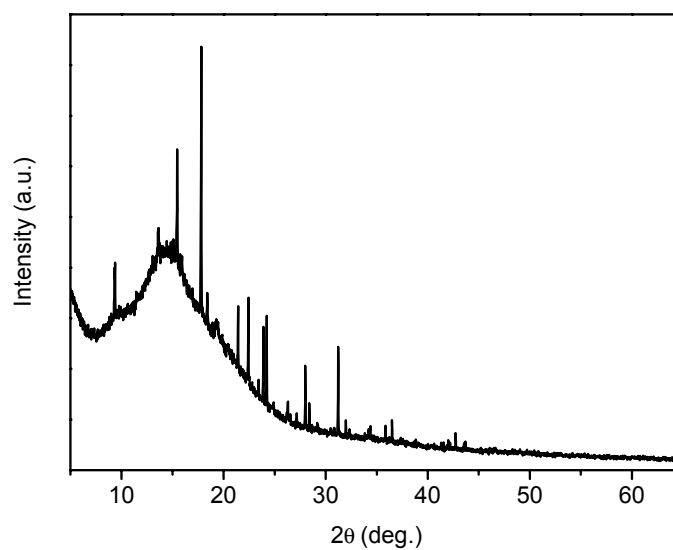
The thermal decomposition behaviors of the samples were examined using synchronous TG/DSC/MS (Netzsch STA 449C Jupiter/QMS 403C). Typically, the sample with a weight of about 3 mg was heated to 250 °C at a ramping rate of 2 °C/min. In the thermal analyses measurements, argon (99.999% purity) was used as purge gas. The isothermal dehydrogenation and temperature-programmed desorption (TPD) measurements (with a typical sample amount of around 100 mg) were performed using a carefully calibrated Sievert's type apparatus. Precise pressure measurement was accomplished using a high-precision pressure transducer. Typically, the dehydrogenation measurements were performed under an initial pressure < 100Pa.

The samples were characterized by XRD (Rigaku D/max 2500, Cu K $\alpha$  radiation), FTIR (Bruker Tensor 27, 4 cm<sup>-1</sup> resolution) and solid-state <sup>11</sup>B MAS NMR (Varian Infinityplus-400, operated at 9.4 T with a <sup>11</sup>B resonance frequency of 128.3 MHz). To determine the crystal structure of NaMg(NH<sub>2</sub>BH<sub>3</sub>)<sub>3</sub>, the sample was examined by high-resolution synchrotron X-ray powder diffractometer at the BL14B beamline of Shanghai Synchrotron Radiation Facility (SSRF), Shanghai.

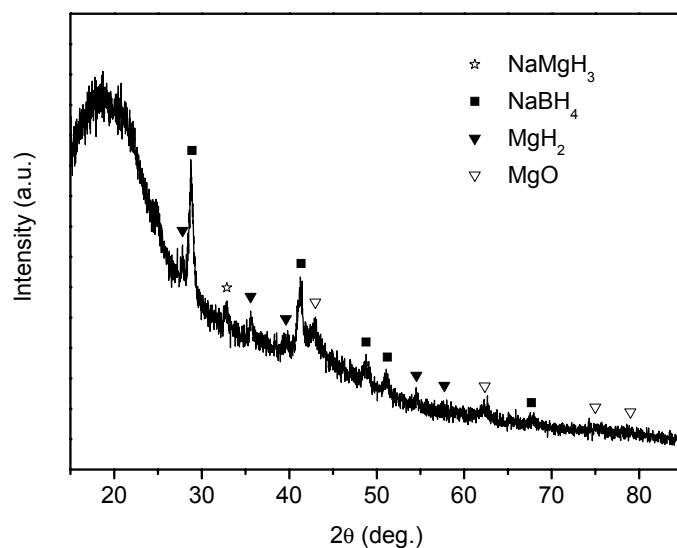
All the sample handlings were carried out in the argon-filled glovebox, and special measures were taken to minimize H<sub>2</sub>O/O<sub>2</sub> contamination during the sample transferring processes. The FTIR spectra were collected at room temperature using KBr-pellet method and the obtained spectra were normalized using OPUS 6.5 software. In the solid-state NMR measurements, solid samples were packed into a ZrO<sub>2</sub> rotor and spun at 12 kHz under nitrogen atmosphere. <sup>11</sup>B chemical shifts were referenced to solid NaBH<sub>4</sub> (-41 ppm). Proton decoupled, Bloch decay <sup>11</sup>B{<sup>1</sup>H} experiments were run using a 3.5 μs 90° pulse, 64 kHz decoupling and a 10 s pulse delay. Each spectrum was accumulated for 16 scans.



