Gas Emission Properties of the MgH$_x$-Zn(BH$_4$)$_2$ Systems

T. Nakagawa$^1$, T. Ichikawa$^2$, Y. Kojima$^2$ and H. Fujii$^2$

$^1$Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8530, Japan
$^2$Institute for Advanced Materials Research, Hiroshima University, Higashi-Hiroshima 739-8530, Japan

The gas emission properties of MgH$_x$-Zn(BH$_4$)$_2$ and Mg-Zn(BH$_4$)$_2$ systems have been investigated to design a new Metal-B-H system which has superior hydrogen storage properties. Thermal decomposition properties of two-layered samples with MgH$_2$ on Zn(BH$_4$)$_2$, Mg on Zn(BH$_4$)$_2$, the mixture of Mg and Zn(BH$_4$)$_2$, and the mixture of MgH$_2$ and Zn(BH$_4$)$_2$, were investigated by DTA-MS. The experimental results indicated that the B$_2$H$_6$ emission decreases in the case of the two-layered samples and the mixtures when compared with that of Zn(BH$_4$)$_2$, as a result of reaction of the solid MgH$_2$ or Mg with B$_2$H$_6$. Then, the reactions between Mg and Zn(BH$_4$)$_2$ as well as MgH$_2$ and Zn(BH$_4$)$_2$ were exothermic. In the case of the Mg-Zn(BH$_4$)$_2$ mixture, the reaction between Mg and Zn(BH$_4$)$_2$ surprisingly proceeded below 100°C before the decomposition of Zn(BH$_4$)$_2$ occurred. This indicates that the reaction between Mg and Zn(BH$_4$)$_2$, proceeds by a solid-solid reaction.

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1. Introduction

Zinc borohydride (Zn(BH$_4$)$_2$) is a very attractive hydrogen storage material because it has a large hydrogen capacity (8.4 mass%) and a low decomposition temperature (~85°C). In addition, Zn(BH$_4$)$_2$ can be synthesized easily by reacting ZnCl$_2$ with MBH$_4$ in a solvent or by milling them, which is expressed as follows:

\[
\text{ZnCl}_2 + 2\text{MBH}_4 \rightarrow \text{Zn(BH}_4)_2 + 2\text{MCI}
\]  

(1)

where M is Li or Na. However, Zn(BH$_4$)$_2$ desorbs hydrogen with diborane (B$_2$H$_6$) after melting with increasing temperature. This reaction can be described as follows:

\[
\text{Zn(BH}_4)_2 \rightarrow \text{Zn} + 2\text{B}_2\text{H}_6 + \text{H}_2
\]  

(2)

Unfortunately, the toxic B$_2$H$_6$ gas is desorbed from Zn(BH$_4$)$_2$. For designing useable H$_2$ storage, the promotion of H$_2$ desorption to decomposition of B$_2$H$_6$ is necessary, so we paid attention to the following reactions: (a) In the Li-N-H system, LiH reacts with ammonia (NH$_3$) generated by the decomposition of LiNH$_2$ and desorbs H$_2$; (b) In the Li-Mg-B-H system, LiH and MgB$_2$ are formed by the reaction between LiBH$_4$ and MgH$_2$ under suitable hydrogen pressure accompanied by H$_2$ desorption, and the rehydrogenation of MgH$_2$ and LiH can proceed more easily (0.5MPaH$_2$, 330°C) than that of LiH and B to LiBH$_4$ (35MPaH$_2$, 600°C). (c) There are some reports of reactions between metal hydride and diborane (B$_2$H$_6$) in the solvent, which is described by the following equation:

\[
\text{MH}_4-(\text{solvent}) + x/2\text{B}_2\text{H}_6 \rightarrow \text{M(BH}_4)_x-(\text{solvent})
\]  

(3)

where M is Li, Na, K, Mg, etc, and x is 1 ~ 4. However, direct gas-solid reactions between solid-state metal hydride and B$_2$H$_6$, as well as the reaction between metal and B$_2$H$_6$ have not been reported yet as far as we know. Thus, in the case of M = Mg without solvent, we expect that the resultant product due to reaction between the solid MgH$_2$ (x = 0, 2) and B$_2$H$_6$ could be MgB$_2$, where the reaction is described by the following equation:

\[
\text{MgH}_4 + 2\text{B}_2\text{H}_6 \rightarrow \text{MgB}_2 + (3 + x/2)\text{H}_2
\]  

