On the reversible hydrogen storage in $\text{Mg}(\text{BH}_4)_2$ under moderate conditions

Yigang Yan,¹ Daniel Rentsch,² Arndt Remhof¹

¹*Empa, Materials for Energy Conversion, Duebendorf 8600, Switzerland*

²*Empa, Functional Polymers, Duebendorf 8600, Switzerland*

Abstract: $\text{Mg}(\text{BH}_4)_2$ contains 14.9 mass% of hydrogen and is considered as a promising hydrogen storage material. Reversible hydrogen sorption under moderate conditions represents a main challenge for $\text{Mg}(\text{BH}_4)_2$ being utilized for solid-state hydrogen storage. Here, we achieve the reversible storage of 4.0 mass% of hydrogen at 265°C in $\text{Mg}(\text{BH}_4)_2$. That is, desorption of 7.5 mass% H at 265°C under vacuum and absorption of 4.0 mass% at 265°C and 160 bar H_2 . ^{11}B MAS NMR measurements indicate that the reversible hydrogen sorption involves the formation of a decisive intermediate which shows a major resonance with a chemical shift at -50.0 ppm. The phase evolution in the hydrogen cycles as well as the capacity loss in the hydrogen sorption cycles is discussed.

Introduction

Safe and efficient hydrogen storage is one of the key technologies challenging hydrogen as a widely used fuel. Owing to high gravimetric and volumetric densities of hydrogen, metal borohydrides have been intensively investigated for solid state hydrogen storage over the last decade.¹⁻⁵ $\text{Mg}(\text{BH}_4)_2$ is a typical example in the group of metal borohydrides, which shows a high hydrogen capacity of 14.9 mass%. Furthermore, the overall dehydrogenation reaction (eq.1) shows an enthalpy change of -39 kJ/mol H_2 which thermodynamically allows the hydrogen desorption at around room temperature and makes $\text{Mg}(\text{BH}_4)_2$ an attractive material for reversible hydrogen storage under moderate conditions.⁶⁻⁸

Reversible hydrogen sorption according to eq. 1 has been experimentally verified, however, it only was observed at elevated temperatures (e.g., around 400°C) and high hydrogen pressure (e.g., 400 to 950 bar).⁹⁻¹¹ The harsh conditions are owing to slow kinetics in terms of large energy barrier for the formation of B-H bonds, migration of atoms, etc. Nanostructured $\text{Mg}(\text{BH}_4)_2$ shows enhanced hydrogen sorption kinetics, where the reversible reaction of eq.1 could be carried out at 200°C.¹²

Numerous studies have revealed that the decomposition reaction (eq.1) occurs in multi steps involving the formation of Mg-B-H ternary intermediates.¹³⁻¹⁶ Since B-H bonds retain in the Mg-B-H intermediates, the kinetic barrier for the reformation of $\text{Mg}(\text{BH}_4)_2$ could be largely reduced, which favors the rehydrogenation reaction under more moderate conditions. The study on rehydrogenation from the intermediates was mainly focusing on $\text{Mg}(\text{B}_3\text{H}_8)_2$.^{15, 17, 18} By controlling the decomposition in a relatively low temperature range from 200 to 285°C, $\text{Mg}(\text{BH}_4)_2$ was partially decomposed into $\text{Mg}(\text{B}_3\text{H}_8)_2$. The reversible formation of $\text{Mg}(\text{BH}_4)_2$ from $\text{Mg}(\text{B}_3\text{H}_8)_2$ can be achieved at 250°C and 120 bar H_2 .¹⁷

However, reversible hydrogen storage capacity is only limited to 2.5 mass% (eq. 2). To make better use of the high hydrogen density of $\text{Mg}(\text{BH}_4)_2$, the dehydrogenation reaction needs to go further beyond the formation of $\text{Mg}(\text{B}_3\text{H}_8)_2$. Other Mg-B-H intermediates such as $\text{Mg}(\text{B}_4\text{H}_9)_2$ and $\text{Mg}(\text{B}_5\text{H}_8)_2$ have been suggested, although further evidence for their phase identification are still required.¹⁹ Stable closo-borates such as $\text{MgB}_{12}\text{H}_{12}$ and stable Mg-B-H polymers have also been widely discussed as the intermediates, which will hinder the reversible hydrogen sorption.^{11, 12, 20}

Apparently, the higher the borate formed in the desorption process, the more hydrogen might reversibly be stored. However, as soon as closo borates such as $\text{MgB}_{12}\text{H}_{12}$ or polymers containing closo borates are formed, the reversibility of the reaction is reduced. Therefore, the control of the decomposition step is crucial to obtain high reversible hydrogen capacity under moderate conditions.

