Supplementary Information for

Synthesis, formation mechanism, and dehydrogenation properties of the long-sought Mg(NH₂BH₃)₂ compound

Junhong Luo,† Xiangdong Kang,† and Ping Wang*,†

† Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, 110016, China.

E-mail: pingwang@imr.ac.cn
Table S1. The mass changes of the post-milled 2AB/Mg and 2AB/MgH$_2$ samples during the storage period in an Ar-filled glove-box.

<table>
<thead>
<tr>
<th></th>
<th>Theor. Values for forming</th>
<th>Sample1- Aged for 45days (wt%)</th>
<th>Sample 2- Aged for 45days (wt%)</th>
<th>Sample 3- Aged for 45days (wt%)</th>
<th>Sample 4- Aged for 45days (wt%)</th>
<th>Sample 5- Aged for 45days (wt%)</th>
<th>Sample 6- Aged for 45days (wt%)</th>
<th>Sample 7- Aged for 1year (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2AB/Mg</td>
<td>2.32</td>
<td>2.86</td>
<td>2.96</td>
<td>2.85</td>
<td>2.91</td>
<td>2.86</td>
<td>2.92</td>
<td>3.2</td>
</tr>
<tr>
<td>2AB/MgH$_2$</td>
<td>4.54</td>
<td>4.28</td>
<td>4.29</td>
<td>4.27</td>
<td>4.24</td>
<td>4.37</td>
<td>4.36</td>
<td>4.38</td>
</tr>
</tbody>
</table>

Notes: 1. The weight losses of the post-milled 2AB/MgH$_2$ and 2AB/Mg samples were measured using a balance with an accuracy of 0.1 mg. Since the two kinds of samples give total weight losses of around 15 and 10 mg, respectively, the weight loss percentages of these samples determined could be pretty accurate.

2. The weight losses of the samples were measured in the following procedures: first, the net weight of the post-milled sample (W1) and the total weight of the post-milled sample + test tube (W2) were measured and recorded; then, after the aging completed, the total weight of the aged sample + test tube (W3) was measured and recorded. Here, the test tube was opened for a while to enable the evolved H$_2$ to escape prior to sample weighing; finally, the weight losses of the post-milled samples (WL\%) were calculated via the following formula: \( WL\% = (W2 - W3)/W1 \times 100\% \).

3. For both kinds of samples, samples numbered from 1 to 6 were aged for around 45 days while samples 7 were stored in the glove-box for over 1 year. The samples aged for about 45 days should have largely completed the conversion reactions that lead to the formation of MgAB, as evidenced by the absence of crystalline AB. Since further aging of MgAB did not result in appreciable mass changes, as indicated by the 1 year-aged sample 7, the stability of MgAB was verified. In contrast, LiAB and NaAB were found to undergo self-decomposition appreciably during the storage period at room temperature.\[^{[1]}\]
**Fig. S1** FTIR profiles of (a) the aged 2AB/Mg (2.9 wt% weigh loss) and (b) the aged 2AB/MgH₂ (4.3 wt% weight loss) after dehydrogenation at 450 °C. The lines are added only to guide the eye.

**Fig. S2** Dehydrogenation profiles of the aged 2AB/Mg (2.9 wt% weigh loss, black) and the aged 2AB/MgH₂ (4.3 wt% weight loss, red). The samples were heated to 450 °C at a ramping rate of 2 °C min⁻¹ and then held at this temperature until the dehydrogenation profiles leveled off.
Analysis of Fig. S1 and S2:

