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Solvent-free synthesis and stability of MgB₁₂H₁₂ \dagger

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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⁻¹ H₂ 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 °C 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

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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 and 600 °C, preceded by a possible polymerization process. The formation mechanism of $MgB_{12}H_{12}$ and its role in the decomposition process of $Mg(BH_4)_2$ are discussed.

solvent-free MgB₁₂H₁₂. 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(H₂O)₆B₁₂H₁₂·6H₂O tend to decompose in the drying process, owing to the dihydrogen bonds between H₂O and the $[B_{12}H_{12}]^{2-}$ 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 B_2H_6 and the metal borohydrides such as $LiBH_4$,³¹ NaBH₄ (ref. 32) and Y(BH₄)₃ (ref. 33) has been demonstrated. In the present study, we first investigated the reaction between bulk Mg(BH₄)₂ and B_2H_6 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 $ZnCl_2$ (99.9%) and $Mg(BH_4)_2$ (>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 a vacuum at 50 °C.³⁴ MgH₂ nanoparticles supported on a carbon matrix (MgH₂/carbon), with a load ratio of 10 wt% and an average diameter of 10 nm, were prepared *via* melt infiltration.³⁵ A Mg(BH₄)₂/carbon nanocomposite was synthesized by ball milling of MgH₂/carbon in a B₂H₆/H₂ atmosphere for 3 days at room temperature.³⁶ NaZn(BH₄)₃, synthesized by milling a mixture of ZnCl₂ and

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NaBH₄, was used as a B_2H_6 source which releases B_2H_6 and H_2 above 90 °C according to eqn (1).³⁷

$$NaZn(BH_4)_3 \rightarrow NaBH_4 + Zn + B_2H_6 + H_2$$
(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 a B_2H_6/H_2 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 \approx 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 NaZn(BH₄)₃ as a B₂H₆ source. Subsequently, the sample holder was heated up to 100 °C with a ramp of 10 °C min⁻¹ by an oven below it. The *in situ* measurement was started right after the temperature was achieved at 100 °C.

Solid-state ¹¹B magic angle spinning (MAS) NMR measurements were performed on a Bruker Avance-400 NMR spectrometer using a 4 mm CP-MAS probe. The ¹¹B 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 μ s (π /12 pulse) and 3.0 μ s were applied for the excitation and echo pulses, respectively. For selected samples, ¹¹B cross-polarization magic angle spinning (CP-MAS) NMR experiments were performed using weak radio-frequency powers for spin locking of the ¹¹B nucleus on resonance as described elsewhere.17,38 Solution-state NMR experiments with dimethyl sulfoxide (DMSO-d₆) as the solvent were carried out using a 5 mm inverse broadband probe at 25 °C. ¹¹B NMR chemical shifts were reported in parts per million (ppm) externally referenced to a 1 M B(OH)₃ aqueous solution at 19.6 ppm as an external standard sample.

Results

Synthesis of MgB₁₂H₁₂

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 a 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.

To further understand the reaction between Mg(BH₄)₂ and B₂H₆, the reactive ball milling of bulk Mg(BH₄)₂ in a B₂H₆/H₂ atmosphere was carried out at 100 and 150 °C, respectively, for 24 h. The two samples obtained were investigated by ¹¹B MAS NMR (Fig. 2a) and solution-state ¹¹B NMR using DMSO-d₆ as the solvent (Fig. 2b). In Fig. 2a, the new species at around -15.0 ppm observed in both samples indicated the formation of MgB₁₂H₁₂. The $[B_{12}H_{12}]^{2-}$ species were readily soluble in DMSO-d₆ 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-d₆.