(4)

Finally, the reaction between MgH$_2$ and Zn(BH$_4$)$_2$ proceeds according to the following reaction equation:

\[
\text{MgH}_4 + \text{Zn(BH}_4)_2 \rightarrow \text{Zn} + \text{MgB}_2 + (4 + x/2)\text{H}_2
\]  

(5)

Therefore, the purpose of this study is to improve the hydrogen storage properties of the M-B-H system on the analogy of the above three reactions so far reported (gas-solid reaction in Li-N-H system, good reversibility of MgB$_2$ generating reaction in Li-Mg-B-H system, and a reaction between metal hydride and B$_2$H$_6$). Especially, gas emission properties of the MgH$_x$-Zn(BH$_4$)$_2$ systems (x = 0 or 2) were investigated in details.

2. Experimental

The starting materials are MgH$_2$ powder (95 mass% purity, Gelas Inc.), Nb$_2$O$_5$ (99.5 mass% purity, mesoporous, 3.2 nm, Sigma-Aldrich), ZnCl$_2$ (99.995+ mass% purity, Sigma-Aldrich), NaBH$_4$ powder (98 mass% purity, Sigma-Aldrich). In this work, Zn(BH$_4$)$_2$ was synthesized by ball-milling a mixture of ZnCl$_2$ and NaBH$_4$ with a molar ratio of 1 : 2 for 2 h, whereas Nb$_2$O$_5$-doped MgH$_2$ was prepared by ball-milling the mixture of MgH$_2$ and 1 mol% Nb$_2$O$_5$ for 20 h at room temperature. Then, the MgH$_x$-Zn(BH$_4$)$_2$ composite samples were prepared by ball-milling the mixtures with 20 steel balls (7 mm in diameter) in a Cr-steel pot under 1.0 MPa hydrogen atmosphere, using a planetary ball mill (Fritsch, P7) at 400 rpm. The dehydrogenated state of MgH$_2$ with the Nb$_2$O$_5$ catalyst was realized by heating up to 200°C under vacuum condition for 8 h, which is the same procedure as a paper reported by Hanada, et al. In order to confirm the gas-solid reaction of MgH$_2$ (x = 0, 2) and B$_2$H$_6$, the decomposition processes of Zn(BH$_4$)$_2$ (with 2NaCl), two kinds of two-layered samples composed of Zn(BH$_4$)$_2$ and much larger amount of MgH$_2$ than Zn(BH$_4$)$_2$ (molar ratio of MgH$_2$ and Zn(BH$_4$)$_2$ is around 15 : 1) were investigated by the differential thermal analysis and thermal desorption mass spectrometry (DTA-MS, Anelva M-QA200TS) measurements.
The schematic diagrams of sample arrangement are shown in Fig. 1. Then, the gas emission and thermal analysis of the mixtures of MgH$_2$-Zn(BH$_4$)$_2$ (molar ratio of MgH$_2$ and Zn(BH$_4$)$_2$ is 1:1) prepared by hand with an agate mortar and pestle were also investigated by DTA-MS. All the gas emission properties and thermal analyses by DTA-MS were performed with a heating rate of 5°C/min to 150°C under a high-purity He gas (6 N) flow, realizing zero partial pressure of hydrogen. All the synthesized samples were identified by the X-ray diffraction (XRD) measurements (Rigaku RINT2000, Cu Kα) before and after the DTA-MS measurements of Zn(BH$_4$)$_2$ and the DTA-MS measurements of the MgH$_2$-Zn(BH$_4$)$_2$ mixtures. All the sample preparation and measurements were carried out in a glovebox filled with purified argon to minimize oxidation and water adsorption by the gas recycling purification system (MP-P60W, Miwa Mfg. Co., Ltd.).

