Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Experimental

The reference samples of amorphous boron and $Mg(BH_4)_2$ (purities > 95%) were purchased from Sigma-Aldrich and $K_2B_{12}H_{12}$ from Katchem. $MgB_{12}H_{12}$ was synthesized via the reaction between $Mg(BH_4)_2$ and B_2H_6.[1] D_2O and anhydrous DMSO-d_6 (d_6 means all the six hydrogen atoms ("H") in DMSO are replaced with their isotope deuterium ("D")) were purchased from ARMAR Chemicals.

To perform the decomposition of $Mg(BH_4)_2$, 150 mg of sample was filled in a stainless steel autoclave which was sealed air tight and transferred into a custom-made pressure-composition-temperature (*pcT*) apparatus.[2] Initially the sample was evacuated at room temperature to a vacuum below 10^{-4} mbar and subsequently heated to different temperatures at a vacuum of 10^{-4} mbar. The amounts of hydrogen released during the heating process were recorded via a mass flow controller/meter connected to the *pcT* apparatus. The $Mg(BH_4)_2$ samples after heating at different temperature from 265 to 500ºC were cooled to room temperature for characterization by X-ray diffraction (XRD), FT-IR, and ^{11}B NMR. The rehydrogenation was carried out at 265ºC and 160 bar H_2 for 20h. Throughout this study, the samples were handled in a glove box filled with purified Ar gas (H_2O < 1 ppm, O_2 < 1 ppm).

XRD measurements were performed using a Bruker D8 diffractometer equipped with a Goebel mirror selecting Cu Kα radiation (λ = 1.5418 Å) and a linear detector system (Vantec). Samples for XRD measurements were filled and sealed under an argon atmosphere into glass capillaries (diameter 0.7 mm; wall thickness 0.01 mm).

FT-IR measurements were carried out at room temperature under protective Ar atmosphere using a Bruker Alpha spectrometer equipped with a platinum ATR single reflection diamond ATR module.

^{11}B magic angle spinning (MAS) NMR experiments were performed at 128.38 MHz on a Bruker Avance 400 NMR spectrometer using a 4 mm CP-MAS probe at room temperature. The spectra were recorded at 12 kHz sample rotation applying a “Hahn echo” pulse sequence for suppression of the probe background signal. Pulse lengths of 1.5 μs (π/12 pulse) and 3.0 μs were applied for the ^{11}B excitation and echo pulses, respectively and during acquisition xy kHz SPINAL64 decoupling of the ^1H frequency was applied.

^{11}B solution-state NMR spectra were recorded on a 5 mm inverse broadband probe at 298 K. The as-prepared samples were homogenously ground under inert atmosphere for 5 min. For each measurement, amounts of ≈ 10 mg solid samples and about 5 mL of water or DMSO were weighed into tight vials and the suspensions were stirred on a shaker (KS 250, JANKE & KUNKEL, IKA Labortechnik) for at least half an hour to facilitate dissolution. Undissolved solids were removed by filtration of the suspensions over Celite. ^{11}B NMR chemical shifts are reported in parts per million (ppm), externally referenced to a 1.0 M $B(OH)_3$ aqueous solution at 19.6 ppm, and ^1H NMR chemical shifts are referenced to the resonances of water (4.7 ppm) or DMSO (2.49 ppm). For the quantitative analysis of boron-containing species in solution, a DMSO (12 mM) and an aqueous solution (46 mM) of $K_2B_{12}H_{12}$ were used as external references. The concentrations of soluble species were determined by comparing the resonance areas of measured species with that of the reference sample applying the ERETIC method.[3]

References

1. A. Remhof, Y. Yan, D. Rentsch, A. Borgschulte, C. M. Jensen and A. Züttel, *Journal of Materials Chemistry A*, 2014, **2**, 6.
2. M. Bielmann, S. Kato, P. Mauron, A. Borgschulte and A. Zuttel, *Rev Sci Instrum*, 2009, **80**.
3. D. I. Hoult, *Concept Magnetic Res*, 2000, **12**, 173-187.
4. Y. G. Yan, A. Remhof, P. Mauron, D. Rentsch, Z. Lodziana, Y. S. Lee, H. S. Lee, Y. W. Cho and A. Zuttel, *J Phys Chem C*, 2013, **117**, 8878-8886.

