Reactivity of magnesium borohydride – Metal hydride composites, γ-Mg(BH₄)₂-MHₓ, M = Li, Na, Mg, Ca

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Reactivity of magnesium borohydride – metal hydride composites,

$\gamma$-Mg(BH$_4$)$_2$-MH$_x$, $M$ = Li, Na, Mg, Ca

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Abstract

The reactivity and thermal decomposition of $\gamma$-Mg(BH$_4$)$_2$-MH$_x$, $M$ = Li, Na, Mg, and Ca composites has been examined with the objective of studying the hydrogen storage capability of the composites. The samples were prepared by manual grinding $\gamma$-Mg(BH$_4$)$_2$ with a metal hydride to obtain homogenous mixtures. In-situ synchrotron radiation powder X-ray diffraction (SR-PXD) and simultaneous thermogravimetric analysis, differential scanning calorimetry, and mass spectrometry was performed to analyse the decomposition mechanism, whereas solid-state $^{11}$B nuclear magnetic resonance spectroscopy and SR-PXD was used to investigate the decomposition products. Interestingly, substitution reactions take place between magnesium borohydride and lithium, sodium and calcium hydride forming the more stable metal borohydrides, M(BH$_4$)$_x$, $M$ = Li, Na or Ca. The composite $\gamma$-Mg(BH$_4$)$_2$-LiH has a hydrogen release at $T \sim 380 - 420$ °C, which indicates the formation of amorphous LiBH$_4$ during decomposition. For the composites $\gamma$-Mg(BH$_4$)$_2$-NaH, formation of crystalline NaBH$_4$ is observed by SR-PXD from $T = 150 - 450$ °C, and hydrogen release ascribed to NaBH$_4$ is observed in MS data at $T = 460 - 480$ °C. $\gamma$-Mg(BH$_4$)$_2$-MgH$_2$ composite decomposes as the individual constituents. $\beta$-Ca(BH$_4$)$_2$ is formed at $T = 175 - 375$ °C in the composites of $\gamma$-Mg(BH$_4$)$_2$-
CaH$_2$. Bragg diffraction from CaB$_6$ at $T > 370$ °C is detected by SR-PXD for γ-Mg(BH$_4$)$_2$-CaH$_2$ (1:0.5) but not for samples richer in CaH$_2$. Release of diborane was not observed for any of the magnesium borohydride metal hydride composites.

Keywords: Hydrogen storage, magnesium borohydride, reactive hydride composites, in-situ powder X-ray diffraction, thermal decomposition

1 Introduction

Hydrogen is the lightest element in the periodic table and has the highest gravimetric energy density of all known substances. Therefore, hydrogen is considered a strong candidate as a future energy carrier [1-5]. A main obstacle in the transition to a “hydrogen economy” is the storage of hydrogen. The complex metal hydrides were first discovered in 1940 and in 1997 they were for the first time suggested as a hydrogen storage medium [6-9]. Metal borohydride materials have attracted much attention [10, 11] as potential H$_2$ storage materials/carriers due to the low atomic weight of boron (10.8 g/mol), the high hydrogen content, often in the given range 10-18 wt.%, and the extreme structural flexibility makes the BH$_4^-$ complex anion an ideal building unit for rational design of novel metal borohydrides interesting for hydrogen storage [12]. For example monometallic borohydrides, lithium and magnesium borohydride, LiBH$_4$ and Mg(BH$_4$)$_2$ have a great potential to store large quantities of hydrogen due to their very high gravimetric (18.5 and 14.9 wt.%, respectively) and volumetric (124 and 117 g H$_2$/L, respectively) hydrogen densities. However, the practical use of complex hydrides is hampered due to slow kinetics for the release of hydrogen and often high thermodynamic stability [12].

The hydrogen release temperature is correlated inversely with the Pauling electronegativity of the metal coordinating directly to the borohydride anion [13]. This correlation may be a way to design new metal borohydrides for hydrogen storage [13-17]. Unfortunately the bi- and trimetallic borohydrides often decompose to the stable monometallic borohydrides. The slow kinetics of hydrogen release and uptake is caused by the often complex reaction mechanisms further complicated
by the fact that the reaction pathway may be dependent on pressure and temperature. In addition, the reversibility of metal borohydrides is often poor, as elevated temperatures and pressures are required (e.g. $T = 600 \, ^\circ\text{C}$, $p(\text{H}_2) = 350 \, \text{bar}$ for LiBH$_4$) and even then the reactions are relatively slow [18].

Lately several strategies have focused on tailoring the properties of metal borohydrides in order to improve the hydrogen storage. One approach is to incorporate metal hydrides to form reactive hydride composites, $M(\text{BH}_4)_n-M'H_m$, $M, M' = \text{metals and } n, m = \text{oxidation state of the metal}$ [19-25]. This can potentially change the reaction pathway and maybe improve both the thermodynamic and kinetic hydrogen release and uptake properties. Reactive hydride composites have an average hydrogen storage capacity of the individual compounds but improved thermodynamic properties. This has been demonstrated for 2LiBH$_4$-MgH$_2$ [19, 26], where magnesium diboride forms in the dehydrogenated state. Various systems have been investigated in order to destabilize the Mg(BH$_4$)$_2$ to lower the hydrogen release temperature and one of them are the composite Mg(BH$_4$)$_2$ – LiNH$_2$ where the release temperature is 160 $^\circ\text{C}$ [27]. Another composite is the Mg(BH$_4$)$_2$ – LiBH$_4$, where an eutectic melting is observed and 7.0 wt.% of hydrogen is released at 270 $^\circ\text{C}$ [28]. Similarly it has been demonstrated that the Mg(BH$_4$)$_2$ – LiH composite can reversible store 3.8 wt% H$_2$ at 180 $^\circ\text{C}$ [29]. It has been suggested that the layered compound MgB$_2$ is an compound, which can be hydrogenated under less harsh conditions compared to e.g. amorphous elemental boron [26]. This has prompted the present investigation, which focuses on tailoring the properties of magnesium borohydride, $\gamma$-Mg(BH$_4$)$_2$, by adding metal hydrides of lithium, sodium, magnesium, and calcium. The recently discovered polymorph of magnesium borohydride, $\gamma$-Mg(BH$_4$)$_2$, has received considerable interest as a potential hydrogen storage medium owing to high hydrogen content ($\rho_m = 14.9 \, \text{wt.\%}$) combined with the permanent high porosity and ability to store molecular hydrogen [30]. However, the dehydrogenation/hydrogenation conditions of $\gamma$-Mg(BH$_4$)$_2$ are still far from those required for practical application, and the mechanism for dehydrogenation is not yet fully understood [31-36]. In this work, the decomposition behaviour of magnesium borohydride and lithium, sodium, magnesium, or calcium hydride composites are investigated using in-situ synchrotron radiation powder X-ray diffraction (SR-PXD) and coupled thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and mass spectroscopy (MS), and solid-state $^{11}$B magic angle spinning (MAS)
nuclear magnetic spectroscopy (NMR). For the purpose of establish understanding of the decomposition mechanism of the composites and reaction intermediates, as well as if the composites can release hydrogen prior to the pristine $\gamma$-Mg(BH$_4$)$_2$.

