Solvent-Free Synthesis and Stability of MgB₁₂H₁₂

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MgB₁₂H₁₂ has been widely discussed as an intermediate in the hydrogen sorption cycles of Mg(BH₄)₂, but its properties such as stability and reactivity are still unknown. We achieved the synthesis of MgB₁₂H₁₂ via the reaction between Mg(BH₄)₂ and B₂H₆ at 100 to 150 °C. When bulk Mg(BH₄)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(BH₄)₂ nanoparticles. The as-synthesized MgB₁₂H₁₂ decomposed into boron between 400 to 600 °C, preceded by a possible polymerization process. The formation mechanism of MgB₁₂H₁₂ and its role in the decomposition process of Mg(BH₄)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(BH₄)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 H₂ in the overall decomposition reaction corresponding to hydrogen desorption at around room temperature.

Mg(BH₄)₂ presents complex crystal structures with different polymorphs at different temperatures.^{4,13} The major desorption reaction of Mg(BH₄)₂ occurs above 270 °C through multiple steps, regardless of the initial crystal structure.^{6-8,16} Within the multi-step decomposition process, MgB₁₂H₁₂ 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 MgB₁₂H₁₂.⁷ 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 MgB₁₂H₁₂. Some metal dodecaborates such as Li₂B₁₂H₁₂ can be synthesized through the thermohydrolysis of their hydrated salts.²⁶⁻²⁸ However, the [B₁₂H₁₂]²⁻ species in Mg(H₂O)₆B₁₂H₁₂·6H₂O tend to decompose in the drying process, owing to the dihydrogen bonds between H₂O and the [B₁₂H₁₂]²⁻ anion.²⁹ Another wet method via the reaction between B₁₀H₁₄ and Mg(BH₄)₂ in THF to produce MgB₁₂H₁₂ was also hindered by desolvation in the final product.²⁸ The reaction between MgH₂ nanoparticles with B₂H₆ leads to the formation of MgB₁₂H₁₂ together with other Mg-B-H species, which is restricted within nanopores.³⁰

Synthesis of metal dodecaborates from the reactions between B₂H₆ and the metal borohydrides such as LiBH₄,³¹ NaBH₄,³² and Y(BH₄)₃³³ has been demonstrated. In present study, we first investigated the reaction between bulk Mg(BH₄)₂ and B₂H₆ at 100 to 150 °C with the intention to synthesize MgB₁₂H₁₂. Second, we promoted the formation of MgB₁₂H₁₂ by using Mg(BH₄)₂ nanoparticles as a starting material. Finally, we investigated the thermal stability and the decomposition process of MgB₁₂H₁₂, and discussed its role in the hydrogen desorption process of Mg(BH₄)₂.

Experimental

The samples of ZnCl₂ (99.9%) and Mg(BH₄)₂ (> 95%) were purchased from Sigma-Aldrich and NaBH₄ (95%), K₂B₁₀H₁₀ and K₂B₁₂H₁₂ from Katchem. Mg(B₃H₈)₂ was synthesized via reaction between borane THF and magnesium mercury amalgams, followed by desolvation in vacuum at 50 °C.³⁴ MgH₂ nanoparticles supported on carbon matrix (MgH₂/carbon), with a load ratio of 10 wt% and an average diameter of 10 nm, were prepared via melt infiltration.³⁵ Mg(BH₄)₂/carbon nanocomposite was synthesized by ball milling of MgH₂/carbon in B₂H₆/H₂ atmosphere for 3 days at room temperature.³⁶ NaZn(BH₄)₃, synthesized by milling a mixture of ZnCl₂ and NaBH₄, was used as a B₂H₆ source which releases B₂H₆ and H₂ above 90 °C according to eq. 1.³⁷

Reactive ball milling of bulk Mg(BH₄)₂ in B₂H₆/H₂ at 100 and 150 °C for 24 h, respectively, was carried out analogous to the procedure as described previously.³³ The reaction of Mg(BH₄)₂/carbon with B₂H₆ was performed at 150 °C for 24 h in B₂H₆/H₂ atmosphere without ball milling.

