

Effects of TiO_2 and Nb_2O_5 on Hydrogen Desorption of $\text{Mg}(\text{BH}_4)_2$

Wipada Ploysuksai, Pramoch Rangsunvigit, Santi Kulprathipanja

Abstract—In this work, effects of catalysts (TiO_2 , and Nb_2O_5) were investigated on the hydrogen desorption of $\text{Mg}(\text{BH}_4)_2$. LiBH_4 and MgCl_2 with 2:1 molar ratio were mixed by using ball milling to prepare $\text{Mg}(\text{BH}_4)_2$. The desorption behaviors were measured by thermo-volumetric apparatus. The hydrogen desorption capacity of the mixed sample milled for 2 h was 4.78 wt% with a 2-step released. The first step occurred at 214 °C and the second step appeared at 374 °C. The addition of 16 wt% Nb_2O_5 decreased the desorption temperature in the second step about 66 °C and increased the hydrogen desorption capacity to 4.86 wt% hydrogen. The addition of TiO_2 also improved the desorption temperature in the second step and the hydrogen desorption capacity. It decreased the desorption temperature about 71°C and showed a high amount of hydrogen, 5.27 wt%, released from the mixed sample. The hydrogen absorption after desorption of $\text{Mg}(\text{BH}_4)_2$ was also studied under 9.5 MPa and 350 °C for 12 h.

Keywords— hydrogen storage, LiBH_4 , metal hydride, $\text{Mg}(\text{BH}_4)_2$

I. INTRODUCTION

THE acceleration of global climate change and the energy crisis caused by the wide use of fossil fuels have encouraged the development of hydrogen as a clean secondary energy source. Hydrogen, a renewable, high burning heat, energy source and low environmental pollution can be used as an alternative fuel for vehicles. One of the challenges in the development of the hydrogen economy is the storage of hydrogen with reliability and safety along with high density, low cost, and a fast releasing rate. As a target given by the U.S. Department of Energy (DOE), the storage criteria for vehicular applications are 6 wt% storage capacity at a temperature below 200°C with low cost and low toxicity [1].

Currently, four methods are available for hydrogen storage: high-pressure gas cylinders, liquid hydrogen in cryogenic tanks, absorption by metal hydride or adsorption on materials with a large surface area, and chemical hydrogen storage (including off-board regeneration). However, some storage methods cannot meet the requirement for hydrogen as a fuel

in car engines or aircraft turbines because of the low hydrogen uptake and ungovernable hydrogen desorption rate. For example, high pressure storage needs high strength containers and has a limited volume capacity including safety problems [2]. Therefore, chemical or physically combined storage of hydrogen in other materials has potential advantages over other storage methods because this process may provide high volumetric and gravimetric storage capacities. However, due to the strong interaction between the adsorbate and surface, reversibility can only be observed at high temperatures [3].

Hydrogen forms metal hydrides with some metals and alloys leading to solid-state storage under a moderate temperature and pressure that gives them the important safety advantage over the gas and liquid storage methods. Metal hydrides have higher hydrogen-storage density (6.5 H atoms/cm³ for MgH_2) than hydrogen gas (0.99 H atoms/cm³) or liquid hydrogen (4.2 H atoms/cm³). Hence, metal hydride storage is a safe, volume-efficient storage method for on-board vehicle applications. A group of Mg-based hydrides stands as a promising candidate for competitive hydrogen storage with reversible hydrogen capacity up to 7.6 wt% for on-board applications [4]. Furthermore, borohydrides have been considered interesting candidates for hydrogen storage applications due to their high gravimetric hydrogen content [5].

Among all possible complex hydride candidates, magnesium borohydride [$\text{Mg}(\text{BH}_4)_2$] seems to have the potential to satisfy the performance targets proposed by the U.S. Department of Energy because it contains not only high gravimetric (14.8 wt%) and volumetric (112 g/l) hydrogen densities, but also a low hydrogen binding enthalpy. Moreover, research results concerning the correlation between the thermodynamic stability of $\text{M}(\text{BH}_4)_n$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Ca}, \text{Mg}, \text{Zn}, \text{Sc}, \text{Zr}$ and Hf ; $n = 1-4$) and the electronegativity of M suggest that $\text{Mg}(\text{BH}_4)_2$ is one of the most attractive borohydrides for hydrogen storage owing to its favorable desorption hydrogen enthalpy. However, the high decomposition temperature of about 300 °C makes it unfavorable for practical fuel cell applications [6].