The relative amounts of different B–H species were calculated based on ¹¹B NMR spectra recorded in DMSO-d₆, as shown in Table 1. Approximately 8.7 and 10.2 mol% of MgB₁₀H₁₀ and MgB₁₂H₁₂, respectively, were obtained by ball milling of Mg(BH₄)₂ in B₂H₆ at 100 °C. More MgB₁₀H₁₀ (23.6 mol%) and MgB₁₂H₁₂ (22.3 mol%) were formed when the reaction was carried out at 150 °C. The incomplete reaction of Mg(BH₄)₂ with B₂H₆ can be attributed to a passivation layer formed by the new species such as Mg(B₃H₈)₂, MgB₁₀H₁₀ and MgB₁₂H₁₂. This passivation layer separated bulk Mg(BH₄)₂ and B₂H₆, as shown in Scheme 1, analogous to the core–shell behavior observed in the reaction between LiH and B₂H₆.⁴¹ Nevertheless, the above results demonstrated the possibility to synthesize MgB₁₂H₁₂*via* the reaction between Mg(BH₄)₂ and B₂H₆ according to eqn (2).

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

In order to promote the gas–solid reaction between $Mg(BH_4)_2$ and B_2H_6 , the $Mg(BH_4)_2$ /carbon nanocomposite was utilized as a starting material, as described in Scheme 1. The assynthesized $MgB_{12}H_{12}$ /carbon composite was characterized by ¹¹B NMR spectroscopy. In Fig. 3a, the ¹¹B MAS NMR spectrum of



Fig. 2 ¹¹B NMR spectra of bulk Mg(BH₄)₂ after ball milling in B₂H₆ at 100 and 150 °C, respectively: (a) solid-state ¹¹B MAS NMR spectra and (b) solution-state ¹¹B{¹H} NMR spectra recorded in DMSO-d₆. Resonance assignments: $-35.2 \text{ ppm} [BH_4]^-$, $-15.3 \text{ ppm} [B_{12}H_{12}]^{2^-}$, $-0.5 \& -28.5 \text{ ppm} [B_{10}H_{10}]^{2^-}$, $-16.5 \text{ ppm} [B_{11}H_{11}]^{2^-,39}$ and $-29.2 \text{ ppm} [B_3H_8]^-$. Broad resonance (a) between 0 and 20 ppm was attributed to boron oxides.⁴⁰

Table 1 Relative amounts of the B–H species in bulk Mg(BH₄)₂ after ball milling in B₂H₆, compared with the MgB₁₂H₁₂/carbon composite synthesized by using the Mg(BH₄)₂ nanocomposite. The calculation of amounts of the B–H species was based on proton-coupled ¹¹B NMR spectra recorded in DMSO-d₆. ¹¹B NMR chemical shifts were reported relative to the 1 M B(OH)₃ aqueous solution at 19.6 ppm. The coupling constants J_{B-H} were determined based on proton-coupled ¹¹B NMR spectra

			Amount/mol%		
			Bulk sample		MgB12H12/
Species	δ $^{\rm 11}{\rm B/ppm}$	$J_{\rm B-H}/{\rm Hz}$	100 $^{\circ}\mathrm{C}$	150 $^{\circ}\mathrm{C}$	carbon composite
$[BH_4]^-$	-35.2	82	75.9	53.3	3.5
$[B_{3}H_{8}]^{-}$	-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

this composite showed a main resonance at -15.6 ppm assigned to MgB₁₂H₁₂. The small shoulder at -40.8 ppm originated from the Mg(BH₄)₂ residue. The yield of MgB₁₂H₁₂ was found to be 92.5 mol% by solution-state ¹¹B NMR recorded in DMSO-d₆, as shown in Fig. 3b. Only small amounts of MgB₁₀H₁₀ (4 mol%) and Mg(BH₄)₂ (3.5 mol%) were observed. Considering that the amount of MgH₂ in the starting MgH₂/carbon sample was 10 wt%, the amount of MgB₁₂H₁₂ was calculated to be about 40 wt% in the as-synthesized MgB₁₂H₁₂/carbon composite.

