Supplementary Information

Facile synthesis and regeneration of $Mg(BH_4)_2$ by high energy reactive ball milling of MgB_2

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Experimental details

Materials and Methods

Mechanochemical processing: mechanochemical hydrogenation of MgB_2 was performed in a planetary mill (Fritsch P-7) under H_2 atmosphere. A custom designed vial (ca. 95 ml), which is made of 316 grade steel with hardened stainless steel liner, is capable of operating at up to 5000 psi. MgB_2 was purchased from Alfa Aesar (99 %, ~100 mesh) and used without further purification. The purity of MgB_2 was confirmed by ^{11}B solid-state (SS)NMR and power X-ray diffraction (XRD). High purity H_2 gas was purchased from Linweld (99.999 %). About 1 g of MgB_2 was milled with ca. 160 g of steel balls (20 ball of ca. 8 g each) at 400 rpm. The milling direction was alternatively changed every 30 min separated by 5 min pauses to avoid excessive heating inside the vials. Due to the amorphous form of milled samples, ^{11}B SSNMR spectroscopy was used for the analysis products and intermediates. All manipulations, before and after the reactions, were carried out under high purity argon atmosphere in a glove box that was maintained at H_2O and O_2 levels of less than 1 ppm.

Volumetric analysis: The thermal desorption of hydrogen from the milled samples was studied using Sievert's-type pressure-composition-temperature apparatus (PCTPro-200, Hy-Energy LLC). 150-200 mg of each sample was loaded in an autoclave followed by the volume calibration of the free sample space. The samples were heated up to 390 °C with 5 °C/min ramping and held the temperature for 2-3 h until the dehydrogenation was no longer observed. The gas composition was analyzed by the residual gas analyzer (SRS RGA100) directly connected to the PCT autoclave. In all samples, the emission of impurities such as diborane (B_2H_6), if any, was lower than the detection limit ($5x10^{-14}$ Torr) of the spectrometer, which corresponds to <1parts per million (pm) by volume.

X-ray powder diffraction analysis

The reaction products were analyzed by X-ray powder diffraction at room temperature on a PANalytical X'Pert powder diffractometer using Cu Kα radiation in the range of Bragg angles

2θ from 10° to 80°, with a 0.02° 2θ step. During the measurements a polyimide (Kapton) film was used to protect the samples from air. The use of film resulted in an amorphous like background in the XRD patterns in the 2θ range of 13–20°.

Solid-state NMR. The SSNMR experiments were performed at 9.4 T on a Chemagnetics Infinity 400 spectrometer, equipped with a 3.2-mm magic angle spinning (MAS) probe operated at a MAS rate of 21~23 kHz. The samples were packed in MAS zirconia rotors in a glove box under argon atmosphere and sealed with double O-ring caps to minimize the possibility of oxygen and moisture contamination. The direct-polarization (DP)MAS spectra of ^{11}B nuclei were acquired using a single pulse excitation, the radio frequency (RF) magnetic field of ~150 kHz, and a small flip angle of 15° for quantitative accuracy.[1,2] The cross-polarization (CP)MAS NMR spectra were also observed, using ^{11}B RF field of ~60 kHz for CP, and ^{1}H RF fields of 100 kHz and ~84 kHz for $\pi/2$ pulse and CP, respectively. In both DPMAS and CPMAS experiments, a ^{1}H two-pulse phase-modulation (TPPM) decoupling[3] at an RF field of 104 kHz was used during the acquisition of ^{11}B signal. The ^{11}B shifts were referenced to diethyl ether-boron trifluoride complex ($BF_3 \cdot OEt_2$, δ ^{11}B = 0 ppm), based on the measurement of a secondary reference (0.1 M aqueous solution of boric acid at 19.4 ppm).[4]

H_2 desorption

Table S1: The amount of thermally released hydrogen from MgB_2 samples mechanochemically hydrogenated at various milling times and a constant H_2 pressure of 350 bar.

Time (h)	H_2 desorption (wt %)
3.5	1.34
7	1.94
15	3.04
30	3.6
40	3.9
60	3.87

Table S2: The amount of thermally released hydrogen from MgB_2 samples mechanochemically hydrogenated at various H_2 pressures and a constant ball-milling time of 15 h.

Pressure (Bar)	H_2 desorption (wt %)
50	1.68
100	2.14
150	2.61
200	2.82
250	3.13
300	3.21
350	3.87

XRD analysis

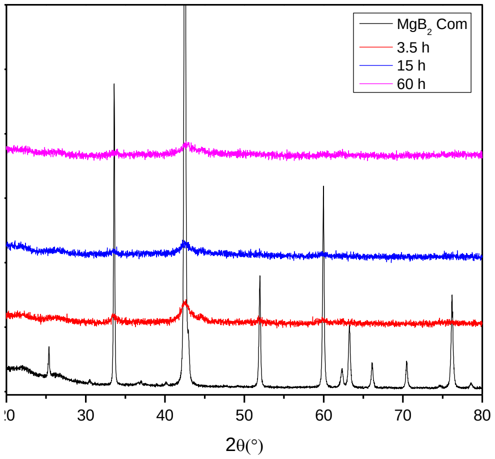

Figure S1: Powder x-ray diffraction of MgB_2 samples milled under hydrogen atmosphere (p_{H2} = 350 bar) after different milling times. Only the broad peaks from MgB_2 are seen after milling. However, the center of the broad peaks do not shift with respect to the stating MgB_2 indicating little or no incorporation of Fe in the MgB_2 lattice.

^{11}B DPMAS spectra of reference samples

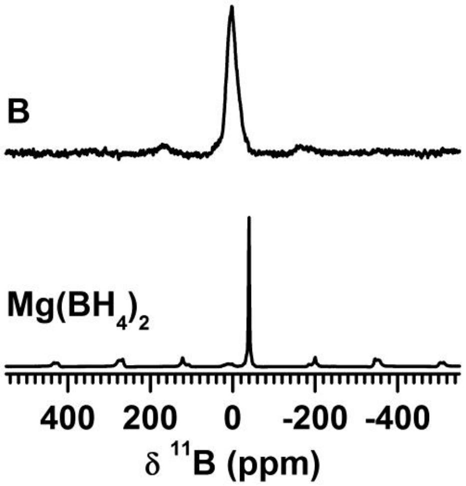

Figure. S2 ^{11}B DPMAS spectra of reference samples: elemental boron and $Mg(BH_4)_2$.

References

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