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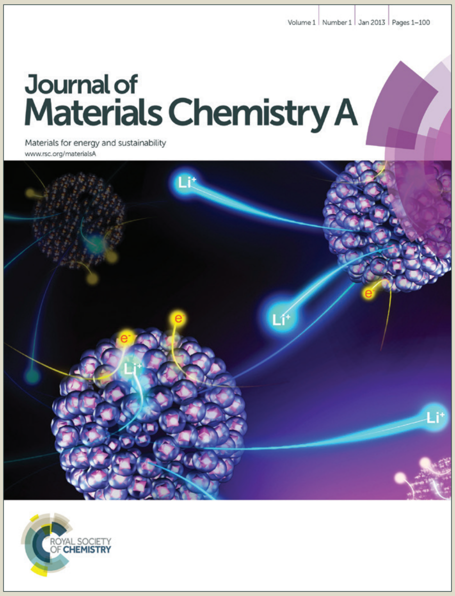

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ARTICLE TYPE

Solvent-Free Synthesis and Stability of $MgB_{12}H_{12}$

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$MgB_{12}H_{12}$ has been widely discussed as an intermediate in the hydrogen sorption cycles of $Mg(BH_4)_2$, but its properties such as stability and reactivity are still unknown. We achieved the synthesis of $MgB_{12}H_{12}$ via the reaction between $Mg(BH_4)_2$ and B_2H_6 at 100 to 150 °C. When bulk $Mg(BH_4)_2$ was used as the starting material, a yield of 10.2 to 22.3 mol% was obtained, which was improved to 92.5 mol% by using $Mg(BH_4)_2$ nanoparticles. The as-synthesized $MgB_{12}H_{12}$ decomposed into boron between 400 to 600 °C, preceded by a possible polymerization process. The formation mechanism of $MgB_{12}H_{12}$ and its role in the decomposition process of $Mg(BH_4)_2$ were discussed.

Introduction

Storing hydrogen in safe and efficient media is a key technology for the widespread utilization of hydrogen as a clean energy carrier.[1] Due to the combined high volumetric and gravimetric hydrogen densities, light-metal complex hydrides have been widely investigated for solid hydrogen storage.[2,3] Among them, magnesium borohydride $Mg(BH_4)_2$ is currently one of the most discussed light-metal complex hydrides.[4-16] It exhibits a hydrogen density of 14.9 wt% and an enthalpy change of -39 kJ/mol H_2 in the overall decomposition reaction corresponding to hydrogen desorption at around room temperature.

$Mg(BH_4)_2$ presents complex crystal structures with different polymorphs at different temperatures.[4,13] The major desorption reaction of $Mg(BH_4)_2$ occurs above 270 ºC through multiple steps, regardless of the initial crystal structure.[6-8,16] Within the multi-step decomposition process, $MgB_{12}H_{12}$ has been widely discussed as an intermediate based on Raman spectroscopy and nuclear magnetic resonance (NMR) measurement results.[7,8,11,17-20] This point was also supported by theoretical predictions.[21-25] H.-W. Li et al. observed that 6.1 mass% of hydrogen can be reversibly stored after the initial dehydrogenation, possibly through the formation of $MgB_{12}H_{12}$.[7] In spite of the important role of this intermediate, its properties such as stability and reactivity are still unknown and its role in the de-/re-hydrogenation processes has not yet been fully understood. One reason for this situation is the difficulty in synthesis of solvent-free $MgB_{12}H_{12}$. Some metal dodecaborates such as $Li_2B_{12}H_{12}$ can be synthesized through the thermohydrolysis of their hydrated salts.[26-28] However, the $[B_{12}H_{12}]^{2-}$ species in $Mg(H_2O)_6B_{12}H_{12}\cdot 6H_2O$ tend to decompose in the drying process, owing to the dihydrogen bonds between H_2O and the $[B_{12}H_{12}]^{2-}$ anion.[29] Another wet method via the reaction between $B_{10}H_{14}$ and $Mg(BH_4)_2$ in THF to produce $MgB_{12}H_{12}$ was also hindered by desolvation in the final product.[28] The reaction between MgH_2 nanoparticles with B_2H_6 leads to the formation of $MgB_{12}H_{12}$ together with other Mg-B-H species, which is restricted within nanopores.[30]