Stability of MgB₁₂H₁₂

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 °C under vacuum and subsequently



cooled to room temperature for ¹¹B 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 °C. Note that after heat-treatment at 350 °C, no soluble species in DMSO-d₆ was observed by solution-state ¹¹B 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. Similar polymerization between $Li_2B_{12}H_{12}$ monomers upon heating has been reported previously.^{42,43}



Fig. 3 (a) ¹¹B MAS NMR spectra of the as-synthesized MgB₁₂H₁₂/ carbon composite and the samples heated at 350 to 600 °C, respectively, and ¹¹B CP-MAS spectra (dashed) for the samples heated at 400 and 500 °C, respectively. K₂B₁₂H₁₂ was used as the reference. The star indicates the Mg(BH₄)₂ residue. (b) Solution-state ¹¹B{¹H} NMR spectra of the as-synthesized MgB₁₂H₁₂/carbon composite recorded in DMSO-d₆.

Heating to 400 and 500 °C led to the further shifting of $MgB_{12}H_{12}$ resonance to -11.4 and -5.6 ppm, respectively. To verify whether these shifts are due to the formation of H-free species such as amorphous boron, the ¹¹B CP-MAS measurements were carried out, by which the signal from the H-free species can be suppressed. For the sample heated at 400 °C, the ¹¹B 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 °C. For the sample heated at 500 °C, only a 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 °C, the resonance shifted to around 0 ppm, close to the chemical shift of amorphous

boron.¹⁷ Furthermore, no ¹¹B signal was observed in the ¹¹B CP-MAS spectrum (not shown), indicating the decomposition of the $[B_{12}H_{12}]^{2-}$ species into amorphous boron at 600 °C according to eqn (3).

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

Discussion

We achieved the synthesis of MgB12H12 via the reaction of Mg(BH₄)₂ with B₂H₆ at 150 °C. By using Mg(BH₄)₂ nanoparticles, the yield of MgB₁₂H₁₂ 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 B2H6 or BH₃ units are ready to react with $[BH_4]^-$ to form higher boranes.44-46 The improved formation of MgB12H12 was possibly due to the shortened diffusion distance of B₂H₆ or BH₃ 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. 2a). 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(BH₄)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 B₂H₆ or BH₃ units play important roles in the decomposition process of $Mg(BH_4)_2$.

The as-synthesized MgB₁₂H₁₂/carbon composite was a physical mixture of MgB₁₂H₁₂ 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 MgB₁₂H₁₂.^{36,47,48} The as-synthesized MgB₁₂H₁₂ particles may be in the nanoscale, which tend to agglomerate upon heating. Consequently, the investigation of the stability of the MgB₁₂H₁₂/carbon composite was considered to be instructive for understanding the role of MgB₁₂H₁₂ in the decomposition of bulk Mg(BH₄)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 °C and slowly decomposed into amorphous boron above 400 °C, whereas $Mg(BH_4)_2$ starts to decompose at 250 to 270 °C.^{6–8,16} The slow self-decomposition of $MgB_{12}H_{12}$ above 400 °C seems not to match with one of the hydrogen desorption events of $Mg(BH_4)_2$ which shows three major desorption steps between 250 and 400 °C.^{6–8,16} MgH_2 or Mg formed from the decomposition of $Mg(BH_4)_2$ might destabilize $MgB_{12}H_{12}$ resulting in the formation of MgB_2 , as suggested by theoretical predictions.²¹

Conclusions

We have successfully synthesized solvent-free $MgB_{12}H_{12}$ *via* a 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 the $Mg(BH_4)_2$ /carbon nanocomposite to overcome the kinetic barrier from the passivation layer.

The as-synthesized MgB₁₂H₁₂ was readily soluble in DMSOd₆ with a chemical shift of -15.3 ppm and coupling constant J_{B-H} of 125 Hz. After being treated at 350 °C, the sample was no longer soluble in DMSO-d₆, implying the occurrence of polymerization between MgB₁₂H₁₂ monomers. Upon further heating at 400 to 600 °C, MgB₁₂H₁₂ slowly decomposed into amorphous boron. This decomposition behavior does not match with one of the hydrogen desorption events of Mg(BH₄)₂ occurring between 250 and 400 °C.

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