3. Results and Discussion

Figures 2(a), (b) and (c) shows the thermal decomposition properties of Zn(BH$_4$)$_2$ and the two-layered sample of Nb$_2$O$_5$-doped MgH$_2$ ($x = 0$, 2) on Zn(BH$_4$)$_2$, respectively. In the case of Fig. 2(a), the Zn(BH$_4$)$_2$ (including 2NaCl) powder denoted in Fig. 1(a) emits H$_2$ and B$_2$H$_6$ from ~85°C and the peak temperatures of these gases are located around 125°C. From their profiles, we cannot quantitatively estimate the amount of H$_2$ or B$_2$H$_6$ because B$_2$H$_6$ has so many fragments. However, we can qualitatively evaluate the degree of diminution of B$_2$H$_6$ by estimating the peak area ratio of B$_2$H$_6$ to H$_2$. The ratio of B$_2$H$_6$/H$_2$ in the profile of gas emission of Zn(BH$_4$)$_2$ (Fig. 2(a)) is 17.2%. For the two-layered samples, in which the Nb$_2$O$_5$-doped MgH$_2$ or Mg powders were put directly on the Zn(BH$_4$)$_2$ powder in sample pans shown in respective Fig. 1(b), we notice that the B$_2$H$_6$ emission is significantly suppressed when compared with the gas emission from Zn(BH$_4$)$_2$ itself, where the B$_2$H$_6$/H$_2$ ratio of Fig. 2(b) and (c) are 5.4% and 2.1%, respectively. These results indicate that the MgH$_2$ samples react with B$_2$H$_6$ desorbed from Zn(BH$_4$)$_2$ by a gas-solid reaction, such as the experiment reported by Ichikawa et al. However, we could not confirm what products were generated after the gas-solid reaction, although we expect that these products are Mg(BH$_4$)$_2$ or MgB$_2$.

Figures 2(d) and (e) show the thermal decomposition properties of the mixtures of Nb$_2$O$_5$-doped MgH$_2$ ($x = 0$ or 2) and Zn(BH$_4$)$_2$. The B$_2$H$_6$ emission is also suppressed in both cases when compared with that of Zn(BH$_4$)$_2$ itself.
shown in Fig. 2(a), where the \( B_2H_6/H_2 \) ratios of Figs. 2(d) and (e) are 6.0% and 8.0%, respectively. These values are larger than their two-layered samples because the amounts of Mg and MgH\(_2\) in the mixtures of MgH\(_2\)–Zn(BH\(_4\))\(_2\) are much smaller than their two-layered samples. In addition, it is noteworthy that the shape of gas emission curve in Figs. 2(d) and (e) significantly changes when compared with those of Figs. 2(b) and (c), and the peak temperatures corresponding to the mixtures of MgH\(_2\)–Zn(BH\(_4\))\(_2\) decrease below 100°C, where the peak temperatures of MgH\(_2\)–Zn(BH\(_4\))\(_2\) and Mg–Zn(BH\(_4\))\(_2\) are 100 and 89°C, respectively. These reactions are exothermic as shown in Figs. 3(b) and (c), whereas the decomposition of Zn(BH\(_4\))\(_2\) is endothermic as shown in Fig. 3(a). This indicates that the absolute value of the enthalpy changes of the reactions between MgH\(_2\) and B\(_2\)H\(_6\) (exothermic) are larger than that of the decomposition of Zn(BH\(_4\))\(_2\) (endothermic). In the case of the mixture of Mg and Zn(BH\(_4\))\(_2\), hydrogen is desorbed before the decomposition of Zn(BH\(_4\))\(_2\) as shown in Fig. 3(c), indicating that Mg directly reacts with Zn(BH\(_4\))\(_2\) by a solid-solid reaction without mediating B\(_2\)H\(_6\).