2 Experimental section

2.1 Sample preparation. Magnesium borohydride, $\gamma$-Mg(BH$_4$)$_2$, was synthesized from a dimethyl sulphide borane complex, (CH$_3$)$_2$S-BH$_3$, (2 M in toluene, Sigma Aldrich) and di-$n$-butyl magnesium, Mg($n$-Bu)$_2$, (1 M in heptane, Sigma Aldrich) according to a literature procedure [30]. Samples of $\gamma$-Mg(BH$_4$)$_2$-$\gamma$-MH$_x$, $M$ = Li, Na, Mg, Ca (> 95 %, Sigma Aldrich) were prepared by manually mixing $\gamma$-Mg(BH$_4$)$_2$ with a metal hydride by mortar and pestle to obtain a homogenous mixture. all sample handling was carried out in an MBraun Unilab glovebox with a circulation purifier ($p$(O$_2$, H$_2$O) < 1 ppm). Selected samples were then heated to $T$ = 50, 100, and 150 °C for $t$ = 90 min. Table 1 provides an overview of the synthesised samples and their composition. All samples were analysed by in-situ SR-PXD and simultaneous TGA-DSC-MS. Selected samples were heated to $T$ = 50, 100, and 150 °C and held at this temperature for $t$ = 90 min and subsequently analysed by $^{11}$B.

Table 1. Overview of the samples synthesised and investigated indicating sample name, the calculated molar ratio and molar fraction of the reactants and the calculated hydrogen content of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Relative molar ratio</th>
<th>Sample preparation</th>
<th>Molar fraction (x hydride)</th>
<th>Gravimetric H$_2$ content (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s1</td>
<td>$\gamma$-Mg(BH$_4$)$_2$</td>
<td>-</td>
<td>(CH$_3$)$_2$S-BH$_3$, Mg($n$-Bu)$_2$</td>
<td>-</td>
<td>14.93</td>
</tr>
<tr>
<td>s2</td>
<td>$\gamma$-Mg(BH$_4$)$_2$, LiH</td>
<td>1.00:0.50</td>
<td>Mortar and pestle</td>
<td>0.33</td>
<td>14.78</td>
</tr>
<tr>
<td>s3</td>
<td>$\gamma$-Mg(BH$_4$)$_2$, LiH</td>
<td>1.00:0.97</td>
<td>Mortar and pestle</td>
<td>0.51</td>
<td>14.65</td>
</tr>
<tr>
<td>s4</td>
<td>$\gamma$-Mg(BH$_4$)$_2$, LiH</td>
<td>1.00:1.89</td>
<td>Mortar and pestle</td>
<td>0.65</td>
<td>14.42</td>
</tr>
<tr>
<td>s5</td>
<td>$\gamma$-Mg(BH$_4$)$_2$, NaH</td>
<td>1.00:0.51</td>
<td>Mortar and pestle</td>
<td>0.34</td>
<td>12.98</td>
</tr>
<tr>
<td>s6</td>
<td>$\gamma$-Mg(BH$_4$)$_2$, NaH</td>
<td>1.00:1.06</td>
<td>Mortar and pestle</td>
<td>0.51</td>
<td>11.63</td>
</tr>
<tr>
<td>s7</td>
<td>$\gamma$-Mg(BH$_4$)$_2$, NaH</td>
<td>1.00:2.03</td>
<td>Mortar and pestle</td>
<td>0.67</td>
<td>9.88</td>
</tr>
<tr>
<td>s8</td>
<td>$\gamma$-Mg(BH$_4$)$_2$, MgH$_2$</td>
<td>1.00:0.50</td>
<td>Mortar and pestle</td>
<td>0.34</td>
<td>13.51</td>
</tr>
<tr>
<td>s9</td>
<td>$\gamma$-Mg(BH$_4$)$_2$, MgH$_2$</td>
<td>1.00:0.99</td>
<td>Mortar and pestle</td>
<td>0.50</td>
<td>12.55</td>
</tr>
<tr>
<td>s10</td>
<td>$\gamma$-Mg(BH$_4$)$_2$, CaH$_2$</td>
<td>1.00:0.50</td>
<td>Mortar and pestle</td>
<td>0.33</td>
<td>12.09</td>
</tr>
<tr>
<td>s11</td>
<td>$\gamma$-Mg(BH$_4$)$_2$, CaH$_2$</td>
<td>1.00:0.99</td>
<td>Mortar and pestle</td>
<td>0.50</td>
<td>10.49</td>
</tr>
<tr>
<td>s12</td>
<td>$\gamma$-Mg(BH$_4$)$_2$, LiH</td>
<td>1.00:1.89</td>
<td>50 °C, 90 min</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>s13</td>
<td>$\gamma$-Mg(BH$_4$)$_2$, LiH</td>
<td>1.00:1.89</td>
<td>100 °C, 90 min</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>s14</td>
<td>$\gamma$-Mg(BH$_4$)$_2$, LiH</td>
<td>1.00:1.89</td>
<td>150 °C, 90 min</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
2.2 Laboratory powder X-ray diffraction (PXD). Samples and reaction products were investigated by PXD data collected on a Rigaku Smart Lab diffractometer using Cu $K_{\alpha}$ radiation ($\lambda = 1.5418$ Å) and a parallel beam multilayer. Diffraction patterns were collected in the range $2\theta = 10^\circ - 80^\circ$ at $5^\circ$/min and obtained with a D/TeX Ultra detector at room temperature (RT). The powders were packed in 0.5 mm boron silica glass capillaries in a glove box and sealed with silicon grease.

