Synthesis and Hydrogen Storage Properties of a Single-Phase Magnesium Borohydride Mg(BH₄)₂

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A single phase Mg(BH₄)₂ was successfully synthesized and its hydrogen storage properties were systematically investigated. Depending on the synthesis conditions, Mg(BH₄)₂ forms low- and high-temperature phases with different crystal structures. The dehydriding reaction of Mg(BH₄)₂ starts at approximately 500 K, and 14.4 mass% of hydrogen is released through a multi-step reaction. Furthermore, 6.1 mass% of hydrogen can be rehydrided for the sample of Mg(BH₄)₂ after the dehydriding reaction, through the formation of a possible intermediate compound such as MgB₁₂H₂. [doi:10.2320/matertrans.MA200807]

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1. Introduction

Metal borohydrides M(BH₄)n with high hydrogen densities, have been attracting great interest as one of the potential candidates for advanced hydrogen storage materials.¹⁻³ For instance, LiBH₄ can release 13.8 mass% of hydrogen by decomposing into LiH and B, whereas its dehydriding temperature was reported to above 700 K, much higher than the practical demand.⁴⁻⁶) For this reason, extensive investigations on LiBH₄ have been carried out, such as structural analysis including intermediate compounds, reversible storage properties, microwave irradiation effects, and so on.⁴⁻²³)

Recently, we have systematically investigated the correlation between the thermodynamic stability of M(BH₄)n (M = Li, Na, K, Cu, Mg, Zn, Sc, Zr and Hf; n = 1–4) and the electronegativity of M.²⁴⁻²⁶) The results indicated that the dehydriding temperature of M(BH₄)n decreased with increasing the number of the electronegativity of M. That is, χP of M is concluded to be an important indicator for estimating the thermodynamical stability of M(BH₄)n.

Among the above-mentioned M(BH₄)n, Mg(BH₄)₂, which has a high hydrogen density (14.9 mass%, twice of common research targets) and a small enthalpy change of the supposed dehydriding reaction to Mg (41 kJ/mol H₂, theoretically estimated²⁷), possesses a fairly high potentiality for hydrogen storage materials. However, the synthesis process is still uncertain at present and the hydrogen storage properties have not been systematically studied yet.²⁸⁻³¹)

In this study, a single phase Mg(BH₄)₂ was chemically synthesized by means of the metathesis reaction of MgCl₂ with NaBH₄ in diethyl ether, and its hydrogen storage properties on dehydriding and rehydriding reactions were also investigated. These results provide valuable insights for hydrogen storage technologies.

2. Experimental

The starting materials, anhydrous MgCl₂ (95% purity) and NaBH₄ (99.99% purity), were purchased from Aldrich Co., Ltd. The organic solvent of diethyl ether (dehydrated, Cica-Reagent) was purchased from Kanto Chemical Co., Inc.

Mg(BH₄)₂ was synthesized by means of the metathesis reaction of MgCl₂ with NaBH₄ according to the following reaction.²⁸⁻³⁰

MgCl₂ + 2NaBH₄ → Mg(BH₄)₂ + 2NaCl (1)

The detailed synthesis procedure is shown as follows: a mixture of anhydrous MgCl₂ (0.70 g) and NaBH₄ (0.56 g) was premixed manually using an agate mortar and pestle, and then mechanically milled to promote the synthesis reaction (1), by planetary ball milling (Fritsch P-7) under 0.1 MPa Ar for 2 h. Subsequently, the sample was transferred into a glass flask, into which approximately 50 ml of diethyl ether was then introduced. After refluxing at the boiling point of diethyl ether for 60 h, the mixed solution was cooled down to room temperature and then filtered to remove the precipitate of NaCl. The filtrate was evacuated and then dried at 443 or 513 K; subsequently a white powder, Mg(BH₄)₂, was obtained.

The samples were examined by powder X-ray diffraction measurements (PAAnalytical XPERT with Cu-Kα radiation), Raman spectroscopy (Nicolet, Almega-HD), thermogravimetry (TG) and differential thermal analysis (DTA, Rigaku TG-8210, He flow of 150 ml/min and heating rate of 5 K/min) and quadrupole mass spectroscopy (QMS, Anelva M-QA200TS, directly connected with TG-DTA), and pressure-composition-temperature (PCT) measurements (Suzuki Shokan, PCT-4SDWIN). The dehydriding reactions of the Mg(BH₄)₂ sample after the dehydriding reaction were conducted by using a Sievelts apparatus at 543 K in hydrogen at 40 MPa for 48 h.