In-situ observation of the reaction between bulk Mg(BH₄)₂ and B₂H₆ at 100 °C by Raman spectroscopy was conducted with a Bruker Senterra instrument of 5 cm⁻¹ spectral resolution (spatial resolution ≈ 5 μm) using a 532 nm laser. Pure Mg(BH₄)₂ powder was compressed into a small pellet (diameter and thickness: 1 mm) which was placed in a gas-tight sample holder together

with some $\text{NaZn}(\text{BH}_4)_3$ as B_2H_6 source. Subsequently, the sample holder was heated up to 100°C with a ramp of $10^\circ\text{C}/\text{min}$ by an oven below it. The in-situ measurement was started right after the temperature was achieved at 100°C .

5 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 $1.5\ \mu\text{s}$ ($\pi/12$ pulse) and $3.0\ \mu\text{s}$ 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 $\text{B}(\text{OH})_3$ aqueous solution at 19.6 ppm as external standard sample.

Results

Synthesis of $\text{MgB}_{12}\text{H}_{12}$

The reaction of bulk $\text{Mg}(\text{BH}_4)_2$ with B_2H_6 was first investigated by in-situ Raman spectroscopy. The evolution of vibration modes of $\text{Mg}(\text{BH}_4)_2$ in $\text{B}_2\text{H}_6/\text{H}_2$ atmosphere at 100°C is presented in Fig. 1. The reference spectra of $\text{K}_2\text{B}_{12}\text{H}_{12}$ and $\text{K}_2\text{B}_{10}\text{H}_{10}$ are shown in Fig. S1 (†ESI). In Fig. 1, $\text{Mg}(\text{BH}_4)_2$ 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 $\text{Mg}(\text{BH}_4)_2$ 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 $\text{K}_2\text{B}_{12}\text{H}_{12}$ and $\text{K}_2\text{B}_{10}\text{H}_{10}$ (Fig. S1).

Fig. 1 In-situ observation of $\text{Mg}(\text{BH}_4)_2$ reacting with B_2H_6 at 100°C within 80 min by Raman spectroscopy.

Fig. 2 ^{11}B NMR spectra of bulk $\text{Mg}(\text{BH}_4)_2$ after ball milling in B_2H_6 at 100 and 150 $^\circ\text{C}$, respectively: (a) solid-state ^{11}B MAS NMR spectra and (b) solution-state $^{11}\text{B}\{^1\text{H}\}$ NMR spectra recorded in DMSO-d_6 . Resonance assignments: -35.2 ppm $[\text{BH}_4]^-$, -15.3 ppm $[\text{B}_{12}\text{H}_{12}]^{2-}$, -0.5 & -28.5 ppm $[\text{B}_{10}\text{H}_{10}]^{2-}$, -16.5 ppm $[\text{B}_{11}\text{H}_{11}]^{2-}$,³⁹ and -29.2 ppm $[\text{B}_3\text{H}_8]^-$. 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 $\text{Mg}(\text{BH}_4)_2$ after ball milling in B_2H_6 , compared with $\text{MgB}_{12}\text{H}_{12}$ /carbon composite synthesized by using $\text{Mg}(\text{BH}_4)_2$ 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 $\text{B}(\text{OH})_3$ aqueous solution at 19.6 ppm. The coupling constants $J_{\text{B-H}}$ were determined based on proton-coupled ^{11}B NMR spectra.