2.3 Synchrotron radiation powder X-ray diffraction (SR-PXD). The reaction mechanism of the decomposition was investigated using in-situ time resolved SR-PXD. SR-PXD data were collected at beamline I711, MAX II laboratory in Lund, Sweden. The selected wavelengths were $\lambda = 0.99242(2)$ Å (samples: s1, s7, s8) and $\lambda = 0.99203(2)$ Å (samples: s4, s5, s6, s9, s10, s11), and $\lambda = 1.00982(2)$ Å (sample: s2). In-situ time resolved SR-PXD data were also collected at P02.1 at Petra III, Germany. The selected wavelength was $\lambda = 0.2072(1)$ Å (sample: s3). The powdered samples were loaded in a single-crystal sapphire (Al$_2$O$_3$) tube (o.d. 1.09 mm, i.d. 0.79 mm) in an argon-filled glove box ($p$(O$_2$, H$_2$O) < 0.5 ppm) and mounted on an in-house designed sample holder [37] allowing control of temperature, pressure, and gas composition. The sample temperature was controlled with a thermocouple placed in the sapphire tube close to the sample. During experiments, the samples were heated from $T = RT - 500$ °C with a heating rate of $\Delta T/\Delta t = 5$ °C/min. The raw data files were analysed by the program FIT2D by masking diffraction spots originating from the single-crystal sapphire tubes and calibrating the wavelength using a NIST 660a LaB$_6$ standard and subsequently transforming the raw 2D diffraction data to 1D powder diffraction patterns.

2.4 Thermal analysis and mass spectroscopy (TGA-DSC-MS). Decomposition reactions were further studied by combined thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and mass spectroscopy (MS) using a PerkinElmer STA 6000 apparatus connected to a Hiden Analytical HPR-20 QMS system. Samples were transferred to Al$_2$O$_3$ crucibles under argon atmosphere and measured from $T = RT - 500$ °C under an argon flow (65 mL/min) and a heating rate of $\Delta T/\Delta t = 5$ °C/min. The outlet gaseous species H$_2$ (m/z = 2) and B$_2$H$_6$ (m/z = 26) were monitored by mass spectroscopy.

2.5 Solid-state magic angle spinning nuclear magnetic resonance (ss MAS NMR). $^{11}$B MAS NMR spectra were obtained on an Agilent 600 MHz (14.1 T) NMR spectrometer using spinning speeds in
the range 6.5 - 15 kHz. The Larmor frequency was 599.74 MHz for $^{11}$B nucleus. The samples were packed in a 3.2 mm rotor in a glovebox ($p$(O$_2$,H$_2$O) < 0.5 ppm) to avoid exposure to air/oxygen. The magic angle was adjusted by minimising the line widths for the spinning sidebands of $^{23}$Na resonance in NaNO$_3$. Single pulse $^{11}$B MAS NMR spectra were obtained using a short pulse to ensure quantitative spectra. The $^{11}$B spectra were referenced using 0.5 M H$_3$BO$_3$ ($\delta = 19.6$ ppm) and H$_2$O ($\delta = 4.6$ ppm) as external references, respectively. The obtained spectra were analysed using VnmrJ 4.2 and MestReNova 6.1.1. A minor variation in the chemical shift is observed due to a small drift in the magnetic field.

3 Results and discussion

3.1 Thermal decomposition of magnesium borohydride, $\gamma$-Mg(BH$_4$)$_2$

Initially the thermal decomposition mechanism of $\gamma$-Mg(BH$_4$)$_2$ (s1) is investigated at the same conditions as the composite samples investigated in this work. The total mass loss from room temperature to 500 °C detected by TGA is 14.6 wt.%, which corresponds well with the calculated hydrogen content, $\rho_m$(Mg(BH$_4$)$_2$) = 14.9 wt.%, see Figure S1 (ESI). A polymorphic transition $\gamma$- to $\beta'$.Mg(BH$_4$)$_2$ is observed at $T = 155$ °C in the DSC data (Figure S1) and SR-PXD (Figure S2) [31, 32]. At $T = 260$ °C, $\beta'$.Mg(BH$_4$)$_2$ decomposes to an amorphous material leaving a featureless X-ray diffractogram, which corresponds well with previous data, where Bragg diffraction is lost at $T = 215 - 284$ °C [31-33]. Two endothermic events are recognised in the DSC curve at $T = 290$ and 360 °C, which are ascribed to the decomposition of Mg(BH$_4$)$_2$ and MgH$_2$, respectively [34]. Diffraction reflections from Magnesium metal appear in the SR-PXD data at $T = 370$ °C. Magnesium reacts with boron forming magnesium diboride, MgB$_2$, at $T \sim 470$ °C (Figure S2). This is seen from the integrated and normalised diffracted intensities in the SR-PXD data (Figure S3) and is in agreement with earlier observations, where formation of MgH$_2$. Mg and MgB$_2$ is observed during the decomposition of Mg(BH$_4$)$_2$ during the following reaction schemes [31, 32, 36].

$$\text{Mg(BH}_4\text{)}_{2(s)} \rightarrow \text{MgH}_2_{(s)} + 2\text{B}_{(s)} + \text{H}_2{(_g)} \quad (1)$$

$$\text{MgH}_2_{(s)} \rightarrow \text{Mg}_{(s)} + \text{H}_2{(_g)} \quad (2)$$
Mg(s) + 2B(s) → MgB\textsubscript{2}(s) \hspace{1cm} (3)

Mass spectroscopy reveals a major hydrogen release in the temperature range ~270 to 400 °C with three peak values at $T = 300$, 350 and 375 °C (Figure S1) coinciding with the hydrogen release previously observed during temperature-programmed desorption [31]. Bragg diffraction peaks of the polymorph $\varepsilon$-Mg(BH\textsubscript{4})\textsubscript{2} [31, 32] and magnesium hydride are not observed by PXD in the present study.