Synthesis of metal dodecaborates from the reactions between B_2H_6 and the metal borohydrides such as $LiBH_4$,[31] $NaBH_4$[32] and $Y(BH_4)_3$[33] has been demonstrated. In present study, we first investigated the reaction between bulk $Mg(BH_4)_2$ and B_2H_6 at 100 to 150 °C with the intention to synthesize $MgB_{12}H_{12}$. Second, we promoted the formation of $MgB_{12}H_{12}$ by using $Mg(BH_4)_2$ nanoparticles as a starting material. Finally, we investigated the thermal stability and the decomposition process of $MgB_{12}H_{12}$, and discussed its role in the hydrogen desorption process of $Mg(BH_4)_2$.

Experimental

The samples of $ZnCl_2$ (99.9%) and $Mg(BH_4)_2$ (> 95%) were purchased from Sigma–Aldrich and $NaBH_4$ (95%), $K_2B_{10}H_{10}$ and $K_2B_{12}H_{12}$ from Katchem. $Mg(B_3H_8)_2$ was synthesized via reaction between borane THF and magnesium mercury amalgams, followed by desolvation in vaccum at 50 ºC.[34] MgH_2 nanoparticles supported on carbon matrix (MgH_2/carbon), with a load ratio of 10 wt% and an average diameter of 10 nm, were prepared via melt infiltration.[35] $Mg(BH_4)_2$/carbon nanocomposite was synthesized by ball milling of MgH_2/carbon in B_2H_6/H_2 atmosphere for 3 days at room temperature.[36] $NaZn(BH_4)_3$, synthesized by milling a mixture of $ZnCl_2$ and $NaBH_4$, was used as a B_2H_6 source which releases B_2H_6 and H_2 above 90 ºC according to eq. 1.[37]

$$NaZn(BH_4)_3 \rightarrow NaBH_4 + Zn + B_2H_6 + H_2 \quad (1)$$

Reactive ball milling of bulk $Mg(BH_4)_2$ in B_2H_6/H_2 at 100 and 150 °C for 24 h, respectively, was carried out analogous to the procedure as described previously.[33] The reaction of $Mg(BH_4)_2$/carbon with B_2H_6 was performed at 150 °C for 24 h in B_2H_6/H_2 atmosphere without ball milling.

In-situ observation of the reaction between bulk $Mg(BH_4)_2$ and B_2H_6 at 100 °C by Raman spectroscopy was conduct with a Bruker Senterra instrument of 5 cm^{-1} spectral resolution (spatial resolution ≈ 5 µm) using a 532 nm laser. Pure $Mg(BH_4)_2$ powder was compressed into a small pellet (diameter and thickness: 1mm) which was placed in a gas-tight sample holder together with some $NaZn(BH_4)_3$ as B_2H_6 source. Subsequently, the sample holder was heated up to 100 °C with a ramp of 10 °C/min by an oven below it. The in-situ measurement was started right after the temperature was achieved at 100 °C.

Solid-state ^{11}B magic angle spinning (MAS) NMR measurements were performed on a Bruker Avance-400 NMR spectrometer using a 4 mm CP-MAS probe. The ^{11}B NMR spectra were recorded at 128.38 MHz at 12 kHz sample rotation applying a Hahn echo pulse sequence to suppress the broad background resonance of boron nitride of the probe. Pulse lengths of 1.5 μs (π/12 pulse) and 3.0 μs were applied for the excitation and echo pulses, respectively. For selected samples, ^{11}B cross polarization magic angle spinning (CP-MAS) NMR experiments were performed using weak radio-frequency powers for spin locking of the ^{11}B nucleus on resonance as described elsewhere.[17, 38] Solution-state NMR experiments with Dimethyl sulfoxide (DMSO-d_6) as the solvent were carried out using a 5 mm inverse broadband probe at 25 °C. ^{11}B NMR chemical shifts were reported in parts per million (ppm) externally referenced to a 1M $B(OH)_3$ aqueous solution at 19.6 ppm as external standard sample.

