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Facile synthesis and regeneration of Mg(BH$_4$)$_2$ by high energy reactive ball milling of MgB$_2$

Shalabh Gupta,$^a$ Ihor Z. Hlova,$^{ab}$ Takeshi Kobayashi,$^a$ Roman V. Denys,$^c$ Fu Chen,$^a$
Ihor Y. Zavalij,$^c$ Marek Pruski$^{a,ad}$ and Vitalij K. Pecharsky$^{a,ab}$

We report direct hydrogenation of MgB$_2$ in a planetary ball mill. Magnesium borohydride, Mg(BH$_4$)$_2$, and various polyhedral borane anion salts have been synthesized at pressures between 50 and 350 bars H$_2$ without the need for subsequent isothermal hydrogenation at elevated pressure and temperature. The obtained products release ~4 wt% H$_2$ below 390 °C, and a major portion of Mg(BH$_4$)$_2$ transforms back to MgB$_2$ at around 300 °C, demonstrating the possibility of reversible hydrogen storage in an Mg(BH$_4$)$_2$–MgB$_2$ system.

Light metal borohydrides, M(BH$_4$)$_n$ (M = Li, Mg, Ca; $n$ is the valence of M), are promising materials for hydrogen storage.$^{1,2}$ In particular, Mg(BH$_4$)$_2$ has been broadly studied because of its favorable enthalpy of dehydrogenation.$^{1,8}$ Complete dehydrogenation yields 14.8 wt% of H$_2$ via multiple competing processes, ultimately leading to the formation of MgB$_2$. Thus, hydrogenation of MgB$_2$ at reasonably low hydrogen pressure is of great interest. Partial hydrogenation of MgB$_2$ was achieved in two recent works through coupling mechanochemical processing with subsequent isothermal hydrogenation at high temperature and pressure. Severa et al. achieved ~75% yield of β-Mg(BH$_4$)$_2$ by heating ball-milled MgB$_2$ to 400 °C under 950 bars H$_2$ for 10 hours.$^6$ Li et al. reported 25% yield of Mg(BH$_4$)$_2$ by milling MgB$_2$ under 10 bars H$_2$ for 10 hours followed by isothermal hydrogenation at 400 °C and 400 bars H$_2$ for 24 hours.$^7$ Here, we examine the hydrogenation of MgB$_2$ solely by mechanochemical processing$^{a,e}$ under high-pressure hydrogen at room temperature, and study (de)hydrogenation pathways using temperature-programmed desorption (TPD) and solid-state (SS) NMR spectroscopy.

MgB$_2$ (Alfa Aesar, 99% purity) was hydrogenated in a planetary ball mill (Fritsch P-7) using different milling times $\tau_{BM}$ at constant H$_2$ pressure, $p_H = 350$ bars, or different $p_H$ at constant $\tau_{BM} = 15$ hours.

The thermal dehydrogenation was studied by TPD with 5°C min$^{-1}$ ramping up to 390°C using an automated Sievert’s type PCT (pressure–composition–temperature) instrument (PCTPro-2000, Hy-Energy LLC). All manipulations were performed under an Ar atmosphere in a glove box. Additional experimental details have been reported elsewhere.$^9$

Noting that not all of the hydrogen adsorbed during the ball milling is necessarily released below 390°C, for $\tau_{BM} \leq 15$ hours the amount of desorbed hydrogen increases linearly up to 3.1 wt%, reaching a plateau of 3.9 wt% of H$_2$ at $\tau_{TM} \approx 45$ hours (Fig. 1a). Similarly, hydrogen desorption increases with $p_{H1}$, before leveling off at 3.2 wt% for $p_{H1} = 300$ bars (Fig. 1b). Fig. 1c shows the transient of hydrogen desorption from the sample ball-milled under 350 bars H$_2$ for 15 hours. The curve indicates two-step dehydrogenation, with peaks observed at 300 and 355°C. The subsequent SSNMR experiments provided further insight into the hydrogenation and dehydrogenation pathways.

Fig. 2 shows the $^{11}$B direct polarization magic-angle spinning (DPMAS) spectra of the hydrogenated products, measured using a small flip angle ($<15$°).$^{10,11}$ All spectra consist largely of two manifolds of spinning sidebands, with isotropic peaks (centerbands) located at about 98 ppm and −39 ppm. These were assigned to...
MgB₂ and Mg(BH₄)₂, respectively, based on the spectra of reference compounds (see ESI†).

Quantitative ¹¹B NMR measurements are challenging due to the complex nutation behaviour of quadrupolar nuclei (for ¹¹B, I = 3/2) following rf-pulse excitation.¹⁰ In this case, an added difficulty is apparent, since the observed manifolds of spinning sidebands do not originate from the typically encountered quadrupolar or chemical shift anisotropies, but stem mainly from the broadening due to bulk magnetic susceptibility (BMS). The large BMS in the hydrogenated products is due to ferromagnetic impurity (metallic bcc Fe from the milling medium) as substantiated by SEM-EDX (scanning electron microscopy–energy dispersive X-ray spectroscopy) analysis and the attraction of the samples to the magnet. The resulting local magnetic fields are of dipolar form and are responsible for the observed effects.¹²,¹³ Despite these complexities, one may assume that in each sample the widths of BMS-induced sideband patterns are similar for all peaks, and simply use the centerband intensities to estimate the relative concentrations of species. From SEM-EDX analysis, 10–15 wt% Fe impurity is present in MgB₂ are retained, and new (undesirable) B–B bonds are created as well. Theoretical study of the hydrogenation of MgB₂ suggests that hydrogen is present on the MgB₂ surface in an atomic form due to low activation energy for dissociation.¹⁷ Thus, higher pₜH increases the concentration of atomic hydrogen on the MgB₂ surface, favouring the formation of B–H bonds over the B–B bonds. The retention and regeneration of B–B bonds lead to stable polyhedral borane salts, and therefore, reduce the efficiency of mechanochemical formation of Mg(BH₄)₂. In earlier studies, mechanochemical processing alone was insufficient to hydrogenate MgB₂, and additional isothermal hydrogenation at high pressure was required.¹⁸ Nevertheless, the product contained a significant amount of MgB₂H₁₂. The high intensity of mechanical energy used here together with moderately high pₜH leads to a more efficient cleaving of the B–B bonds under milder conditions (temperature and tₜM).