3.2 Magnesium borohydride lithium hydride composites, $\gamma$-Mg(BH\textsubscript{4})\textsubscript{2}-LiH

Three samples of $\gamma$-Mg(BH\textsubscript{4})\textsubscript{2}-LiH 1.00:0.50 (s2), 1.00:0.97 (s3), and 1.00:1.89 (s4) were prepared and in-situ SR-PXD data for s4 are shown (Figure 1). Data for s2 are shown in supplementary information Figure S4. The diffracted intensity of $\gamma$-Mg(BH\textsubscript{4})\textsubscript{2} and LiH observed in figure 1 decreases relatively fast at $T < 100$ °C and then slower at $T > 100$ °C and disappears at $T = 150$ and 350 °C, respectively (Figure 1 and Figure 2). $\beta'$-Mg(BH\textsubscript{4})\textsubscript{2} is observed at $T = 150 - 240$ °C. Magnesium hydride forms at $T \sim 175$ °C, which is 150 °C lower than observed for $\gamma$-Mg(BH\textsubscript{4})\textsubscript{2}, which is properly due to a substitution reaction between LiH and Mg(BH\textsubscript{4})\textsubscript{2} [36]. Magnesium hydride decomposes to magnesium at $T \sim 370$ °C. Two thermal events in the DSC data is seen at $T = 150 - 175$ °C, most pronounced for s2 (Figure 3). No mass loss is associated with this event and it might be assigned to the polymorphic transition to $\varepsilon$- followed by the transition to $\beta'$-Mg(BH\textsubscript{4})\textsubscript{2} polymorph, which have been reported to occur in the temperature range $T = 165-210$ °C [31, 32]. No diborane is detected by mass spectroscopy during heating from $RT$ to 500 °C. The Mg(BH\textsubscript{4})\textsubscript{2}-LiH composites show a different hydrogen release profile compared to $\gamma$-Mg(BH\textsubscript{4})\textsubscript{2} as observed from MS data (Figure 3). A hydrogen release at $T = 380 - 420$ °C is observed s3 (1.00:0.97) and s4 (1.00:1.89), respectively, see Figure 3. This observation is assigned to decomposition of LiBH\textsubscript{4}, as the decomposition of LiBH\textsubscript{4} is reported in this temperature interval [38, 39]. The hydrogen observed at $T \sim 300$ °C for $\gamma$-Mg(BH\textsubscript{4})\textsubscript{2} is not present in the Mg(BH\textsubscript{4})\textsubscript{2}-LiH composites. This combined with the hydrogen release at $T = 380 - 420$ °C suggests the following substitution reaction during thermal decomposition:

$$\text{Mg(BH}_4\text{)}_2(s) + 2\text{LiH}(s) \rightarrow 2\text{LiBH}_4(s) + \text{MgH}_2(s)$$ \hspace{1cm} (4)
However, no Bragg diffraction from LiBH$_4$ is observed in any SR-PXD patterns of the three γ-Mg(BH$_4$)$_2$-LiH composites, suggesting the presence of amorphous LiBH$_4$. Amorphous LiBH$_4$ has been observed to form during decomposition of 3LiBH$_4$-YCl$_3$ [40]. The initial molar ratio of the reactants, γ-Mg(BH$_4$)$_2$ and LiH, influences the amount of LiBH$_4$ formed, and s4 (1.00:1.89) has the highest hydrogen release at $T = 420$ °C, ascribed to decomposition of LiBH$_4$. TGA data (Figure 3) show a total mass loss in the temperature range $T = 150 - 500$ °C of 15.5, 14.3, 13.0 wt.% for s2 (1.00:0.50), s3 (1.00:0.97), and s4 (1.00:1.89), respectively, which compares fairly well to calculated hydrogen contents of 14.8, 14.7 and 14.4 wt.% H$_2$, respectively. The deviation in calculated and observed mass loss for s2 at 150 °C is assigned to remaining solvent in the sample of γ-Mg(BH$_4$)$_2$.

![Figure 1. In-situ SR-PXD pattern of γ-Mg(BH$_4$)$_2$-LiH 1.00:1.89 (s4) from $T = RT$ to 500 °C, $\Delta T/\Delta t = 5$ °C/min under static vacuum ($\lambda = 0.99203$ Å, MAX II laboratory, Sweden). Symbols: ▼ = γ-Mg(BH$_4$)$_2$, ▲ = β’-Mg(BH$_4$)$_2$, □ = Mg, ○ = MgH$_2$, ● = MgB$_2$, * = MgO, ▼ = LiH.](image-url)
Figure 2. Normalised integrated diffracted intensities for the compounds observed during thermal treatment of $\gamma$-Mg(BH$_4$)$_2$-LiH 1.00:1.89 (s4). Symbols: ▼ = $\gamma$-Mg(BH$_4$)$_2$, ▲ = $\beta'$-Mg(BH$_4$)$_2$, ○ = MgH$_2$, □ = Mg, ▼ = LiH.