Results

Synthesis of $MgB_{12}H_{12}$

The reaction of bulk $Mg(BH_4)_2$ with B_2H_6 was first investigated by in-situ Raman spectroscopy. The evolution of vibration modes of $Mg(BH_4)_2$ in B_2H_6/H_2 atmosphere at 100 °C is presented in Fig. 1. The reference spectra of $K_2B_{12}H_{12}$ and $K_2B_{10}H_{10}$ are shown in Fig. S1 (†ESI). In Fig. 1, $Mg(BH_4)_2$ shows the bending vibration modes at Raman shifts 1180 and 1387 cm^{-1} and stretching modes at 2210 and 2230 cm^{-1}. The vibrations of gaseous B_2H_6 exhibit sharp lines at 577, 804, 1025, 2114 and 2530 cm^{-1}. With the increase of the reaction time, the vibrations of $Mg(BH_4)_2$ declined and new vibration modes became pronounced at 730 and 2560 cm^{-1}. The new vibration modes can be assigned to the B-H vibrations of closo structures, as compared with Raman spectra of $K_2B_{12}H_{12}$ and $K_2B_{10}H_{10}$ (Fig. S1).

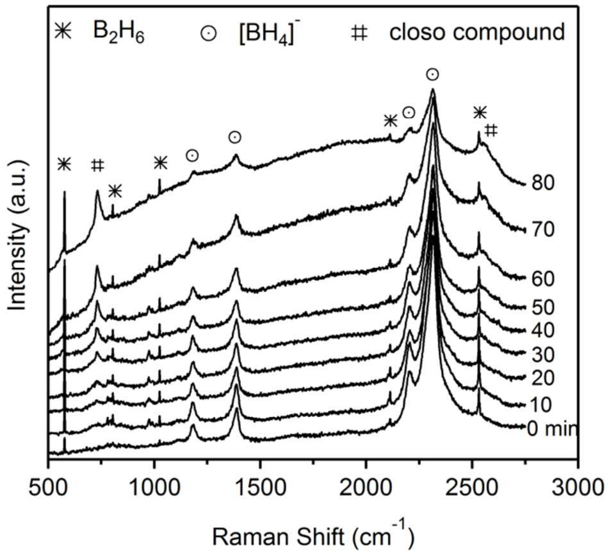


Fig. 1 In-situ observation of $Mg(BH_4)_2$ reacting with B_2H_6 at 100 °C within 80 min by Raman spectroscopy.