All the samples were always handled in a glove box filled with purified Ar/He gas (dew point below 183 K, oxygen
concentration lower than 1 ppm) in order to avoid (hydro-) oxidation.

3. Results and Discussion

3.1 Synthesis of a single phase Mg(BH\(_4\))\(_2\)

Figure 1 shows the powder X-ray diffraction profiles of the samples obtained from (a) precipitation, and filtrate followed by desolvation at (b) 443 K and (c) 513 K, respectively. That is, (a) NaCl, (b) \(\alpha\)-Mg(BH\(_4\))\(_2\) and (c) \(\beta\)-Mg(BH\(_4\))\(_2\). The profiles for the starting materials of (d) MgCl\(_2\) and (e) NaBH\(_4\) are also shown for references. The inset shows the differential thermal analysis curves of \(\alpha\)-Mg(BH\(_4\))\(_2\), which transforms into \(\beta\)-Mg(BH\(_4\))\(_2\) at approximately 460 K.

![Figure 1](image1.png)

![Figure 2](image2.png)

![Figure 3](image3.png)

3.2 Dehydriding properties of a single phase Mg(BH\(_4\))\(_2\)

As mentioned above, \(\alpha\)-Mg(BH\(_4\))\(_2\) transforms into \(\beta\)-Mg(BH\(_4\))\(_2\) at approximately 460 K, which is lower than the initial dehydriding temperature (Fig. 3). That is, hydrogen is released via the decomposition of \(\beta\)-Mg(BH\(_4\))\(_2\). Then the
The dehydriding properties of Mg(BH$_4$)$_2$ upon heating with He flow were measured by TG-DTA and the corresponding results are shown in Fig. 3. The dehydriding reaction starts at approximately 500 K and a weight loss of approximately 14.4 mass% is confirmed up to 800 K. Only hydrogen was detected from the thermal desorption measurement of Mg(BH$_4$)$_2$ by mass spectroscopy within our experimental accuracy.\(^{33}\)

Two sharp endothermic peaks with small shoulders are observed at 572 and 643 K, as shown in the DTA curve (Fig. 3). Correspondingly, at least three overlapped peaks are confirmed in the mass spectra of Mg(BH$_4$)$_2$ (not shown). Furthermore, the TG differentiation curve, which clearly expresses the change in the slope of the TG curve, indicates a four-step dehydriding reaction. These results strongly indicate a multi-step (more than two steps) dehydriding process, which suggests the presence of an intermediate compound, similar to that in the case of LiBH$_4$.\(^{14,15}\)

In order to clarify the dehydriding process of Mg(BH$_4$)$_2$, the sample was heated to above each peak in the TG differentiation curve (Fig. 3) and subsequently cooled at a rate of approximately 20 K/min down to room temperature. The X-ray diffraction profiles of the samples heated to the respective stages are shown in Fig. 4. Compared with the as-synthesized Mg(BH$_4$)$_2$, the diffraction peaks of the sample heated to 566 K become weak, and the sample shows a weight loss of 3.3 mass%. When the sample is heated to 593 K, the diffraction peaks disappear and are replaced by a broad maximum, which suggests the absence of long-range ordered atomic arrangements; the weight loss is observed to be 5.9 mass%. The MgH$_2$ phase and a broad maximum are confirmed in the X-ray diffraction profile for the sample heated to 638 K. The corresponding weight loss of 11.0 mass%, which is fairly consistent with the theoretical value (11.2 mass%) for the dehydriding reaction from Mg(BH$_4$)$_2$ to MgH$_2$, suggests that the broad maximum might result from the amorphous boron. The Mg phase is identified for the sample heated to 733 K and the final weight loss is 14.4 mass%. When the sample is heated to 870 K, the formation of MgB$_2$ is confirmed, as shown in Fig. 4. The presence of MgO may result from the reaction between the decomposed material and a background level of oxygen in the analysis chamber. Both the TG and the corresponding X-ray diffraction results consistently indicate the formation of some intermediate compounds at approximately 593 K during the dehydriding process from Mg(BH$_4$)$_2$ to MgH$_2$. Consequently, the dehydriding reaction of Mg(BH$_4$)$_2$ might proceed via some intermediate compounds according to the following multi-step reaction:\(^{33}\)

\[
\begin{align*}
\text{Mg(BH}_4\text{)}_2 & \rightarrow \text{some intermediate compounds} \\
& \rightarrow \text{MgH}_2 + 2\text{B} + 3\text{H}_2 \\
& \rightarrow \text{Mg} + 2\text{B} + 4\text{H}_2
\end{align*}
\]