Figure 3. Thermal analysis of $\gamma$-Mg(BH$_4$)$_2$-LiH 1.00:0.50 (s2), 1.00:0.97 (s3) and 1.00:1.89 (s4) heated from RT to 500 °C at $\Delta T/\Delta t = 5$ °C/min under an argon flow (65 mL/min) combining thermogravimetry (top), differential scanning calorimetry (middle), and mass spectrometry (bottom). Data for the reference material $\gamma$-Mg(BH$_4$)$_2$ (s1) is plotted with a dotted line for comparison.

3.3 Magnesium borohydride sodium hydride composites, $\gamma$-Mg(BH$_4$)$_2$-NaH

Three composite samples of $\gamma$-Mg(BH$_4$)$_2$-NaH 1.00:0.51 (s5), 1.00:1.06 (s6) and 1.00:2.03 (s7) were prepared. The TGA-DSC-MS and SR-PXD results are displayed in Figure 4 to Figure 6 and in Figure
S5 and S6. The powder diffractogram of the three $\gamma$-Mg(BH$_4$)$_2$-NaH composites shows a relatively fast decrease of diffracted intensity of NaH at $T \sim 100$ °C (Figure 5 and Figure 6) followed by a slower decrease in the temperature range $T = 100 - 150$ °C. From 150 °C a faster reduction of intensity of NaH is simultaneous to an abrupt decrease in diffraction of $\gamma$-Mg(BH$_4$)$_2$, which transforms to $\beta'$-Mg(BH$_4$)$_2$ at $T = 155$ °C. For s5 (1.00:0.51) and s6 (1.00:1.06), formation of crystalline NaBH$_4$ starts at $T \sim 150$ °C, continues to $T \sim 225$ °C where the intensity decreases until $T \sim 275$ °C and a new maximum for the diffracted intensity is observed at $T \sim 350$ °C (Figure S5 and Figure S6). Other studies have also showed formation of NaBH$_4$ from reactive hydride composites such as NaH and MgB$_2$, where NaBH$_4$ is formed at 380 °C and a modified system of NaF-NaH-MgB$_2$, where the NaBH$_4$ formation is observed as low as 204 °C [41, 42]. For s7 (1.00:2.03) the temperature, at which the two maxima occur, is slightly higher, $T = 250$ and 425 °C, respectively (Figure 6). In all three $\gamma$-Mg(BH$_4$)$_2$-NaH composites, Bragg diffraction of NaBH$_4$ disappears at $T = 450$ °C. The fact that NaBH$_4$ is observed in the SR-PXD patterns indicates that the following substitution reaction proceed during the thermal treatment at $T > 150$ °C:

$$\text{Mg(BH}_4\text{)}_{2(s)} + 2\text{NaH}_{(s)} \rightarrow 2\text{NaBH}_4_{(s)} + \text{MgH}_2_{(s)}$$  \hspace{1cm} (5)

TGA data (Figure 4) reveal a total mass loss of 12.2, 9.5, and 9.2 wt. % for s5, s6, and s7 at $T = 150 - 500$ °C in accordance with the calculated hydrogen contents of 13.0, 11.6, and 9.8 wt.% H$_2$, respectively. The decomposition of NaBH$_4$ is seen in the MS data (Figure 4) at $T = 460 - 480$ °C as a broad hydrogen release peak (NaBH$_4$ decomposes at $T = 500$ °C according to literature [43]). No diborane was detected by mass spectroscopy during heating from $RT$ to 500 °C. Mass spectroscopy and TGA data indicate that the samples contain increasing amounts of NaBH$_4$, i.e. $\gamma$-Mg(BH$_4$)$_2$-NaH 1.00:0.51 (s5) < 1.00:1.06 (s6) < 1.00:2.03 (s7). The DSC curves s5, s6, and s7 show an exothermic event observed at $T = 210$ °C, which contrasts the data for $\gamma$-Mg(BH$_4$)$_2$ and the $\gamma$-Mg(BH$_4$)$_2$-LiH composites (s1, s2 and s3). The magnitude of the exothermic peak increases with the increasing sodium hydride content of the samples. This event may be due to the formation of NaBH$_4$ and coincides with a decrease of diffracted intensity of Mg(BH$_4$)$_2$ as discussed above.
Figure 4. Thermal analysis of $\gamma$-Mg(BH$_4$)$_2$-NaH 1.00:0.51 (s5), 1.00:1.06 (s6) and 1.00:2.03 (s7) heated from $T = RT - 500 ^\circ$C at $\Delta T/\Delta t = 5 ^\circ$C/min under argon flow (65 mL/min) combining thermogravimetry (top), differential scanning calorimetry (middle) and mass spectroscopy (bottom). Data of $\gamma$-Mg(BH$_4$)$_2$ (s1) is given as dotted line for comparison.

Figure 5. In-situ SR-PXD pattern of $\gamma$-Mg(BH$_4$)$_2$-NaH 1.00:0.51 (s5) heated from $T = RT$ to 515 °C at 5 °C/min under static vacuum ($\lambda = 0.99203$ Å, MAX II laboratory, Sweden). Symbols: ▼ = $\gamma$-Mg(BH$_4$)$_2$, ▲ = $\beta$'-Mg(BH$_4$)$_2$, ■ = Mg, ● = MgH$_2$, * = MgO, ▼ = NaBH$_4$, ○ = NaH.
Figure 6. Normalised integrated diffracted intensities for the compounds present in the γ-Mg(BH$_4$)$_2$-NaH 1.00:0.51 composite sample (s5). Symbols: ▼ = γ-Mg(BH$_4$)$_2$, ▲ = β'-Mg(BH$_4$)$_2$, ■ = Mg, ○ = MgH$_2$, ▼ = c-NaBH$_4$, ● = NaH.