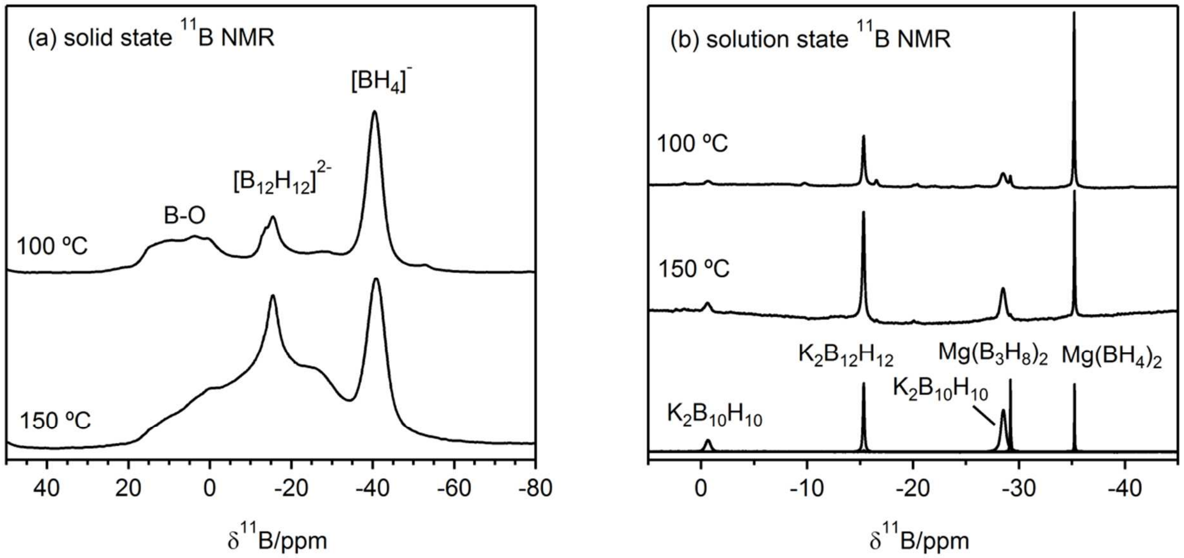


Fig. 2 ^{11}B NMR spectra of bulk $Mg(BH_4)_2$ after ball milling in B_2H_6 at 100 and 150 °C, respectively: (a) solid-state ^{11}B MAS NMR spectra and (b) solution-state $^{11}B\{^1H\}$ NMR spectra recorded in DMSO-d_6. Resonance assignments: -35.2 ppm $[BH_4]^-$, -15.3 ppm $[B_{12}H_{12}]^{2-}$, -0.5 & -28.5 ppm $[B_{10}H_{10}]^{2-}$, -16.5 ppm $[B_{11}H_{11}]^{2-}$,[39] and -29.2 ppm $[B_3H_8]^-$. Broad resonance in (a) between 0 and 20 ppm was attributed to boron oxides.[40]

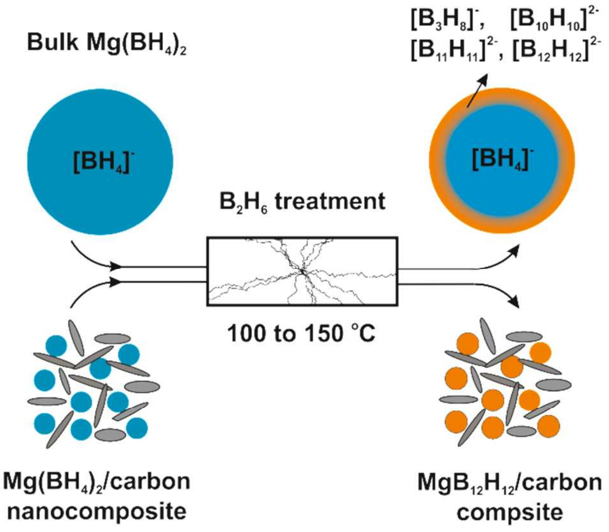
Table 1 Relative amounts of the B-H species in bulk $Mg(BH_4)_2$ after ball milling in B_2H_6, compared with $MgB_{12}H_{12}$/carbon composite synthesized by using $Mg(BH_4)_2$ nanocomposite. The calculation of amounts of the B-H species was based on proton-coupled ^{11}B NMR spectra recorded in DMSO-d_6. ^{11}B NMR chemical shifts were reported relative to the 1M $B(OH)_3$ aqueous solution at 19.6 ppm. The coupling constants J_{B-H} were determined based on proton-coupled ^{11}B NMR spectra.

Species	δ^{11}B / ppm	J_{B-H} / Hz	Amount /mol%		
			Bulk sample		$MgB_{12}H_{12}$/carbon composite
			100 °C	150 °C	
$[BH_4]^-$	-35.2	82	75.9	53.3	3.5
$[B_3H_8]^-$	-29.2	33	3.2	0.5	-
$[B_{10}H_{10}]^{2-}$	-0.5 & -28.5	125	8.7	23.6	4.0
$[B_{11}H_{11}]^{2-}$	-16.5	125	2.0	0.3	-
$[B_{12}H_{12}]^{2-}$	-15.3	125	10.2	22.3	92.5

To further understand the reaction between $Mg(BH_4)_2$ and B_2H_6, the reactive ball milling of bulk $Mg(BH_4)_2$ in B_2H_6/H_2 atmosphere were carried out at 100 and 150 °C, respectively, for 24 h. The two samples obtained were investigated by ^{11}B MAS NMR (Fig. 2a) and solution-state ^{11}B NMR using DMSO-d_6 as the solvent (Fig. 2b). In Fig. 2a, the new species at around -15.0 ppm observed in both samples indicated the formation of $MgB_{12}H_{12}$. The $[B_{12}H_{12}]^{2-}$ species were readily soluble in DMSO-d_6 with a chemical shift of -15.3 ppm, as shown in Fig. 2b. Other species such as $[B_3H_8]^-$ (-29.2 ppm), $[B_{10}H_{10}]^{2-}$ (-0.5 & -28.5 ppm) and $[B_{11}H_{11}]^{2-}$ (-16.5 ppm)[39] were also observed when the two samples were dissolved in DMSO-d_6.