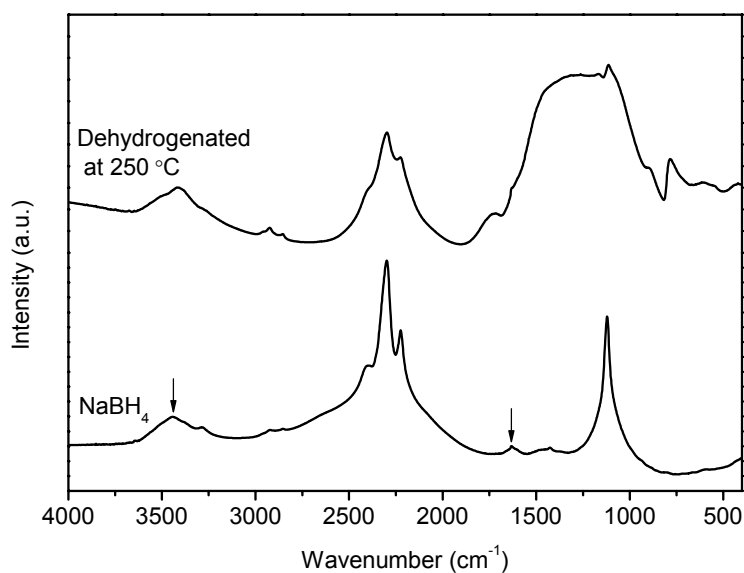
**Fig. S1**  $^{11}\text{B}\{^1\text{H}\}$  MAS NMR spectra of the 3AB/NaMgH<sub>3</sub> sample at varied states.



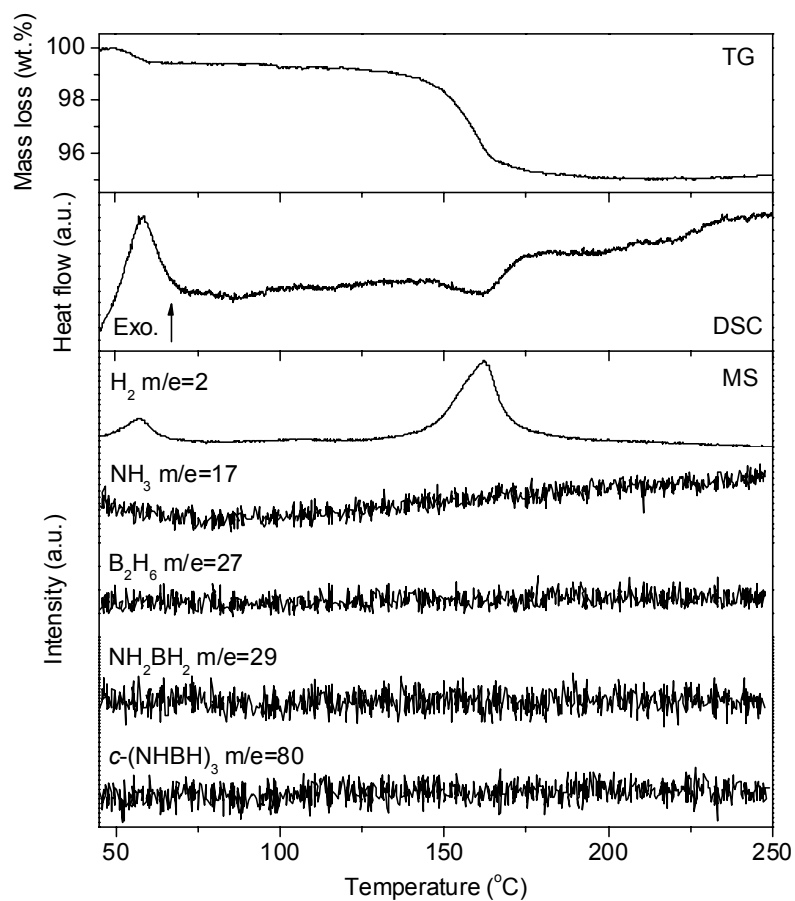
**Fig.S2** Synchrotron X-ray diffraction pattern of the post-treated 3AB/NaMgH<sub>3</sub> sample at 45 °C. The wavelength of the synchrotron X-ray diffractometer is 1.2398Å.