### 3.3 Rehydriding properties of Mg(BH$_4$)$_2$ after dehydriding reaction

The rehydriding reaction of the dehydrided Mg(BH$_4$)$_2$ was conducted with a Sievelts apparatus at 543 K in hydrogen at 40 MPa for 48 h. In this study, the dehydrided Mg(BH$_4$)$_2$, which indicates the sample prepared by dehydriding of Mg(BH$_4$)$_2$ from 10 to 2 MPa at 573 K using the PCT apparatus, i.e. dehydriding of Mg(BH$_4$)$_2$ into a mixture of MgH$_2$ and amorphous boron, is called ‘the sample before the rehydriding reaction’.

No apparent changes but the diffraction peaks of MgH$_2$ are observed between the X-ray diffraction profiles (not shown) of the samples before and after the rehydriding reaction. However, the changes in the TG and QMS curves for the samples before and after the rehydriding reaction are clearly observed, as shown in Fig. 5. The weight loss of the samples before the rehydriding reaction is approximately

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![Fig. 4](image-url)  
**Fig. 4** Powder X-ray diffraction profiles for the samples of Mg(BH$_4$)$_2$ heated to 566, 593, 638, 733 and 870 K, respectively.

![Fig. 5](image-url)  
**Fig. 5** (a) Thermogravimetry curves and (b) mass spectra of the samples before and after the rehydriding reaction, which are shown in dotted and solid curves, respectively. The corresponding results for the sample after rehydriding reaction of the dehydrided Mg(BH$_4$)$_2$ to Mg, are also shown in blue dashed curves.
3.9 mass%, which is in good agreement with that (3.7 mass%) of the last step of the dehydriding reaction in eq. (2), i.e. from MgH$_2$ to Mg. On the other hand, the sample after the rehydriding reaction desorbed approximately 6.1 mass% of hydrogen up to 800 K. Furthermore, when compared with the mass spectrum for the sample before the rehydriding reaction, an additional peak at around 600 K is observed for the sample after the rehydriding reaction. Therefore, it should be emphasized that both the TG and QMS results consistently demonstrate the reversible hydrogen storage property of the dehydrided Mg(BH$_4$)$_2$ to Mg by dehydriding of Mg(BH$_4$)$_2$ under vacuum at 573 K, as shown in Fig. 5.

Correspondingly, the changes in the Raman spectra for the samples before and after the rehydriding reaction are also detected, as shown in Fig. 6. None of the vibrating modes of the B-H bonding is observed for the sample before the rehydriding reaction (Fig. 6(a)). However, it is worth noting that the B-H bending and stretching modes at approximately 500–1000 cm$^{-1}$ and 2200–2600 cm$^{-1}$, respectively, appear in the sample after the rehydriding reaction (Fig. 6(b)). This suggests the formation of a new Mg-B-H compound along with the progress of the rehydriding reaction. These observed B-H vibration modes are consistent with the theoretically calculated phonon density of state (PDOS) for [B$_{12}$H$_{12}$]$^{2-}$ (Fig. 6(c)). Therefore, a possible intermediate compound is considered to be MgB$_{12}$H$_{12}$, similar to the intermediate compound in the case of LiBH$_4$, i.e. Li$_2$B$_{12}$H$_{12}$. 