The relative amounts of different B-H species were calculated based on ^{11}B NMR spectra recorded in DMSO-d_6, as shown in table 1. Approximately 8.7 and 10.2 mol% of $MgB_{10}H_{10}$ and $MgB_{12}H_{12}$, respectively, were obtained by ball milling of $Mg(BH_4)_2$ in B_2H_6 at 100 °C. More $MgB_{10}H_{10}$ (23.6 mol%) and $MgB_{12}H_{12}$ (22.3 mol%) were formed when the reaction was carried out at 150 °C. The incomplete reaction of $Mg(BH_4)_2$ with B_2H_6 can be attributed to a passivation layer formed by the new species such as $Mg(B_3H_8)_2$, $MgB_{10}H_{10}$ and $MgB_{12}H_{12}$. This passivation layer separated bulk $Mg(BH_4)_2$ and B_2H_6, as shown in scheme 1, analogous to the core-shell behavior observed in the reaction between LiH and B_2H_6.[41] Nevertheless, above results demonstrated the possibility to synthesize $MgB_{12}H_{12}$ via the reaction between $Mg(BH_4)_2$ and B_2H_6 according to eq. 2.

$$Mg(BH_4)_2 + 5B_2H_6 \rightarrow MgB_{12}H_{12} + 13H_2 \quad (2)$$



Scheme 1 Illustration of incomplete reaction between bulk $Mg(BH_4)_2$ and B_2H_6, owing to the formation of a passivation layer from the newly-formed species. In contrast, promoted reaction occurs between $Mg(BH_4)_2$/carbon nanocomposite and B_2H_6 forming $MgB_{12}H_{12}$.

In order to promote the gas-solid reaction between $Mg(BH_4)_2$ and B_2H_6, $Mg(BH_4)_2$/carbon nanocomposite was utilized as a starting material, as described in Scheme 1. The as-synthesized $MgB_{12}H_{12}$/carbon composite was characterized by ^{11}B NMR spectroscopy. In Fig. 3a, ^{11}B MAS NMR spectrum of this composite showed a main resonance at -15.6 ppm assigned to $MgB_{12}H_{12}$. The small shoulder at -40.8 ppm originated from the $Mg(BH_4)_2$ residue. The yield of $MgB_{12}H_{12}$ was found to be 92.5 mol% by solution-state ^{11}B NMR recorded in DMSO-d_6, as shown in Fig. 3b. Only small amounts of $MgB_{10}H_{10}$ (4 mol%) and $Mg(BH_4)_2$ (3.5 mol%) were observed. Considering that the amount of MgH_2 in the starting MgH_2/carbon sample was 10 wt%, the amount of $MgB_{12}H_{12}$ was calculated to be about 40 wt% in the as-synthesized $MgB_{12}H_{12}$/carbon composite.

Stability of $MgB_{12}H_{12}$

To examine the stability of $MgB_{12}H_{12}$, the as-synthesized $MgB_{12}H_{12}$/carbon composite was heated to different temperatures from 350 to 600 ºC under vacuum and subsequently cooled to room temperature for ^{11}B NMR measurement. As shown in Fig. 3a, $MgB_{12}H_{12}$ showed a sharp resonance (linewidth 1600 Hz) at -15.6 ppm. This resonance broadened (linewidth 3500 Hz) and slightly shifted downfield to -14.2 ppm after heat treatment at 350 ºC. Note that after heat-treatment at 350 ºC, no soluble species in DMSO-d_6 was observed by solution-state ^{11}B NMR (not shown), indicating the disappearance of $MgB_{12}H_{12}$ monomers. We attributed this slight downfield shift to polymerization between $MgB_{12}H_{12}$ monomers. A similar polymerization between $Li_2B_{12}H_{12}$ monomers upon heating has been reported previously.[42,43]