Figure 4 shows the XRD profiles of (a) mixture of NaBH\(_4\) and ZnCl\(_2\) (B\(_2\)H\(_6\)) synthesized by ball-milling, (b) Zn(BH\(_4\))\(_2\) after heat treatment at 150°C, (c) MgH\(_2\)+Nb\(_2\)O\(_5\)+Zn(BH\(_4\))\(_2\) after heat treatment, (d) Mg\(_2\)+Nb\(_2\)O\(_5\)+Zn(BH\(_4\))\(_2\) after heat treatment, and (e) Mg+nb\(_2\)O\(_5\)+Zn(BH\(_4\))\(_2\) after heat treatment.

\[ \text{Fig. 4 XRD profiles of (a) mixture of NaBH}_4\text{ and ZnCl}_2\text{ (B}_2\text{H}_6\text{) synthesized by ball-milling, (b) Zn(BH}_4\text{)}\(_2\text{) after heat treatment at 150°C, (c) MgH}_2\text{+Nb}_2\text{O}_5\text{+Zn(BH}_4\text{)}\(_2\text{) after heat treatment, (d) Mg}_2\text{+Nb}_2\text{O}_5\text{+Zn(BH}_4\text{)}\(_2\text{) after heat treatment, and (e) Mg+nb}_2\text{O}_5\text{+Zn(BH}_4\text{)}\(_2\text{) after heat treatment.} \]

[![Fig. 4 XRD profiles](image)]

Figure 5 shows the infrared spectra of the mixtures of Nb\(_2\)O\(_5\)-doped MgH\(_2\)-Zn(BH\(_4\))\(_2\) after heat treatment. (a) MgH\(_2\)-Zn(BH\(_4\))\(_2\) before milling, (b) Zn(BH\(_4\))\(_2\) synthesized by ball-milling the mixture of ZnCl\(_2\) and NaBH\(_4\) before heat treatment, (c) after heat treatment, and (d) the mixtures of Nb\(_2\)O\(_5\)-doped MgH\(_2\) with Zn(BH\(_4\))\(_2\) after heat treatment, respectively. In Fig. 4(b), neither ZnCl\(_2\) nor NaBH\(_4\) peaks are observed, but NaCl and many other peaks are observed. In fact, we notice that the profile before milling in Fig. 4(a) is different from the profile after milling in Fig. 4(b). In addition, this profile is almost the same Zn(BH\(_4\))\(_2\) (NaCl) as synthesized by Jeon and Cho, indicating that the reaction (1) completely proceeds by milling. After heating the mixtures of MgH\(_2\)-Zn(BH\(_4\))\(_2\), the Zn and NaCl phases are also observed in XRD profiles in Figs. 4(d) and (e), but magnesium related compounds such as MgB\(_2\), Mg(BH\(_4\))\(_2\), Mg or MgH\(_2\) are not observed, and some unidentified peaks are observed. The Mg-related phases may be nano or amorphous structure which is too small to detect our X-ray equipment or these unidentified peaks are Mg-related phase. In addition, NaBH\(_4\) was observed in the infrared profile after heat treatment of the mixtures of MgH\(_2\)-Zn(BH\(_4\))\(_2\) (Fig. 5). This result indicates that NaCl is involved in this reaction process. Thus, NaCl probably prevent MgB\(_2\) or Mg(BH\(_4\))\(_2\) from generation. In order to clarify how reactions between Zn(BH\(_4\))\(_2\) and MgH\(_2\) proceed, it is necessary to remove NaCl in this system. Therefore, we were not able to identify what reaction proceeded. However, the product of the reaction...
between Mg and Zn(BH$_4$)$_2$ may be MgB$_2$ if this reaction mechanism is a B$_2$H$_6$-mediated reaction which is in the same analogy as in Li-N-H system. It needs more detailed investigation for this system.

4. Conclusion

In this work, we investigated the gas emission properties of the MgH$_2$-Zn(BH$_4$)$_2$ and Mg-Zn(BH$_4$)$_2$ systems. The results indicate that the solid MgH$_2$ or Mg reacts with B$_2$H$_6$ desorbed from Zn(BH$_4$)$_2$ and the desorption temperatures from the MgH$_2$-Zn(BH$_4$)$_2$ mixtures are lower (below 100°C) than that of Zn(BH$_4$)$_2$ itself, where these reactions are exothermic. In addition, the reaction between Mg and Zn(BH$_4$)$_2$ proceeds by a solid-solid reaction. However, these reactions have still not been characterized by XRD.

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