Species	$\delta^{11}\text{B}$ / ppm	$J_{\text{B-H}}$ / Hz	Amount /mol%		
			Bulk sample		$\text{MgB}_{12}\text{H}_{12}$ /carbon composite
			100 $^\circ\text{C}$	150 $^\circ\text{C}$	
$[\text{BH}_4]^-$	-35.2	82	75.9	53.3	3.5
$[\text{B}_3\text{H}_8]^-$	-29.2	33	3.2	0.5	-
$[\text{B}_{10}\text{H}_{10}]^{2-}$	-0.5 & -28.5	125	8.7	23.6	4.0
$[\text{B}_{11}\text{H}_{11}]^{2-}$	-16.5	125	2.0	0.3	-
$[\text{B}_{12}\text{H}_{12}]^{2-}$	-15.3	125	10.2	22.3	92.5

To further understand the reaction between $\text{Mg}(\text{BH}_4)_2$ and B_2H_6 , the reactive ball milling of bulk $\text{Mg}(\text{BH}_4)_2$ in $\text{B}_2\text{H}_6/\text{H}_2$ atmosphere were carried out at 100 and 150 $^\circ\text{C}$, 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 $\text{MgB}_{12}\text{H}_{12}$. The $[\text{B}_{12}\text{H}_{12}]^{2-}$ 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 $[\text{B}_3\text{H}_8]^-$ (-29.2 ppm), $[\text{B}_{10}\text{H}_{10}]^{2-}$ (-0.5 & -28.5 ppm) and $[\text{B}_{11}\text{H}_{11}]^{2-}$ (-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 $\text{MgB}_{10}\text{H}_{10}$ and $\text{MgB}_{12}\text{H}_{12}$, respectively, were obtained by ball milling of

$\text{Mg}(\text{BH}_4)_2$ in B_2H_6 at 100 $^\circ\text{C}$. More $\text{MgB}_{10}\text{H}_{10}$ (23.6 mol%) and $\text{MgB}_{12}\text{H}_{12}$ (22.3 mol%) were formed when the reaction was carried out at 150 $^\circ\text{C}$. The incomplete reaction of $\text{Mg}(\text{BH}_4)_2$ with B_2H_6 can be attributed to a passivation layer formed by the new species such as $\text{Mg}(\text{B}_3\text{H}_8)_2$, $\text{MgB}_{10}\text{H}_{10}$ and $\text{MgB}_{12}\text{H}_{12}$. This passivation layer separated bulk $\text{Mg}(\text{BH}_4)_2$ 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 $\text{MgB}_{12}\text{H}_{12}$ via the reaction between $\text{Mg}(\text{BH}_4)_2$ and B_2H_6 according to eq. 2.

Scheme 1 Illustration of incomplete reaction between bulk $\text{Mg}(\text{BH}_4)_2$ and B_2H_6 , owing to the formation of a passivation layer from the newly-formed species. In contrast, promoted reaction occurs between $\text{Mg}(\text{BH}_4)_2/\text{carbon}$ nanocomposite and B_2H_6 forming $\text{MgB}_{12}\text{H}_{12}$.

In order to promote the gas-solid reaction between $\text{Mg}(\text{BH}_4)_2$ and B_2H_6 , $\text{Mg}(\text{BH}_4)_2/\text{carbon}$ nanocomposite was utilized as a starting material, as described in Scheme 1. The as-synthesized $\text{MgB}_{12}\text{H}_{12}/\text{carbon}$ 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 $\text{MgB}_{12}\text{H}_{12}$. The small shoulder at -40.8 ppm originated from the $\text{Mg}(\text{BH}_4)_2$ residue. The yield of $\text{MgB}_{12}\text{H}_{12}$ was found to be 92.5 mol% by solution-state ^{11}B NMR recorded in $\text{DMSO}-d_6$, as shown in Fig. 3b. Only small amounts of $\text{MgB}_{10}\text{H}_{10}$ (4 mol%) and $\text{Mg}(\text{BH}_4)_2$ (3.5 mol%) were observed. Considering that the amount of MgH_2 in the starting $\text{MgH}_2/\text{carbon}$ sample was 10 wt%, the amount of $\text{MgB}_{12}\text{H}_{12}$ was calculated to be about 40 wt% in the as-synthesized $\text{MgB}_{12}\text{H}_{12}/\text{carbon}$ composite.