In present study, we investigated the reversible hydrogen storage in $\text{Mg}(\text{BH}_4)_2$ under moderate condition. The hydrogen desorption was carried out at 265°C under dynamic vacuum for 20 h and 7.5 mass% H was released in the first cycle. The re-absorption at 265°C / 160 bar H_2 exhibited a reversible hydrogen storage capacity of 4.0 mass% in the second cycle. Furthermore, the phase evolution in the hydrogen sorption cycle was studied by X-ray diffraction (XRD) and ^{11}B magic angle spinning nuclear magnetic resonance (^{11}B MAS NMR).

Experimental

$\text{Mg}(\text{BH}_4)_2$ (purity > 95%) was purchased from Sigma-Aldrich. To perform the hydrogen desorption of $\text{Mg}(\text{BH}_4)_2$, 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.²¹ Initially the sample was evacuated at room temperature to a vacuum below 10^{-4} mbar and subsequently heated to 265°C under vacuum. The amounts of hydrogen released during the heating process were recorded via a mass flow controller/meter connected to the *pcT* apparatus. After hydrogen desorption, 160 bar H_2 (purity, 99.999%) was introduced and kept for 20 h at 265°C . After desorption and re-absorption the samples were cooled to room temperature for further characterization.

XRD measurements were performed using a Bruker D8 diffractometer equipped with a Goebel mirror selecting Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a linear detector system (Vantec). Samples for XRD measurements were filled and sealed under argon atmosphere into glass capillaries (diameter 0.7 mm; wall thickness 0.01 mm).

^{11}B MAS NMR experiments were performed at 128.4 MHz on a Bruker Avance III 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 $1.5 \mu\text{s}$ ($\pi/12$ pulse) and $3.0 \mu\text{s}$ were applied for the ^{11}B excitation and echo pulses, respectively and during acquisition 52 kHz SPINAL64 decoupling of the ^1H frequency was applied.

Solution-state ^{11}B NMR spectra were recorded on a 5 mm CryoProbeTM Prodigy probe at 298 K. The as-prepared samples were homogeneously ground under inert atmosphere for 5 min. Amounts of ≈ 10 mg solid samples and about 5 mL of water 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 $\text{B}(\text{OH})_3$ aqueous solution at 19.6 ppm. D_2O was purchased from ARMAR Chemicals.

Results and discussion

The as-received $\text{Mg}(\text{BH}_4)_2$ was heated up to 265°C and kept for 20 h under vacuum. 7.5 mass% of H was recorded in the 1st desorption process (Figure 1). After 1st desorption, 160 bar H_2 was introduced for re-absorption at 265°C . In the 2nd desorption, 4.0 mass% of H was desorbed at 265°C in 20 h, indicating that 4.0 mass% of H was stored in the re-absorption process.

XRD measurement (Figure 2) indicated that the as-received $\text{Mg}(\text{BH}_4)_2$ show cubic γ -phase (space group: *I*d-3a).²² After the 1st desorption, the reflections of the γ -phase disappeared, and crystalline MgH_2 was formed. Moreover, a halo around $2\theta = 22^\circ$ indicates the formation of an amorphous phase. After re-absorption, the reflections of MgH_2 almost disappeared and

orthorhombic β -phase $\text{Mg}(\text{BH}_4)_2$ (space group: $Fddd$) was formed.²³ In addition, impurity phase of MgO was observed, possibly owing to the presence of contamination from water or oxygen.