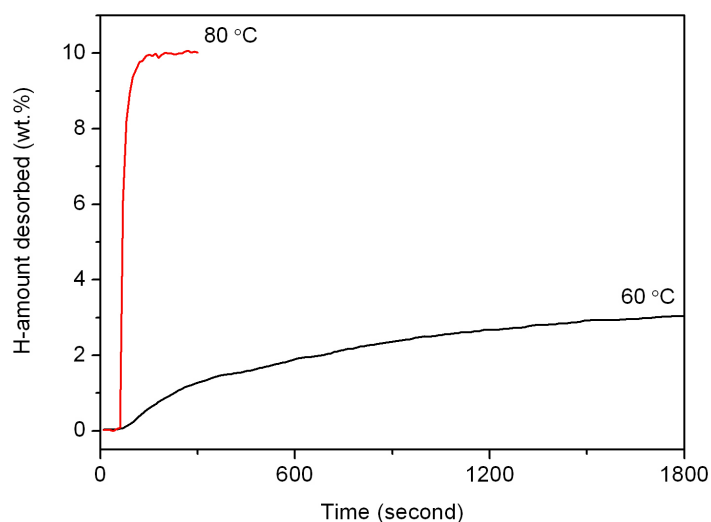
**Fig. S3** XRD pattern of the post-heated 3AB/NaMgH<sub>3</sub> sample at 250 °C. The hump centered at 18.9° comes from the polymer tape that was used to shield sample from H<sub>2</sub>O/O<sub>2</sub> contamination during the XRD measurement.



**Fig. S4** FTIR spectra of the post-heated 3AB/NaMgH<sub>3</sub> sample at 250 °C and the NaBH<sub>4</sub> reference sample. The peaks centered at 3444 and 1631 cm<sup>-1</sup> should be assigned to the H-O bands, which come from the moisture contamination of the samples during the measurement process.



**Fig. S5** TG(top)/DSC(middle)/MS(bottom) profiles of the 1 : 1 AB/NaMgH<sub>3</sub> sample after mechanical milling for 1 h. The ramping rate is 2 °C /min.



**Fig. S6** Comparison of the isothermal dehydrogenation profiles of the post-milled 3AB/NaMgH<sub>3</sub> sample at 80 °C (red line) and 60 °C (black line), respectively.

**Table S1** Comparison of the theoretical and effective hydrogen capacities of NaMg(NH<sub>2</sub>BH<sub>3</sub>)<sub>3</sub> with those of the relevant materials.

Samples	Theoretical H-capacity (wt.%)	Effective H-capacity (wt.%)
NH <sub>3</sub> BH <sub>3</sub>	19.6	13 (below 200 °C)
NaNH <sub>2</sub> BH <sub>3</sub>	9.5	7.6 (release 2 equiv. H <sub>2</sub> )
NaMg(NH <sub>2</sub> BH <sub>3</sub> ) <sub>3</sub>	11	7.4 (release 5 equiv. H <sub>2</sub> )
3NH <sub>3</sub> BH <sub>3</sub> /NaMgH <sub>3</sub>	14.8	11.3 (release 8 equiv. H <sub>2</sub> )

## Analysis of the decomposition products

$\text{NaMgB}_3\text{N}_3\text{H}_5$  gives a nominal composition of the decomposition products of the 3AB/NaMgH<sub>3</sub> sample. XRD pattern of the post-heated sample at 250 °C (Fig. S3) showed the amorphous nature of the majority of solid residue and the presence of NaBH<sub>4</sub>, MgH<sub>2</sub> and NaMgH<sub>3</sub> crystalline phases. The formation of NaBH<sub>4</sub> by-product was further confirmed by the NMR and IR results. As shown in Fig. S1, the characteristic resonances of BH<sub>4</sub> (-41 ppm) species was observed. Likewise, the IR spectra presented in Fig. S4 showed clearly the characteristic bands of NaBH<sub>4</sub> at 2407, 2298, 2224 and 1120 cm<sup>-1</sup>, respectively, which actually dominate the B-H bands in the post-heated sample. Meanwhile, the N-H stretches largely disappeared. These results suggested that the majority of the residual H in the decomposition products exists in the form of NaBH<sub>4</sub>. Similar phenomenon was also observed in the decomposition process of LAB•AB material.<sup>S1</sup> With respect to the destination of the majority of Mg element, one possibility is the formation of magnesium boron nitrides, e.g. Mg<sub>3</sub>BN<sub>3</sub>.<sup>S2</sup> Additionally, the identification of the wide <sup>11</sup>B resonances at 16.8 and 25.9 ppm (Fig. S1) indicates the presence of polyborazine-like [BNH<sub>x</sub>]<sub>n</sub> species in the solid residue. The possibility of BN formation is precluded since the strong characteristic bands of h-BN and c-BN at 1370 and 1065 cm<sup>-1</sup>, respectively, were absent in the IR pattern.

## References

- [S1] C. Z. Wu, G. T. Wu, Z. T. Xiong, X. W. Han, H. L. Chu, T. He, P. Chen, *Chem. Mater.* **2010**, 22, 3.
- [S2] P. Rogl, *Int. J. Inorg. Mater.* **2001**, 3, 201.