Stability of $\text{MgB}_{12}\text{H}_{12}$

To examine the stability of $\text{MgB}_{12}\text{H}_{12}$, the as-synthesized $\text{MgB}_{12}\text{H}_{12}/\text{carbon}$ composite was heated to different temperatures from 350 to 600 °C under vacuum and subsequently cooled to room temperature for ^{11}B NMR measurement. As shown in Fig. 3a, $\text{MgB}_{12}\text{H}_{12}$ 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 °C. Note that after heat-treatment at 350 °C, no soluble species in $\text{DMSO}-d_6$ was observed by solution-state ^{11}B NMR (not shown), indicating the disappearance of $\text{MgB}_{12}\text{H}_{12}$ monomers. We attributed this slight downfield shift to polymerization between $\text{MgB}_{12}\text{H}_{12}$ monomers. A similar polymerization between $\text{Li}_2\text{B}_{12}\text{H}_{12}$ monomers upon heating has been reported previously.^{42,43}

Fig. 3 (a) ^{11}B MAS NMR spectra of the as-synthesized $\text{MgB}_{12}\text{H}_{12}/\text{carbon}$ composite and the samples heated at 350 to 600 °C, respectively, and ^{11}B CP-MAS spectra (dashed) for the samples heated at 400 and 500 °C, respectively. $\text{K}_2\text{B}_{12}\text{H}_{12}$ was used as the reference. The star indicates the $\text{Mg}(\text{BH}_4)_2$ residue. (b) Solution-state $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of the as-synthesized $\text{MgB}_{12}\text{H}_{12}/\text{carbon}$ composite recorded in $\text{DMSO}-d_6$.

Heating to 400 and 500 °C led to the further shifting of $\text{MgB}_{12}\text{H}_{12}$ 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 °C, the ^{11}B CP-MAS spectrum showed a strong resonance at -14.2 ppm which can be assigned to $\text{MgB}_{12}\text{H}_{12}$ polymers, indicative of only partial decomposition occurring at 400 °C. For the sample heated at 500 °C, only weak signal centered at -14.2 ppm was observed, indicating that $\text{MgB}_{12}\text{H}_{12}$ mainly decomposed to the H-free species.

After the sample was heated at 600 °C, 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 $[\text{B}_{12}\text{H}_{12}]^{2-}$ species into amorphous boron at 600 °C according to eq. 3.

5 Discussion

We achieved the synthesis of $\text{MgB}_{12}\text{H}_{12}$ via the reaction of $\text{Mg}(\text{BH}_4)_2$ with B_2H_6 at 150 °C. By using $\text{Mg}(\text{BH}_4)_2$ nanoparticles, the yield of $\text{MgB}_{12}\text{H}_{12}$ was improved to 92.5 mol%, compared to the yield of 10.2 to 22.5 mol% when bulk $\text{Mg}(\text{BH}_4)_2$ was used as the starting material. It has been reported that B_2H_6 or BH_3 units are readily to react with $[\text{BH}_4]^-$ to form higher boranes.^{44–46} The improved formation of $\text{MgB}_{12}\text{H}_{12}$ was possibly due to shortened diffusion distance of B_2H_6 or BH_3 units and accelerated the conversion from $[\text{BH}_4]^-$ to $[\text{B}_{12}\text{H}_{12}]^{2-}$. In this conversion process, the $[\text{B}_3\text{H}_8]^-$, $[\text{B}_{10}\text{H}_{10}]^{2-}$ and $[\text{B}_{11}\text{H}_{11}]^{2-}$ species were observed after the reaction between bulk $\text{Mg}(\text{BH}_4)_2$ and B_2H_6 (Fig. 2). These species may be intermediates for the formation of $[\text{B}_{12}\text{H}_{12}]^{2-}$. A similar B-H conversion process has also been proposed in the decomposition of $\text{Mg}(\text{BH}_4)_2$,¹¹ where $[\text{BH}_4]^-$ gradually grows up to form $[\text{B}_{12}\text{H}_{12}]^{2-}$ via intermediates such as $[\text{B}_3\text{H}_8]^-$ and $[\text{B}_{10}\text{H}_{10}]^{2-}$. This similarity suggests that B_2H_6 or BH_3 units play important roles in the decomposition process of $\text{Mg}(\text{BH}_4)_2$.