To enhance the hydrogen storage capacity, the kinetics and cycle life including decrease their desorption temperature, modified $\text{Mg}(\text{BH}_4)_2$ has been investigated. The kinetics has been improved by adding an appropriate catalyst into the system and by ball-milling that introduces defects with improved surface properties.

From the previous studies, attempts have been made to improve metal hydride properties including hydrogen-storage capacity, kinetics, cyclic behavior, toxicity, pressure and thermal response [4]. In this research, $\text{Mg}(\text{BH}_4)_2$ was

W. P. is with The Petroleum and Petrochemical College; and Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Soi Chula 12, Phayathai Road, Pathumwan, Bangkok 10330, Thailand (e-mail: airvipool@hotmail.com)

P. R. is with Petroleum and Petrochemical College; and Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok 10330, Thailand (Phone: +66-2-218-4139; fax: +66-2-218-4139; e-mail: pramoch.r@chula.ac.th)

S. K. is with UOP, A Honeywell Company, 50 East Algonquin Rd., Des Plaines, IL 60017, USA)

synthesized by a dry process. The hydride was then investigated for its hydrogen storage properties. Effects of catalyst, ball-milling, temperature, and pressure on the hydrogen storage capacity, were reported.

II. EXPERIMENTAL

A. Sample Preparation

For the mixture of LiBH_4 and MgCl_2 , the sample was prepared with a 2:1 molar ratio and mixed with and without a transition metal. A transition metal catalyst - Nb_2O_5 and TiO_2 - was included. The mixing was achieved by a ball-milling technique. For mixed samples, 16 wt% Nb_2O_5 or TiO_2 was added to the sample and milled for 2 and 5 h. The starting materials were used as-received. In the milling process, the sample was milled using a centrifugal ball mill (Retsch ball mill model S100, 250 ml stainless steel vial, stainless steel ball with 1 cm diameter) under nitrogen atmosphere with a ball to powder ratio of 60:1 and a rotation speed of 300 rpm. All material handlings (including weighing and loading) were performed in a glove box filled with nitrogen to keep a low water vapor concentration and avoid exposing the samples to air.

B. Experimental Set up

The thermo-volumetric apparatus was used to study the gas-solid interaction. The schematic diagram of the experimental set-up is shown in Fig. 1. The set-up consisted of a high pressure stainless reactor, which held the sample and part of stainless steel tube as a gas reservoir. The high pressure stainless steel reactor was heated from room temperature to 450°C for the LiBH_4 and MgCl_2 mixture with a heating rate of $2^\circ\text{C}/\text{min}$ via a furnace controlled by a PID temperature controller. Inside the reactor, a K-type thermocouple was placed to measure the temperature. The pressure regulator with 3,000 psig maximum limit was installed to control the gas flow rate into the whole system. The pressure transducer was used to measure pressure of the system for measuring in the range of 0-3,000 psig with 0.13% global error.