3.4 Magnesium borohydride magnesium hydride composites, γ-Mg(BH$_4$)$_2$-MgH$_2$

The results of the thermal analysis of the two γ-Mg(BH$_4$)$_2$-MgH$_2$ 1.00:0.50 (s8) and 1.00:0.99 (s9) composites are shown in Figure 7. The SR-PXD data for the two γ-Mg(BH$_4$)$_2$-MgH$_2$ composites, 1.00:0.99 (s9) and 1.00:0.50 (s8), are similar see Figure 8 and Figure S7, respectively. Diffraction from crystalline γ-Mg(BH$_4$)$_2$ and MgH$_2$ is observed at RT (Figure 8), and the decomposition mechanism of s8 and s9 are identical. The decomposition of γ-Mg(BH$_4$)$_2$ is apparently not affected by the addition of MgH$_2$, which imply no reaction between these compounds [31, 32]. The transformation of γ- to β'-Mg(BH$_4$)$_2$ is recognised at 155 °C as a thermal event in the DSC data (Figure 7). At 260 °C, Bragg diffraction of β'-Mg(BH$_4$)$_2$ disappears possibly due to formation of a solid amorphous material [31, 32]. The diffracted intensity from MgH$_2$ has an abrupt decrease in intensity at ~100 °C, followed by gradual loss of intensity in the temperature range $T = 100$ to ~ 350 °C for both γ-Mg(BH$_4$)$_2$-MgH$_2$ composites. Magnesium is observed at $T \approx 350$ °C and reacts with the amorphous boron at $T > 500$ °C and forms MgB$_2$ (Figure 9) in accord with decomposition of γ-Mg(BH$_4$)$_2$ [31]. The mass spectroscopy data (Figure 7) reveal four events with maximum hydrogen release at $T = 300, 350, 375,$ and 385 °C. The three first are assigned to γ-Mg(BH$_4$)$_2$ [31] and the last to MgH$_2$. No diborane was detected by
mass spectroscopy. Thermogravimetric investigations (Figure 7) reveal a total mass loss in the temperature range $T = 150 - 500 \, ^\circ\text{C}$ of 15.0 and 13.7 wt.% for $\gamma$-Mg(BH$_4$)$_2$-MgH$_2$ 1.00:0.50 (s8) and 1.00:0.99 (s9), respectively, which is slightly higher than the calculated hydrogen contents, 13.5 and 12.6 wt.% H$_2$, respectively.

**Figure 7.** Thermal analysis of $\gamma$-Mg(BH$_4$)$_2$-MgH$_2$ 1.00:0.50 (s8) and 1.00:0.99 (s9) heated from $RT$ to 500 °C at $\Delta T/\Delta t = 5 \, ^\circ\text{C}/\text{min}$ under argon flow (65 mL/min) combining thermogravimetry (top), differential scanning calorimetry (middle) and mass spectroscopy (bottom). Data of $\gamma$-Mg(BH$_4$)$_2$ (s1) is given as dotted line for comparison.
Figure 8. In-situ SR-PXD pattern of $\gamma$-Mg(BH$_4$)$_2$-MgH$_2$ 1.00:0.99 (s9) heated from $T = RT$ to 600 °C at 5 °C/min under static vacuum ($\lambda = 0.99203$ Å, MAX II laboratory, Sweden). Symbols: ▼ = $\gamma$-Mg(BH$_4$)$_2$, ▲ = $\beta'$-Mg(BH$_4$)$_2$, ● = MgH$_2$, ■ = Mg, ◆ = MgB$_2$, ★ = MgO.

Figure 9. Normalised integrated diffracted intensities for the compounds observed during thermal treatment of $\gamma$-Mg(BH$_4$)$_2$-MgH$_2$ 1.00:0.99 (s9). Symbols: ▼ = $\gamma$-Mg(BH$_4$)$_2$, ▲ = $\beta'$-Mg(BH$_4$)$_2$, ● = MgH$_2$, ■ = Mg, ◆ = MgB$_2$.

3.5 Magnesium borohydride calcium hydride composites, $\gamma$-Mg(BH$_4$)$_2$-CaH$_2$

The results of the thermal analysis of the two $\gamma$-Mg(BH$_4$)$_2$-CaH$_2$ 1.00:0.50 (s8) and 1.00:0.99 (s9) composites are shown in Figure 10. SR-PXD patterns measured at RT (Figure 11 and 13) show Bragg diffraction from $\gamma$-Mg(BH$_4$)$_2$ and CaH$_2$. Diffraction from calcium hydride decreases in the temperature
range $T = 100 - 300$ °C. Almost all CaH$_2$ is consumed in a reaction with $\gamma$-Mg(BH$_4$)$_2$ for composite s10 (1.00:0.50), but only ca. 60 % for s11 (1.00:0.99). Thermal analysis under the same physical conditions verifies that CaH$_2$ does not decompose at $T < 500$ °C. Diffraction from $\beta$-Ca(BH$_4$)$_2$ appears in the SR-PXD patterns in the temperature range $T = 175 - 375$ °C with maximum intensity at $T = 270 - 330$ °C suggesting the substitution reaction (3),

$$\text{Mg(BH}_4\text{)}_{2(s)} + \text{CaH}_2(s) \rightarrow \beta\text{-Ca(BH}_4\text{)}_{2(s)} + \text{MgH}_2(s)$$  \hspace{1cm} (6)

Literature reports a polymorphic transition $\alpha$- to $\alpha'$-Ca(BH$_4$)$_2$ and then to the more stable $\beta$-Ca(BH$_4$)$_2$ at $T = 180$ °C [44]. Here $\beta$-Ca(BH$_4$)$_2$ forms directly at slightly lower temperatures, $\beta$-Ca(BH$_4$)$_2$ is then reported to transform into an amorphous phase and decomposes at $T > 380$ °C [44, 45]. At $T > 370$ °C the two $\gamma$-Mg(BH$_4$)$_2$-CaH$_2$ composite samples, s10 and s11, behave differently. s10 (1.00:0.50) shows two endothermic events (Figure 10), corresponding to hydrogen releases in the MS profile (Figure 10), and the presence of Bragg diffraction of CaB$_6$ at $T = 450$ °C (Figure 11 and 12). s11 (1.00:0.99) shows only one endothermic event at $T = 375$ °C and one larger MS hydrogen release (Figure 10) and no Bragg diffraction of CaB$_6$ (Figure 13). No diborane was detected by mass spectroscopy during heating from $T = RT$ to 500 °C. The endothermic DSC events at $T = 370$ and 375 °C corresponding to the hydrogen release with a maximum at $T = 385$ °C, is due to decomposition of the magnesium or calcium containing component.