In the following, we scrutinize the thermal dehydrogenation and subsequent rehydrogenation of a sample hydrogenated at pₜH = 350 bar, tₜM = 15 h and B/S = 160. After dehydrogenation at 300 °C, the sample shows a significantly increased concentration of MgB₂ and a diminished peak due to Mg(BH₄)₂, accompanied by the resonance previously ascribed to [B₆H₆]²⁻ anions (including [B₁₂H₁₄]²⁻) (compare Fig 2a and 4a).¹⁴ Further treatment at 390 °C
results in a complete conversion of Mg(BH$_4$)$_2$ to dehydrogenated products (as evidenced by the lack of $^{11}$B$[^{1}H]$ CPMAS signal in Fig. 4b), with MgB$_2$ being the main product. The minor signal centred at 6 ppm in Fig. 4b is characteristic of amorphous boron.\(^{19}\) Also, in addition to MgB$_2$, the powder X-ray diffraction (XRD) analyses reveal the formation of Mg$_2$H$_6$ and Mg in the samples dehydrogenated at 300 and 390 °C, respectively (Fig. 4d and e). These results suggest the following dehydrogenation pathways in Mg(BH$_4$)$_2$ synthesized by reactive ball milling:

\[
\begin{align*}
\text{Mg(BH}_4\text{)}_2 & \rightarrow \text{MgB}_2 + 4\text{H}_2 \\
\text{Mg(BH}_4\text{)}_2 & \rightarrow 1/6\text{MgB}_12\text{H}_12 + 5/6\text{MgH}_2 + 13/6\text{H}_2 \\
\text{MgB}_12\text{H}_12 & \rightarrow \text{Mg (MgH}_3\text{)} + 12\text{B} + 6\text{H}_2 \\
\text{MgH}_2 & \rightarrow \text{Mg} + \text{H}_2
\end{align*}
\]

Note that in addition to MgB$_2$H$_{12}$, other $[\text{B}_x\text{H}_y]^-$ species are also possible in the sample dehydrogenated at 300 °C. The hydrogen desorption at around 300 °C (Fig. 1c) is attributed to eqn (1) and (2a), while the desorption at around 355 °C is described by eqn (2b) and (2c). An earlier report described multi-step thermal dehydrogenation of crystalline Mg(BH$_4$)$_2$: Mg(BH$_4$)$_2$ $\rightarrow$ MgH$_2$ + $[\text{B}_x\text{H}_y]^-$ + $\text{H}_2$ (between 280 and 350 °C) and MgH$_2$ $\rightarrow$ Mg + $\text{H}_2$ (\~{}310 °C).\(^{5}\) In that study, the formation of MgB$_2$ was only observed after heating to 550 °C. In contrast, MgB$_2$ forms already at 300 °C in the present study, whereas MgH$_2$ and Mg form at temperatures similar to those reported in ref. 5 (Fig. 4d and e). These results imply the feasibility of a direct pathway from Mg(BH$_4$)$_2$ to MgB$_2$ without the formation of stable intermediates (eqn 1), which is likely related to both the nanoscale size and high concentration of defects in Mg(BH$_4$)$_2$ particles formed mechanochemically.

The dehydrogenated product was again hydrogenated by ball milling at $p_H = 350$ bar, $t_{BM} = 15$ h and B/S = 160. The $^{11}$B DPMAS spectrum of the re-hydrogenated sample (Fig. 4c) indicates that most of MgB$_2$ and polyhedral boron species were transformed back to Mg(BH$_4$)$_2$. Taken together, the spectra of Fig. 4a-c suggest a reasonable reversibility between MgB$_2$ and Mg(BH$_4$)$_2$. Compared to the first desorption, nearly 90% of the hydrogen desorption was recovered after the second mechanochemical hydrogenation cycle. The 10% loss of storage capacity may be attributed to the formation of elemental boron that remains unreacted in the rehydrogenated product, and in part to the additional Fe impurity introduced upon successive milling. Further cycling experiments have not been performed due to the difficulties in collecting the dehydrogenated product in quantities sufficient for adequate milling.

In summary, we have demonstrated purely mechanochemical hydrogenation of MgB$_2$ to Mg(BH$_4$)$_2$ by high energy reactive ball milling. The sample prepared at room temperature under 350 bar H$_2$ releases \~{}4 wt% of hydrogen below 390 °C. SSNMR reveals the formation of Mg[BH$_4$]$_2$ as the final product through $[\text{B}_x\text{H}_y]^-$ intermediates. Subsequent thermal dehydrogenation results in complete decomposition of mechanochemically synthesized Mg[BH$_4$]$_2$ and $[\text{B}_x\text{H}_y]^-$ anions, and the recovery of MgB$_2$ below 390 °C. The results suggest that the formation of nanoscale size particles plays a critical role for the reversible hydrogen storage in the Mg(BH$_4$)$_2$–MgB$_2$ system.

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Notes and references