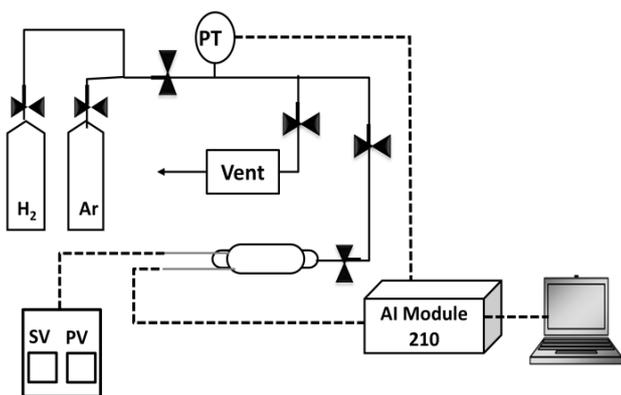


Fig. 1 Schematic diagram of the experimental set-up

C. Hydrogen Sorption Data Collection

The pressure transducers must be calibrated for each desorption experiment. Atmospheric pressure, 14.7 psi, was used as the reference pressure to set the zero span on the transducer to vacuum. The amount of sample used in each experiment was about 0.3 g. A sample was placed into the sample holder, and the sample holder volume was determined. The degassing procedure at about 10^{-3} torr and 25°C was conducted to remove the remaining gas for at least an hour. The sample holder was initially pressurized with helium gas at 30 psig. Hence, the valve between the manifold and the sample holder was closed. After that, hydrogen desorption was performed from 25°C to the set point (450°C for the LiBH_4 and MgCl_2 mixture) by a stepwise increase with a heating rate of $2^\circ\text{C}/\text{min}$. A sample was held at 450°C until no further hydrogen desorption was observed. While the above processes were continuing, the pressure values were recorded every 1 min until the pressure in the sample holder was rather constant. The released pressure was cooled down to room temperature to avoid the gas expansion by heat before evaluating the hydrogen capacity.

After completing hydrogen desorption, the sample was compressed under 9.5 MPa hydrogen (99.9999%) at a constant temperature of 350°C for 12 h for hydrogen adsorption. After that, both hydrogen desorption and absorption were repeated in order to investigate the reversibility.

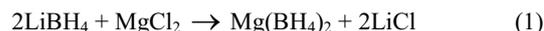
D. Characterization

In order to identify phase transformation during hydrogen desorption and absorption of the samples, X-ray diffraction (XRD, Rigaku) measurement was used at the room temperature over a range of diffraction angles from 20 to 70° with $\text{CuK}\text{-}\alpha$ radiation (40kV, 30 mA). The desorption temperature, phase transformation temperature, and temperature that reactions occurred were measured by differential scanning calorimetry (DSC 822, Mettler Toledo).

III. RESULTS AND DISCUSSION

A. Synthesis of $\text{Mg}(\text{BH}_4)_2$

To synthesize $\text{Mg}(\text{BH}_4)_2$, a mixture of LiBH_4 and MgCl_2 was prepared with a 2:1 molar ratio by ball-milling at 2 and 5 h. The XRD patterns in Fig. 2 provide the phase of the $\text{LiBH}_4/\text{MgCl}_2$ mixture milled for 2 and 5 h and LiBH_4 milled for 5 h. The XRD patterns of the $\text{LiBH}_4/\text{MgCl}_2$ mixture milled for 2 and 5 h (Fig. 2b and 2c) consists of LiMgCl_4 and LiCl peaks whereas the peaks corresponding to LiBH_4 (Fig. 2a) and MgCl_2 disappear. It can be deduced that the ball milling process induces LiBH_4 to react with MgCl_2 through the following reaction [7]-[8]:



Comparison between the XRD patterns of the $\text{LiBH}_4/\text{MgCl}_2$ mixture milled for 2 and 5 h shows that the intensity of the sample ball milled for 5 h (Fig. 2c) is lower than that ball milled for 2 h (Fig. 2b). That is believed to be contributed from the partial decomposition of the $\text{LiBH}_4/\text{MgCl}_2$ mixture to

LiCl and H₂ during the ball milling process. Therefore, the ball milling time of 2 h is expected to be adequate to synthesize Mg(BH₄)₂.

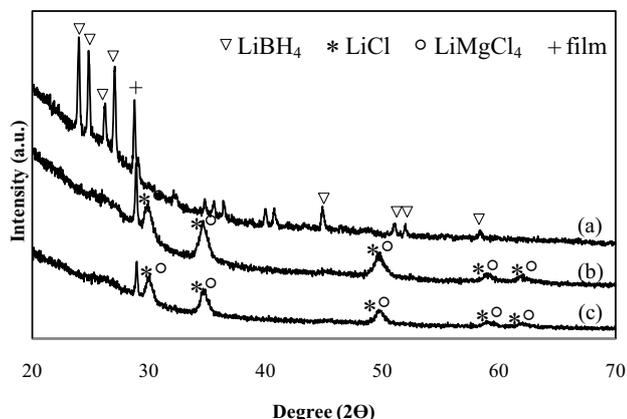
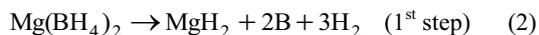


Fig. 2 X-ray diffraction patterns of LiBH₄ milled for 5 h (a), the LiBH₄/MgCl₂ mixture milled for 2 h (b) and 5 h (c)

The reason for the absence of a diffraction pattern of Mg(BH₄)₂ may be that the compound synthesized by the ball milling method is not crystallized sufficiently [9].