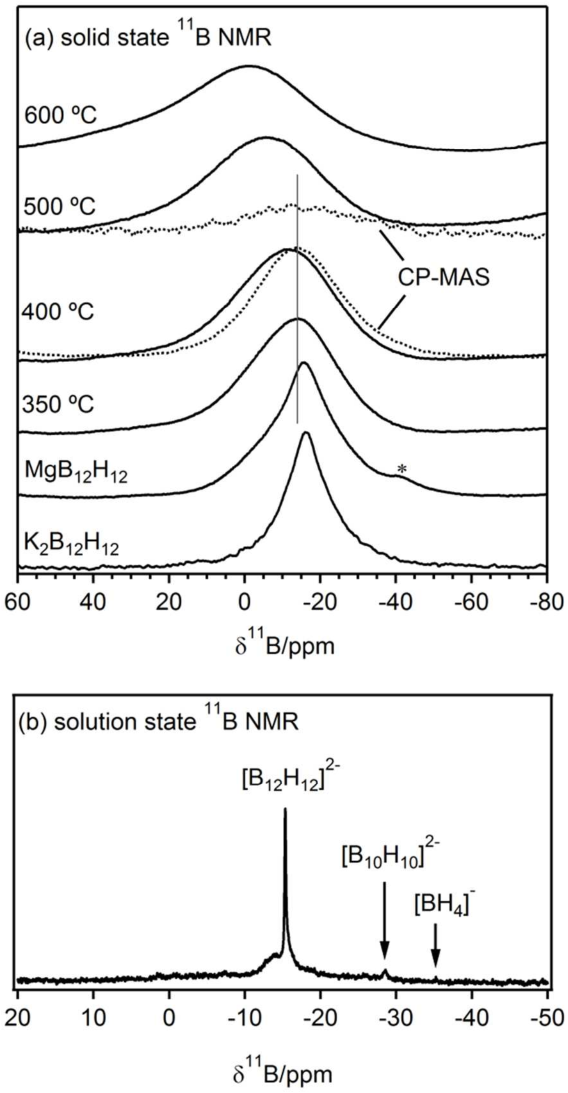


Fig. 3 (a) ^{11}B MAS NMR spectra of the as-synthesized $MgB_{12}H_{12}$/carbon composite and the samples heated at 350 to 600 ºC, respectively, and ^{11}B CP-MAS spectra (dashed) for the samples heated at 400 and 500 ºC, respectively. $K_2B_{12}H_{12}$ was used as the reference. The star indicates the $Mg(BH_4)_2$ residue. (b) Solution-state $^{11}B\{^1H\}$ NMR spectra of the as-synthesized $MgB_{12}H_{12}$/carbon composite recorded in DMSO-d_6.

Heating to 400 and 500 ºC led to the further shifting of $MgB_{12}H_{12}$ resonance to -11.4 and -5.6 ppm, respectively. To verify whether these shifts owed to the formation of the H-free species such as amorphous boron, the ^{11}B CP-MAS measurements were carried out, by which signal from the H-free species can be suppressed. For the sample heated at 400 ºC, the ^{11}B CP-MAS spectrum showed a strong resonance at -14.2 ppm which can be assigned to $MgB_{12}H_{12}$ polymers, indicative of only partial decomposition occurring at 400 ºC. For the sample heated at 500 ºC, only weak signal centered at -14.2 ppm was observed, indicating that $MgB_{12}H_{12}$ mainly decomposed to the H-free species.

After the sample was heated at 600 ºC, the resonance shifted to around 0 ppm, close to the chemical shift of amorphous boron.[17] Furthermore, no ^{11}B signal was observed in the ^{11}B CP-MAS spectrum (not shown), indicating the decomposition of the $[B_{12}H_{12}]^{2-}$ species into amorphous boron at 600 ºC according to eq. 3.

$$MgB_{12}H_{12} \rightarrow Mg + 12B + 6H_2 \quad (400 \text{ to } 600\ °C) \quad (3)$$

Discussion

We achieved the synthesis of $MgB_{12}H_{12}$ via the reaction of $Mg(BH_4)_2$ with B_2H_6 at 150 °C. By using $Mg(BH_4)_2$ nanoparticles, the yield of $MgB_{12}H_{12}$ was improved to 92.5 mol%, compared to the yield of 10.2 to 22.5 mol% when bulk $Mg(BH_4)_2$ was used as the starting material. It has been reported that B_2H_6 or BH_3 units are readily to react with $[BH_4]^-$ to form higher boranes.[44-46] The improved formation of $MgB_{12}H_{12}$ was possibly due to shortened diffusion distance of B_2H_6 or BH_3 units and accelerated the conversion from $[BH_4]^-$ to $[B_{12}H_{12}]^{2-}$. In this conversion process, the $[B_3H_8]^-$, $[B_{10}H_{10}]^{2-}$ and $[B_{11}H_{11}]^{2-}$ species were observed after the reaction between bulk $Mg(BH_4)_2$ and B_2H_6 (Fig. 2). These species may be intermediates for the formation of $[B_{12}H_{12}]^{2-}$. A similar B-H conversion process has also been proposed in the decomposition of $Mg(BH_4)_2$,[11] where $[BH_4]^-$ gradually grows up to form $[B_{12}H_{12}]^{2-}$ via intermediates such as $[B_3H_8]^-$ and $[B_{10}H_{10}]^{2-}$. This similarity suggests that B_2H_6 or BH_3 units play important roles in the decomposition process of $Mg(BH_4)_2$.