A total mass loss of 12.6 and 10.6 wt.% is observed at $T = 150$ to 500 °C for s10 and s11, respectively, which is in agreement with the calculated hydrogen contents of 12.1 and 10.5 wt.% H$_2$. An unidentified Bragg diffraction peak is present at $\theta = 22.85^\circ$ ($d = 2.504$ Å) from $T = 160 - 530$ °C in the SR-PXD of $\gamma$-Mg(BH$_4$)$_2$-CaH$_2$ 1.00:0.99 (s11).
Figure 10. Thermal analysis of $\gamma$-Mg(BH$_4$)$_2$-CaH$_2$ 1.00:0.50 (s10) and 1.00:0.99 (s11) heated from RT to 500 °C at $\Delta T/\Delta t = 5$ °C/min under argon flow (65 mL/min) combining thermogravimetry (top), differential scanning calorimetry (middle) and mass spectroscopy (bottom). Data of $\gamma$-Mg(BH$_4$)$_2$ (s1) are given as dotted line for comparison.

Figure 11. In-situ SR-PXD pattern of $\gamma$-Mg(BH$_4$)$_2$-CaH$_2$ 1.00:0.50 (s10) heated from $T = RT$ to 625 °C at 5 °C/min under static vacuum ($\lambda = 0.99203$ Å, MAX II laboratory, Sweden). Symbols: ▼ = $\gamma$-Mg(BH$_4$)$_2$, ▲ = $\beta$'-Mg(BH$_4$)$_2$, ■ = Mg, ◆ = MgB$_2$, △ = $\beta$-Ca(BH$_4$)$_2$, ○ = CaH$_2$, ◆ = CaB$_6$, * = MgO.
Figure 12. Normalised integrated diffracted intensities for the compounds observed during thermal treatment of $\gamma$-Mg(BH$_4$)$_2$-CaH$_2$ 1.00:0.50 (s10). The intensity of MgH$_2$ in Figure 11 is so low, that it is impossible to integrate. ▼ = $\gamma$-Mg(BH$_4$)$_2$, ▲ = $\beta'$-Mg(BH$_4$)$_2$, □ = Mg, ◇ = CaH$_2$, △ = $\beta$-Ca(BH$_4$)$_2$, ◇ = CaB$_6$.

Figure 13. In-situ SR-PXD pattern of $\gamma$-Mg(BH$_4$)$_2$-CaH$_2$ 1.00:0.99 (s11) heated from $T = RT$ to 530 °C at 5 °C/min under static vacuum ($\lambda = 0.99203$ Å, MAX II laboratory, Sweden). ▼ = $\gamma$-Mg(BH$_4$)$_2$, ▲ = $\beta'$-Mg(BH$_4$)$_2$, □ = Mg, ◆ = MgB$_2$, △ = $\beta$-Ca(BH$_4$)$_2$, ◇ = CaH$_2$, × = CaO, ★ = MgO, + = unknown.
3.6 $^{11}$B MAS NMR of $\gamma$-Mg(BH$_4$_2)-LiH 1:2

For all composites studied in this work, the intensity of the Bragg diffraction peaks from the metal hydride observed in the in-situ SR-PXD decreases rapidly from RT to $\sim$100 °C by 10 – 30% after, which the decrease in intensity is less pronounced as illustrated in, e.g., Figure 2, Figure 9 and Figure 12). This decrease occurs simultaneously with a 20-55% reduction of the diffraction of $\gamma$-Mg(BH$_4$_2) from RT to 100 °C, which could indicate a reaction occurring between $\gamma$-Mg(BH$_4$_2) and the metal hydride. No new Bragg diffraction is seen in the in-situ SR-PXD data; therefore $^{11}$B MAS NMR spectra were recorded for $\gamma$-Mg(BH$_4$_2)-LiH 1.00:1.89 (s4) before and after heat treatment at $T = 50$ °C (s12), 100 °C (s13), and 150 °C (s14) to gain insight into potential amorphous phases. The $^{11}$B MAS NMR spectrum obtained from $\gamma$-Mg(BH$_4$_2)-LiH 1.00:1.89 at RT (s4) (Figure 15) shows the characteristic MAS NMR spectrum of a quadrupole nuclei ($I = 3/2$ for $^{11}$B) influenced by a moderate quadrupole interaction [46], which is different to that observed for $\alpha$-Mg(BH$_4$_2) and $\beta$-Mg(BH$_4$_2) [47].

The $^{11}$B MAS NMR spectrum of $\gamma$-Mg(BH$_4$_2)-LiH (s4) contains four resonances at 22.8, 13.2, 0.4 and -41.1 ppm (Figure 15 and Table 2). The major site (~ 94%) $\delta_{iso}(^{11}$B) = -41 ppm is assigned to boron in...
BH$_4$ anion in $\gamma$-Mg(BH$_4$)$_2$ [32]. The centre band indicates only one boron site in contrast to the two non-equivalent boron sites found for both $\alpha$-Mg(BH$_4$)$_2$ and $\beta$-Mg(BH$_4$)$_2$ [47]. The three resonances at 22.8, 13.2, 0.4 ppm constitute < 6% of the intensity and originate from boron oxide impurities [48], as trigonal (BO$_3$) and tetrahedrally coordinated (BO$_4$) boron have isotropic chemical shift ranges of $\delta = 12 - 25$ and $\delta = -4 - 6$ ppm, respectively [49].