Figure 1. Hydrogen desorption curves in the first two cycles at 265°C under dynamic vacuum. After first desorption, hydrogen re-absorption was conducted at 265°C and 160 bar H_2 for 20h.

Figure 2. XRD patterns of the as-received γ - $\text{Mg}(\text{BH}_4)_2$, and the samples after 1st desorption (265°C, vacuum, 20h) and re-absorption (265°C, 160 bar H_2 , 20h). The intensity of γ - $\text{Mg}(\text{BH}_4)_2$ was reduced by 20 times.

Figure 3. (a) Solid-state ^{11}B MAS NMR and (b) solution-state ^{11}B NMR of samples: after 1st desorption, re-absorption and 2nd desorption. Dashed lines in (a) represent the line shapes of the individual components.

Table 1. Quantitative analysis of individual components based on solid-state ^{11}B MAS NMR in Figure 3.

Samples	Amount / % (FWHM / kHz)			
	-50.0 ppm	-40.3 ppm	-22.0 ppm	0 – 20 ppm
$\text{Mg}(\text{BH}_4)_2$	-	100.0 (0.4)	-	-
1 st desorption	21.2	29.2 (1.60)	38.7	10.9
1 st re-absorption	-	72.2 (0.47)	27.8	-
2 nd desorption	16.8	20.3 (1.40)	54.7	6.8

Regarding the presence of amorphous Mg-B-H compounds in the desorption/re-absorption cycle, ^{11}B NMR experiments were carried out. The solid-state ^{11}B MAS NMR spectra of $\text{Mg}(\text{BH}_4)_2$ and the samples after desorption and re-absorption are shown in Figure 3a and quantitative analysis summarized in Table 1. $\text{Mg}(\text{BH}_4)_2$ displays a single resonance at -40.3 ppm (FWHM = 0.4 kHz). After the 1st desorption, two broad resonances centered at -40.3 (FWHM = 1.6 kHz) and -22.0 ppm, respectively, and a shoulder at -50.0 ppm were observed. After re-absorption, the shoulder at -50.0 ppm disappeared and the resonance at -40.3 ppm narrowed (FWHM = 0.47 kHz), corresponding to the re-formation of crystalline $\text{Mg}(\text{BH}_4)_2$ (Figure 2). While the resonance at -22.0 ppm maintained, its relative amount decreased from 38.7% to 27.8% after the re-hydrogenation step. After the 2nd desorption, the resonance at -40.3 ppm broadened again, the shoulder at -50.0 ppm re-appeared and further, the relative amount of chemical species with a resonance at -22.0 ppm increased to 54.7%.

To further identify the intermediate phases in the hydrogen sorption cycles, all individual samples were dissolved in D_2O and measured by solution-state ^{11}B NMR (Figure 3b). The dissolution of pure $\text{Mg}(\text{BH}_4)_2$ in D_2O resulted in a resonance of $[\text{BH}_4]^-$ at -41.8 ppm and a resonance of the $[\text{B}(\text{OH})_4]^-$ ion at 2.2 ppm originated from the hydrolysis of $[\text{BH}_4]^-$. After 1st desorption, $[\text{B}_3\text{H}_8]^-$ at -30.6 ppm, $[\text{B}_9\text{H}_9]^{2-}$ at -20.5 ppm, $[\text{B}_{11}\text{H}_{11}]^{2-}$ at -17.3 ppm and $[\text{B}_{12}\text{H}_{12}]^{2-}$ at -15.2 ppm were observed in addition to the remaining $[\text{BH}_4]^-$.¹⁶ The species of $[\text{B}_9\text{H}_9]^{2-}$, $[\text{B}_{11}\text{H}_{11}]^{2-}$ and $[\text{B}_{12}\text{H}_{12}]^{2-}$ remained after the re-absorption of hydrogen and the 2nd desorption processes. Apparently, these species are not accessible to the hydrogen absorption reaction. The species $[\text{B}_3\text{H}_8]^-$ disappeared after re-absorption and re-formed after the 2nd desorption, confirming that

Mg(B₃H₈)₂ is one of the intermediate favorable for hydrogen re-absorption. However, in the ¹¹B MAS NMR spectra (Figure 3a), no resonance around -30.0 ppm attributable to Mg(B₃H₈)₂ was detected, implying that the resonance of [B₃H₈]⁻ is overlapped by the broad resonance around -22.0 ppm. The resonance around -50.0 ppm observed by solid-state ¹¹B NMR (Figure 3a) did not appear in the solution-state NMR spectra (Figure 3b), indicating that the formed intermediate assigned to -50 ppm was not soluble or not stable in D₂O.