FTIR analyses of the dehydrogenation products of the aged 2AB/MgH₂ (~4.3 wt% weight loss) and 2AB/Mg (~2.9 wt% weight loss) samples revealed that the hydrogen contained can be mostly detached upon heating to 450 °C, as evidenced by the absence of BH and NH stretches (Fig. S1). This provides us an indirect way to evaluate whether the weight losses that occurred during the aging period of the post-milled 2AB/MgH₂ and 2AB/Mg samples are solely contributed by the loss of H₂. We know the 2AB/MgH₂ and 2AB/Mg samples contain ~15.6 and 13.7 wt% of H (after taking the purity of AB (97%) and MgH₂ (98%) into account), respectively. And after aging treatment, the aged 2AB/MgH₂ and 2AB/Mg samples totally yielded ~11.2 and 11.4 wt% of H₂ upon heating to 450 °C, respectively (Fig. S2). Then the H-capacity gaps should result from the loss of hydrogen during the aging period, which are 4.4 and 2.3 wt% of H for the 2AB/MgH₂ and 2AB/Mg samples, respectively. Since for the 2AB/MgH₂ sample, the determined H-capacity gap is close to the determined weight loss, it should have released H₂ of purity during the aging period. Whereas for the 2AB/Mg sample, the determined weight loss is greater than the determined H-capacity gap, thus indicating that its aging process should have involved the release of heavier gaseous byproduct(s).
**Fig. S3** Enlarged view of the XRD patterns of (a) the aged 2AB/Mg (2.9 wt% weight loss) and (b) the aged 2AB/MgH₂ (4.3 wt% weight loss) samples.

**Fig. S4** H₂ release profiles of the post-milled 2AB/Mg (black) and 2MgH₂ (red) samples when were aged at 40, 60, and 70 °C water bath.
Fig. S5  XRD patterns of the 2AB/MgH₂ sample after aging at 60 °C water bath with varied pre-milling: (a) and (b) milled using a Planetary Fritsch P7 mill at 400 rpm for 5 and 1 h, respectively; (c) milled using a high-energetic Spex8000 mill for 2 h.

Fig. S6  Comparison of the FTIR spectra of Mg(NH₂)₂, Mg₃N₂, and MgAB. It was found that the newly formed IR band peaked at ~565 cm⁻¹ falls in the same range of IR bands of the Mg-N stretch, so the formation of such IR band is indicative of the establishment of Mg-N bonding.
**Fig. S7** FTIR spectra of (a) the postmilled 2AB/MgH$_2$ sample, (b) the aged 2AB/MgH$_2$ sample with ~4.3 wt% weight loss (MgAB), and (c) the dehydrogenation product of MgAB at 300 °C.

**Fig. S8** $^{11}$B MAS NMR spectra of the postmilled 2AB/MgH$_2$ sample (black), the aged 2AB/MgH$_2$ sample with ~4.3 wt% weight loss (MgAB, red), and the dehydrogenation product of the 2AB/MgH$_2$-converted MgAB at 300 °C (blue). ★ indicates the spinning sidebands.
Fig. S9 Comparison of the TG/DSC/MS profiles of the post-milled 2AB/Mg sample (black) and the aged 2AB/Mg sample with ~2.9 wt% weight loss (MgAB, red). The mass spectra represent: m/e=2 (H₂); m/e=17 (NH₃). No B-containing gaseous byproduct was detected.

Fig. S10 Mass spectroscopy of the possible gaseous byproducts from the 2AB/MgH₂-converted MgAB at the ramping rates of 2 (bottom panel), 5 (middle), and 10 (top) °C min⁻¹: m/e=17 (NH₃); m/e=26 (B₂H₆); m/e=29 (NH₃BH₂); m/e=80 (c-(NHBH)₃).
Fig. S11 TG profiles of the aged 2AB/MgH₂ sample (4.3 wt% weight loss) at the ramping rates of 2 (black), 5 (red), and 10 (blue) °C min⁻¹. The dramatic fluctuations of the TG profiles at the ramping rates of 5 and 10 °C min⁻¹ are due to the occurrence of sample foaming, which is associated with the melting of MgAB at these heating rates.