The as-synthesized $MgB_{12}H_{12}$/carbon composite was a physical mixture of $MgB_{12}H_{12}$ and carbon. Physically-mixed carbon is not a catalyst for the hydrogen desorption of boron-based hydrides and thus would not influence the thermal stability of $MgB_{12}H_{12}$.[36,47,48] The as-synthesized $MgB_{12}H_{12}$ particles may be in nanoscale, which tend to agglomerate upon heating. Consequently, the investigation of stability of the $MgB_{12}H_{12}$/carbon composite was considered to be instructive for understanding the role of $MgB_{12}H_{12}$ in the decomposition of bulk $Mg(BH_4)_2$.

As a possible intermediate in the decomposition process of $Mg(BH_4)_2$, $MgB_{12}H_{12}$ shows higher stability than $Mg(BH_4)_2$. $MgB_{12}H_{12}$ possibly polymerized when being heated at 350 ºC and slowly decomposed into amorphous boron above 400 ºC, whereas $Mg(BH_4)_2$ starts to decompose at 250 to 270 ºC.[6-8,16] The slow self-decomposition of $MgB_{12}H_{12}$ above 400 ºC seems not to match with one of the hydrogen desorption events of $Mg(BH_4)_2$ which shows three major desorption steps between 250 to 400 ºC.[6-8,16] MgH_2 or Mg formed from the decomposition of $Mg(BH_4)_2$ might destabilize $MgB_{12}H_{12}$ resulting in formation MgB_2, as suggested by theoretical predictions.[21]

Conclusions

We have successfully synthesized solvent-free $MgB_{12}H_{12}$ via gas-solid reaction between $Mg(BH_4)_2$ and B_2H_6. When bulk $Mg(BH_4)_2$ was used as the starting material, the yield of $MgB_{12}H_{12}$ was limited to 10.2 to 22.3 mol%. The incomplete reaction was attributed to a passivation layer made of newly-formed species such as $Mg(B_3H_8)_2$, $MgB_{10}H_{10}$ and $MgB_{12}H_{12}$. The yield was improved to above 90 mol% by using $Mg(BH_4)_2$/carbon nanocomposite to overcome the kinetic barrier from the passivation layer.

The as-synthesized $MgB_{12}H_{12}$ was readily soluble in DSMO-d_6 with a chemical shift of -15.3 ppm and coupling constant $J_{B\text{-}H}$ of 125 Hz. After being treated at 350 ºC, the sample was no longer soluble in DSMO-d_6, implying the occurrence of polymerization between $MgB_{12}H_{12}$ monomers. Upon further heating at 400 to 600 ºC, $MgB_{12}H_{12}$ slowly decomposed into amorphous boron. This decomposition behavior does not match with one of hydrogen desorption events of $Mg(BH_4)_2$ occurring between 250 to 400 ºC.

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†Electronic Supplementary Information (ESI) available: Raman spectra of reference samples $K_2B_{12}H_{12}$ and $K_2B_{10}H_{10}$. See DOI: 10.1039/b000000x/

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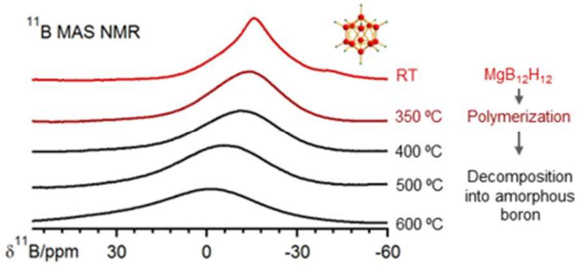

We synthesized solvent-free $MgB_{12}H_{12}$ via the reaction between $Mg(BH_4)_2$ and B_2H_6, and investigated its thermal stability and decomposition process.