Judged from the above mentioned experimental results of Raman spectrometry, TG and QMS, MgB$_{12}$H$_{12}$ might be highly regarded as one of the intermediate compounds. In this case, the dehydriding process of Mg(BH$_4$)$_2$ might be expressed as follows:

\[
\text{Mg(BH}_4\text{)}_2 \rightarrow 1/6\text{MgB}_{12}\text{H}_{12} + 5/6\text{MgH}_2 + 13/6\text{H}_2 \quad (3a) \\
\leftrightarrow \text{MgH}_2 + 2\text{B} + 3\text{H}_2 \quad (3b) \\
\leftrightarrow \text{Mg} + 2\text{B} + 4\text{H}_2 \quad (3c)
\]

Accordingly, the desorbed hydrogen (theoretical) at each step of (3a), (3b) and (3c) should be 8.0, 3.1 and 3.7 mass%, respectively. In other words, the amount of hydrogen desorption from the intermediate compound MgB$_{12}$H$_{12}$ to Mg, i.e. in the dehydriding reactions of (3b) and (3c), is approximately 6.8 mass%, which shows considerable agreement with the reversible hydrogen content (6.1 mass%) examined by TG, as shown in Fig. 5(a). That is, not only reaction (3c) but also reaction (3b) is demonstrated to be reversible by the formation of intermediate compounds, such as MgB$_{12}$H$_{12}$.

The reason for the formation of MgB$_{12}$H$_{12}$, rather than Mg(BH$_4$)$_2$, after the rehydriding reaction at the present experimental condition (at 543 K in 40 MPa H$_2$) may be explained from the viewpoint of crystal (cluster) structure. Figure 7 indicates the schematic diagram of the clusters composed of B and/or H atom for B, [B$_{12}$H$_{12}$]$^{2-}$ and [BH$_4^-$], respectively. As mentioned above, the dehydriding products of Mg(BH$_4$)$_2$ at 573 K are MgH$_2$ and B, which are the starting materials for rehydriding reaction. During the rehydriding reaction, once MgH$_2$ reacts with B to form Mg(BH$_4$)$_2$, B-B bond in the icosahedral cluster of B should be broken and the B atoms should migrate to form [BH$_4^-$] spatially. However, the barrier for breaking of the B-B bonds and migration of the B atoms is probably too high to overcome under the present rehydriding condition. On the other hand, the formation of [B$_{12}$H$_{12}$]$^{2-}$ does not need break the B-B bonds and migrate B atoms to a long distance, because almost the same icosahedral cluster for B is clearly observed between B and MgB$_{12}$H$_{12}$, as shown in Fig. 7.

These results suggest that, intermediate compounds, which act as an “intermediate state” for dehydriding/rehydriding reactions, are very important for metal borohydrides, similar to the other complex hydrides such as NaAlH$_4$ and LiNH$_2$, in which dehydriding/rehydriding reactions occur at a relatively low temperature by the formation of intermediate compounds of NaAlH$_6$ and Li$_2$NH, respectively. Further investigations on the atomic and electronic structures of MgB$_{12}$H$_{12}$ and other intermediate compounds are being conducted at present, and they are expected to be helpful in improving the hydrogen storage properties of Mg(BH$_4$)$_2$. 

![Fig. 6 Raman spectra for the samples of (a) the dehydrided Mg(BH$_4$)$_2$ from 10 to 2 MPa at 573 K using the PCT apparatus, (b) after the rehydriding reaction at 543 K in hydrogen at 40 MPa for 48 h. The theoretically calculated phonon density of state (PDOS) for [B$_{12}$H$_{12}$]$^{2-}$ is shown in (c) for reference.](image)

![Fig. 7 Schematic diagram of the clusters composed of B and/or H atom for (a) B, (b) [B$_{12}$H$_{12}$]$^{2-}$ and (c) [BH$_4^-$], respectively.](image)
4. Conclusions

A single phase Mg(BH)\textsubscript{4}, which forms low- and high-temperature phases with different crystal structures, was successfully synthesized according to a metathesis reaction between MgCl\textsubscript{2} and NaBH\textsubscript{4} in diethyl ether. The low(\(\alpha\))-temperature phase transforms into the high(\(\beta\))-temperature one at approximately 460 K. The dehydriding reaction of Mg(BH)\textsubscript{4}\textsuperscript{2} initiates at approximately 500 K, and 14.4 mass\% of hydrogen is released through the following multi-step reaction, Mg(BH)\textsubscript{4} \→ some intermediate compounds \→ MgH\textsubscript{2} + 2B + 3H\textsubscript{2} \→ Mg + 2B + 4H\textsubscript{2}. Furthermore, 6.1 mass\% of hydrogen can be rehydrided at 543 K in 40 MPa H\textsubscript{2} for the sample of Mg(BH)\textsubscript{4}\textsuperscript{2} after the dehydriding reaction, through the formation of a possible intermediate compound such as MgB\textsubscript{12}H\textsubscript{12}.

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