Above all, we have shown the reversible hydrogen storage of 4.0 mass% within two sorption cycles at 265°C in Mg(BH₄)₂. This amount is higher than the reversible reaction involving pristine Mg(B₃H₈)₂ according to eq.2. Meanwhile, only a low amount of Mg(B₃H₈)₂ was observed by NMR (Figure 3b), i.e., only 10.9 mol% of boron atoms existed as [B₃H₈]⁻ after 1st desorption according to Ref.16. Furthermore, the reversible sorption reaction was found to closely relate to the formation of certain intermediate(s) with a boron chemical shift at around -50 ppm in ¹¹B MAS NMR measurement (Figure 3a). Nido-boranes such as [B₅H₈]⁻, arachno- and hypho-boranes such as [B₄H₉]⁻ and [B₅H₉]²⁻ were reported to contain a small portion of boron atoms with ¹¹B chemical shifts around -50 ppm, but the major ¹¹B NMR resonance of these compounds show chemical shifts between -10 to -20 ppm.²⁴ Additional phase characterization of this material is still required to reveal this crucial intermediate(s) for the reversible hydrogen storage in Mg(BH₄)₂ under moderate conditions.

The accumulation of boron atoms which apparently did not participate in the hydrogen re-absorption was observed by ¹¹B MAS NMR (Figure 3a). These borons show chemical shift around -22 ppm. Considering that closo-borates including [B₉H₉]²⁻, [B₁₁H₁₁]²⁻ and [B₁₂H₁₂]²⁻ maintained in the hydrogen sorption cycles (Figure 3b), the broad resonance at -22 ppm in ¹¹B MAS NMR spectra may be attributed to the formation of a polymeric compound composed of closo-borates and [B₃H₈]⁻. In the re-absorption process, the polymeric compound dissociated, where [B₃H₈]⁻ was converted back to [BH₄]⁻ but closo-borates maintained leading to the loss in the hydrogen capacity.¹⁶ Further, ¹¹B MAS NMR data indicated that about 28% of boron atoms maintained after 1st re-absorption cycle (Table 1). However, XRD results (Figure 2) show that MgH₂ was almost fully consumed and a large amount of MgO was observed. As a consequence, the lack of Mg may result in the accumulation of, with respect to the re-hydrogenation reaction nonreactive boron species and therefore loss of hydrogen capacity of the whole system.

Conclusion

We demonstrate the reversible storage of 4.0 mass% of hydrogen in Mg(BH₄)₂ under moderate conditions for the first two sorption cycles. Mg(BH₄)₂ desorbs 7.5 mass% H at 265°C under vacuum in the first cycle and absorbs of 4.0 mass% at 265°C and 160 bar H₂ in the second cycle. We identified Mg(B₃H₈)₂ as intermediate by solution-state ¹¹B NMR, but only in a small amount. ¹¹B MAS NMR data indicate that the reversible hydrogen sorption at 265°C involves the reversible formation of a not yet known intermediate chemical species which shows a major ¹¹B NMR resonance at -50.0 ppm. The capacity loss of this material was attributed to two reasons: the formation of polymeric compounds containing closo-borates such as [B₉H₉]²⁻, [B₁₁H₁₁]²⁻ and [B₁₂H₁₂]²⁻ and hydro (-oxide) contamination leading to the formation of MgO.

Acknowledgement

Y. Yan and A. Remhof would like to acknowledge the financial support granted by Switzerland through the Swiss Contribution to the enlarged European Union. The NMR hardware was partially granted by the Swiss National Science Foundation (SNFS, grant No. 150638).

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