The as-synthesized $\text{MgB}_{12}\text{H}_{12}$ /carbon composite was a physical mixture of $\text{MgB}_{12}\text{H}_{12}$ 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 $\text{MgB}_{12}\text{H}_{12}$.^{36,47,48} The as-synthesized $\text{MgB}_{12}\text{H}_{12}$ particles may be in nanoscale, which tend to agglomerate upon heating. Consequently, the investigation of stability of the $\text{MgB}_{12}\text{H}_{12}$ /carbon composite was considered to be instructive for understanding the role of $\text{MgB}_{12}\text{H}_{12}$ in the decomposition of bulk $\text{Mg}(\text{BH}_4)_2$.

As a possible intermediate in the decomposition process of $\text{Mg}(\text{BH}_4)_2$, $\text{MgB}_{12}\text{H}_{12}$ shows higher stability than $\text{Mg}(\text{BH}_4)_2$. $\text{MgB}_{12}\text{H}_{12}$ possibly polymerized when being heated at 350 °C and slowly decomposed into amorphous boron above 400 °C, whereas $\text{Mg}(\text{BH}_4)_2$ starts to decompose at 250 to 270 °C.^{6–8,16} The slow self-decomposition of $\text{MgB}_{12}\text{H}_{12}$ above 400 °C seems not to match with one of the hydrogen desorption events of $\text{Mg}(\text{BH}_4)_2$ which shows three major desorption steps between 250 to 400 °C.^{6–8,16} MgH_2 or Mg formed from the decomposition of $\text{Mg}(\text{BH}_4)_2$ might destabilize $\text{MgB}_{12}\text{H}_{12}$ resulting in formation MgB_2 , as suggested by theoretical predictions.²¹

45 Conclusions

We have successfully synthesized solvent-free $\text{MgB}_{12}\text{H}_{12}$ via gas-solid reaction between $\text{Mg}(\text{BH}_4)_2$ and B_2H_6 . When bulk $\text{Mg}(\text{BH}_4)_2$ was used as the starting material, the yield of $\text{MgB}_{12}\text{H}_{12}$ 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 $\text{Mg}(\text{B}_3\text{H}_8)_2$, $\text{MgB}_{10}\text{H}_{10}$ and $\text{MgB}_{12}\text{H}_{12}$. The yield was improved to above 90 mol% by using $\text{Mg}(\text{BH}_4)_2$ /carbon nanocomposite to overcome the kinetic barrier from the passivation layer.

The as-synthesized $\text{MgB}_{12}\text{H}_{12}$ was readily soluble in DMSO- d_6 with a chemical shift of -15.3 ppm and coupling constant $J_{\text{B-H}}$ of 125 Hz. After being treated at 350 °C, the sample was no longer soluble in DMSO- d_6 , implying the occurrence of polymerization between $\text{MgB}_{12}\text{H}_{12}$ monomers. Upon further heating at 400 to 600 °C, $\text{MgB}_{12}\text{H}_{12}$ slowly decomposed into amorphous boron.

This decomposition behavior does not match with one of hydrogen desorption events of $\text{Mg}(\text{BH}_4)_2$ occurring between 250 to 400 °C.

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70 Notes and references

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Table of contents entry

We synthesized solvent-free $\text{MgB}_{12}\text{H}_{12}$ via the reaction between $\text{Mg}(\text{BH}_4)_2$ and B_2H_6 , and investigated its thermal stability and decomposition process.