Figure S1

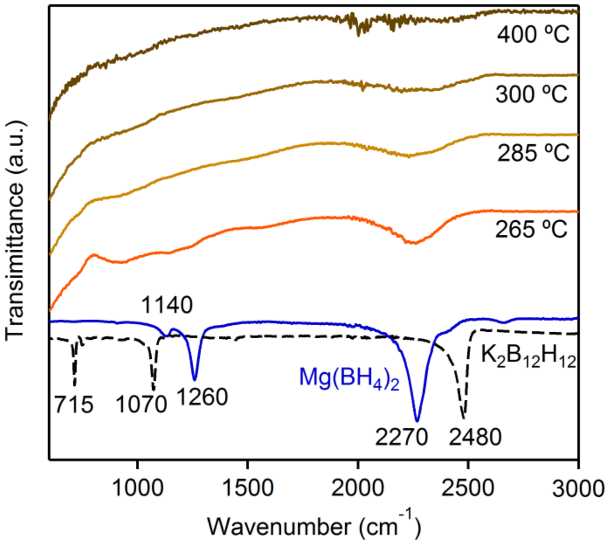

Fig. S1 FT-IR spectra of $Mg(BH_4)_2$ decomposed at 265ºC (20 h), 285ºC (20 h), 300ºC (20 h), and 400ºC (2 h), and reference samples $Mg(BH_4)_2$ and $K_2B_{12}H_{12}$.

Figure S2

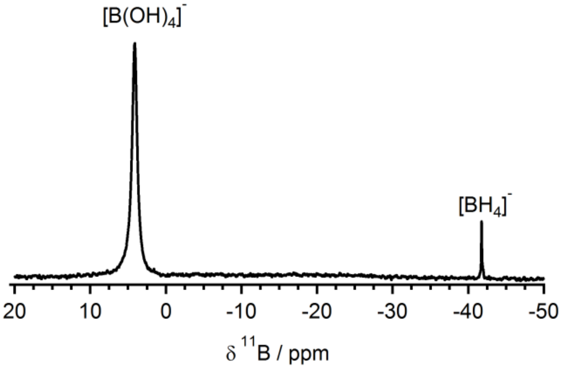

Fig. S2 Solution-state ^{11}B NMR spectrum of hydrolysis products of $Mg(BH_4)_2$ in D_2O.

Figure S3

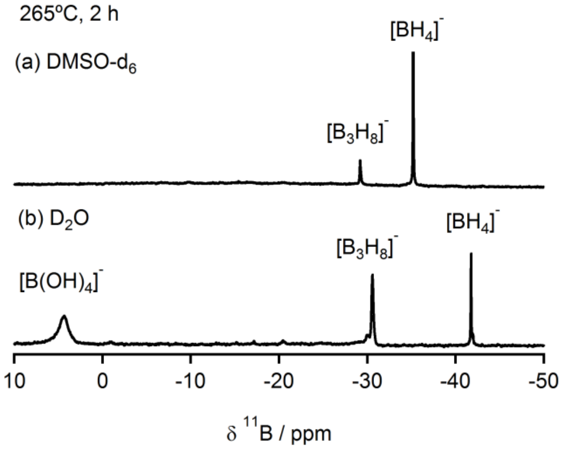

Fig. S3 ^{11}B NMR spectra of $Mg(BH_4)_2$ decomposed at 265ºC for 2h, after dissolution in (a) DMSO and (b) D_2O. Smaller ratio of $[BH_4]^-$ to $[B_3H_8]^-$ in D_2O may be due to the hydrolysis of $[BH_4]^-$. Different solvents also cause different chemical shifts for $[BH_4]^-$ and $[B_3H_8]^-$.