The $^{11}$B MAS NMR spectra $s_{12}$ and $s_{13}$ are comparable to that of $s_4$ except for a slight decrease in relative intensity of the boron oxides (Table 2). After heat treatment of $\gamma$-Mg(BH$_4$)$_2$-LiH 1.00:1.89 at 150 °C ($s_{14}$), one additional resonance with $\delta_{iso}$(11B) = -39.9 ppm is observed (Figure 16 and Table 2) and originates from $\beta'$-Mg(BH$_4$)$_2$ [32, 47]. Thus, $^{11}$B MAS NMR verifies that $\gamma$-Mg(BH$_4$)$_2$ converts to $\beta'$-Mg(BH$_4$)$_2$ at about 150 °C. This is also evident from the spinning side band pattern, as the pattern $s_{14}$ resembles the spinning side band pattern of $\beta'$-Mg(BH$_4$)$_2$ [47]. The $^{11}$B NMR do not show any evidence for other metal borohydride formation during the heat treatment here. Since no substitution reaction is observed during the heat treatment the decrease in reflection intensity of Mg(BH$_4$)$_2$ can not be explained by formation of another metal borohydride. As well as no evidence of amorphous boron being formed during the heat treatment as the ratio between Mg(BH$_4$)$_2$ and amorphous boron is constant.

Figure 15. $^{11}$B MAS NMR spectra of $\gamma$-Mg(BH$_4$)$_2$-LiH 1.00:1.89 at RT ($s_4$) and after heat treatment at 50, 100, and 150 °C. Spinning speed 15 kHz.
Figure 16. Zoom in of $^{11}$B MAS NMR spectra of $\gamma$-Mg(BH$_4$)$_2$-LiH 1.00:1.89 at RT (s4)1 at RT and after heat treatment to treatment to 150 °C. Spinning speed 15 kHz.

Table 2. $^{11}$B NMR isotropic chemical shifts and relative intensity for $\gamma$-Mg(BH$_4$)$_2$-LiH 1.00:1.89 at RT (s4) and after heat treatment to treatment to 50 (s12), 100 (s13) and 150 °C (s14).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Assignment</th>
<th>$\delta$ (ppm) ± 1 ppm</th>
<th>$I_{rel}$ (%) ± 1 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(s4) γ-Mg(BH$_4$)$_2$-LiH 1.00:1.89 at RT</td>
<td>Oxides</td>
<td>-41.1 ± 0.4</td>
<td>94 ± 1</td>
</tr>
<tr>
<td>(s12) γ-Mg(BH$_4$)$_2$-LiH 1.00:1.89 at 50 °C</td>
<td>Oxides</td>
<td>-40.5 ± 0.8</td>
<td>95.4 ± 0.8</td>
</tr>
<tr>
<td>(s13) γ-Mg(BH$_4$)$_2$-LiH 1.00:1.89 at 100 °C</td>
<td>Oxides</td>
<td>-40.9 ± 0.5</td>
<td>98.2 ± 0.4</td>
</tr>
<tr>
<td>(s14) γ-Mg(BH$_4$)$_2$-LiH 1.00:1.89 at 150 °C</td>
<td>Oxides</td>
<td>-41.2 ± 0.1</td>
<td>96.7 ± 0.8</td>
</tr>
</tbody>
</table>

$^a$Total intensity of $\gamma$-Mg(BH$_4$)$_2$ and $\beta$-Mg(BH$_4$)$_2$.

4 Conclusion

In this work, we have investigated the reactivity and thermal decomposition of the magnesium borohydride metal hydride composites, $\gamma$-Mg(BH$_4$)$_2$-$M$H$_x$, $M$ = Li, Na, Mg, Ca. It was found that heat
treatment of $\gamma$-Mg(BH$_4$)$_2$ composite with of LiH, NaH, or CaH$_2$ gave in-situ formation of the metal borohydrides, LiBH$_4$, NaBH$_4$, Ca(BH$_4$)$_2$. This observation is in agreement with the thermodynamic stability of the metal borohydrides, which can be correlated to the electronegativity of the metal ion [16]. Mg(BH$_4$)$_2$ being the least stable and NaBH$_4$ the most stable. However, the decomposition of the $\gamma$-Mg(BH$_4$)$_2$-MgH$_2$ composites was identical to the individual constituents $\gamma$-Mg(BH$_4$)$_2$ and MgH$_2$.

The composite $\gamma$-Mg(BH$_4$)$_2$-LiH showed hydrogen release at $T = 380$ to $420$ °C, which indicated formation of amorphous LiBH$_4$ during thermal decomposition. Crystalline NaBH$_4$ was observed by SR-PXD from $T = 150$ - $450$ °C in the composites of $\gamma$-Mg(BH$_4$)$_2$-NaH and hydrogen release at $T = 460$ - $480$ °C. $\beta$-Ca(BH$_4$)$_2$ formed at $T = 175$ - $375$ °C in the two composites of $\gamma$-Mg(BH$_4$)$_2$-CaH$_2$.

The $\gamma$-Mg(BH$_4$)$_2$-CaH$_2$ composites behave differently during thermal decomposition depending on composition. No diborane was detected in any of the composite samples. $^{11}$B and $^1$H ss NMR was employed to investigate the rapid decrease in intensity observed at $T < 100$ °C in SR-PXD of the Bragg diffraction. Further investigations are needed in order to elaborate further on this matter.

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6 References


Highlights (for review)

- $\gamma$-Mg(BH$_4$)$_2$-LiH a metathesis reaction produce amorphous LiBH$_4$, which release hydrogen at $T \sim 380 - 420 \, ^\circ C$.

- $\gamma$-Mg(BH$_4$)$_2$-NaH form crystalline NaBH$_4$ in the temperature range 150 - 450 °C and release hydrogen at $T > 460 \, ^\circ C$

- $\beta$-Ca(BH$_4$)$_2$ is formed in the temperature range 175 - 375 °C in the composites of $\gamma$-Mg(BH$_4$)$_2$-CaH$_2$

- Bragg diffraction from CaB$_6$ at $T > 370 \, ^\circ C$ $\gamma$-Mg(BH$_4$)$_2$-0.5CaH$_2$ but not for samples more rich in CaH$_2$