Fig. S12 The DSC profiles of the aged 2AB/MgH₂ sample (~4.3 wt% weight loss) at the ramping rate of 2, 5, 10 °C min⁻¹. The inset shows the Kissinger plots of the three dehydrogenation steps. Eₐ₁, Eₐ₂, and Eₐ₃ are the apparent activation energies for the first, the second, and the third dehydrogenation steps, respectively.
**Analysis of Fig. S10~S12:**

1. The appearance of an endothermic signal (at 91 and 97 °C, respectively) before the release of H₂ for samples heating at 5 and 10 °C min⁻¹ should be assigned to the occurrence of melting of MgAB. Presumably, the absence of melting signal for MgAB heated at the ramping rate of 2 °C min⁻¹ should result from the occurrence of solid-phase decomposition of MgAB before reaching its melting point. Actually, similar phenomenon has also been found in the thermolysis of AB.² But except for this physical change, the chemical decomposition of MgAB was not notably altered by the variation of heating rates, as indicated by the combination of MS (Fig. S10) and TG (Fig. S11) results.

2. The apparent activation energies for the three dehydrogenation steps were estimated on the basis of DSC data at varied rates using Kissinger equation,³ which is given by:

\[
d\left[\ln\left(\frac{\beta}{T_p^2}\right)\right]/d(1/T_p) = -\frac{E_a}{R}
\]

where \( T_p \) is the peak temperature, \( \beta \) is the heating rate, \( E_a \) is the apparent activation energy, and \( R \) is the gas constant. The Kissinger plots, i.e., \( \ln[\beta/T_p^2] \) as a function of the inverse of \( T_p \), are given in the inset. For each step, a well-fitted line can be obtained, and from the slope of the fitted line, the apparent activation energies of the first, the second, and the third dehydrogenation steps can be roughly estimated to be 84, 116, and 119 kJ mol⁻¹, respectively.
Fig. S13 Dehydrogenation profiles of AB and the aged 2AB/MgH₂ (4.3 wt% weight loss, MgAB) at 100 °C oil bath.

Fig. S14 TPD profile of MgAB converted from the post-milled 2AB/Mg sample with a ramping rate of 2 °C min⁻¹ to 300 °C and held at this temperature for about 2 h.
**Fig. S15** XRD patterns of the dehydrogenation products of (a) the 2AB/MgH$_2$-converted MgAB and (b) the 2AB/Mg-converted MgAB at 300 °C

\[ \text{Mg} + 2\text{NH}_3\text{BH}_3 \rightarrow [\text{MgH}]^{\delta^+}[\text{NH}_2\text{BH}_3]^{\delta^-} + \text{NH}_3\text{BH}_3 \quad (1) \]

\[ \rightarrow [\text{Mg}^{2\delta^+}\text{H}^{\delta^-}][\text{NH}_2\text{BH}_3]^{\delta^-} + \text{NH}_3\text{BH}_3 \quad (2) \]

\[ \rightarrow [\text{Mg}^{2\delta^+}\text{H}^{\delta^-}][\text{NH}_2\text{BH}_3]^{\delta^-} + \text{H}^{\delta^+}[\text{NH}_2\text{BH}_3]^{\delta^-} \quad (3) \]

\[ \rightarrow \text{Mg}^{2\delta^+}[\text{NH}_2\text{BH}_3]^{\delta^-} + \text{H}_2 \uparrow \]

**Scheme S1.** Conceived scheme of reaction between AB and elemental Mg. First, ammine H$^{\delta^+}$ of AB transfers from AB to Mg, resulting in the formation of a transient $[\text{MgH}]^{\delta^+}[\text{NH}_2\text{BH}_3]^{\delta^-}$ species (step 1); then, charge redistribution occurs in the $[\text{MgH}]^{\delta^+}$ group, leading to the formation of $[\text{Mg}^{2\delta^+}\text{H}^{\delta^-}]$[NH$_2$BH$_3$]$^{\delta^-}$ species with a hydridic H$^{\delta^-}$ on Mg (step 2); finally, the as-formed hydridic H$^{\delta^-}$ in the $[\text{Mg}^{2\delta^+}\text{H}^{\delta^-}]$[NH$_2$BH$_3$]$^{\delta^-}$ species combines with a protic H$^{\delta^+}$ from another AB to generate molecular H$_2$ and results in the formation of MgAB (step 3). But to verify the proposed reaction mechanism, theoretical calculations are still highly needed.

**References:**