Figure S4

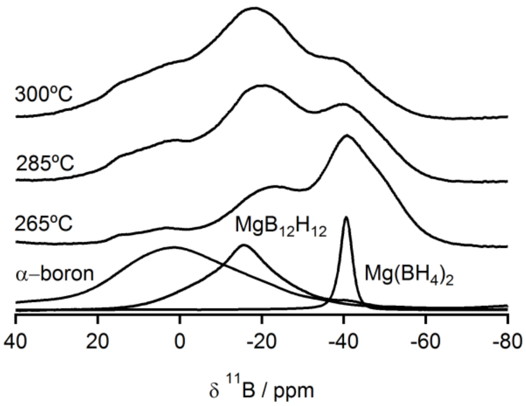

Fig. S4 ^{11}B MAS NMR spectra of $Mg(BH_4)_2$ decomposed at 265°C (20 h), 285°C (20 h), and 300°C (20 h), referred to $Mg(BH_4)_2$, $MgB_{12}H_{12}$ and amorphous boron. The shoulders between 0 to 20 ppm were attributed to boron oxides.[4]

Figure S5

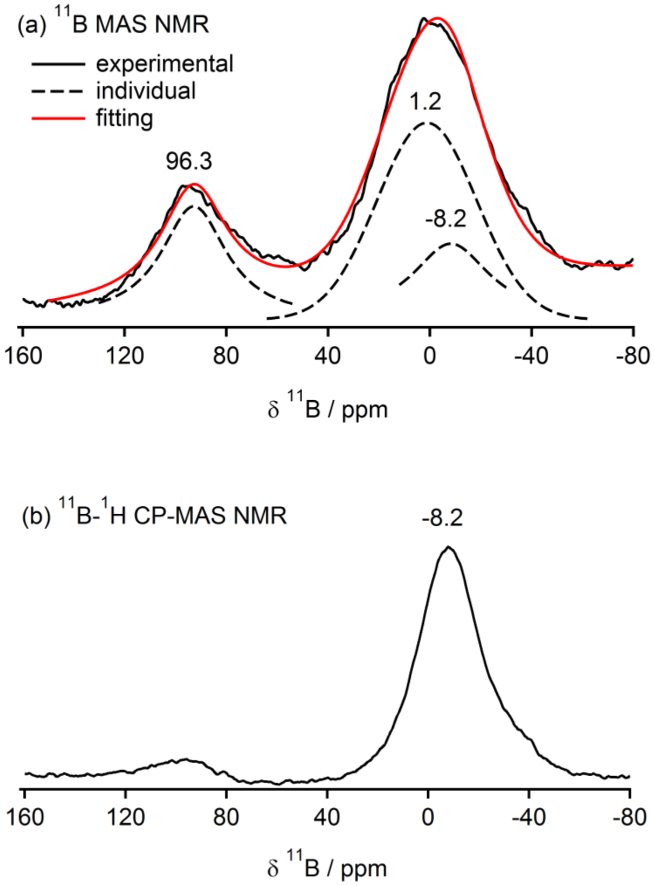

Fig. S5 (a) ^{11}B MAS NMR and (b) ^{11}B-^{1}H CP-MAS NMR spectra of $Mg(BH_4)_2$ decomposed at 400ºC for 2 h. The MAS NMR spectrum was deconvoluted into three individuals at –8.2, 1.2 and 96.3 ppm, respectively.

Figure S6

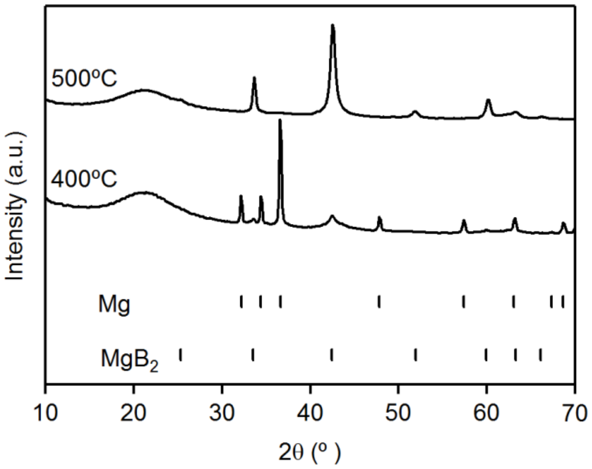

Fig. S6 XRD patterns of $Mg(BH_4)_2$ decomposed at 400°C for 2 h and 500°C for 1h.