B. Hydrogen Desorption of Mg(BH₄)₂

The hydrogen desorption profiles of Mg(BH₄)₂ at different ball milling times are presented in Fig. 3. For the ball milling time of 2 h (Fig. 3a), Mg(BH₄)₂ starts to decompose at 30 °C. The first desorption step occurs at 214 °C and releases about 2.43 wt% hydrogen. The second step releases 2.10 wt% hydrogen and takes place at 374 °C, with a total amount of desorbed hydrogen about 4.78 wt% hydrogen. The results of Mg(BH₄)₂ ball milled for 5 h (Fig. 3b) show similar hydrogen desorption profile to that ball milled for 2 h. It starts to release at 61 °C, while the starts of the first and second desorption are at 226 °C and 374 °C with the accumulated hydrogen of 1.97 and 2.56 wt%, respectively, and a total amount of desorbed hydrogen about 4.76 wt% hydrogen. These results indicate that the hydrogen desorbs in the following two steps [7]-[8]:



Moreover, the results indicate that the mixing between LiBH₄ and MgCl₂ to synthesize MgBH₄ results in the decrease in the desorption temperature compared to LiBH₄ that show the desorption temperature at 380 °C (Fig. 3c). However, LiBH₄ shows a high hydrogen capacity about 6.55 wt% hydrogen.

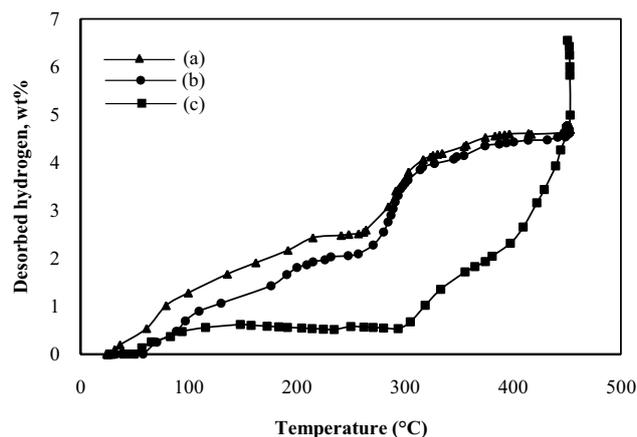


Fig. 3 Hydrogen desorption profiles of the LiBH₄/MgCl₂ mixture milled for 2 h (a) and 5 h (b) and LiBH₄ milled for 5 h (c)

The DSC profiles in Fig. 4 show the phase transformation temperature of the LiBH₄/MgCl₂ mixture milled for 2 and 5 h. The DSC profile of the LiBH₄/MgCl₂ mixture milled for 2 h (Fig. 4a) shows the first step of hydrogen desorption temperature at 212 °C and the second step at 377 °C. For the mixture ball milled for 5 h (Fig. 4b), the result shows hydrogen desorption temperature of the first and second steps at 244 and 380 °C, respectively.

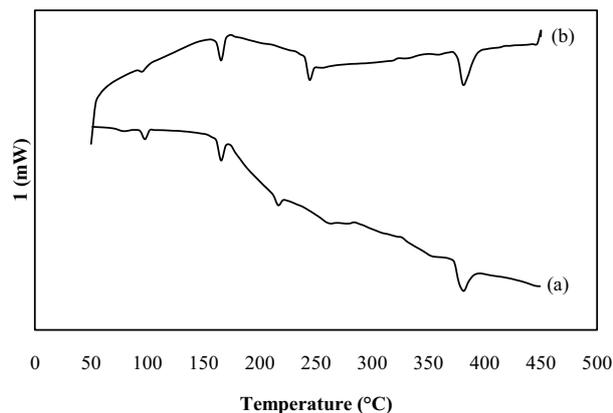


Fig. 4 Differential scanning calorimetry profiles of the LiBH₄/MgCl₂ mixture milled for 2 h (a) and 5 h (b)

The results from Fig. 3 and 4 exhibit that using different ball milling times results in similar hydrogen desorption behavior and desorption temperature. However, the LiBH₄/MgCl₂ mixture milled for 2 h shows a little higher hydrogen capacity than that milled for 5 h.

C. Hydrogen Desorption of Catalyzed Mg(BH₄)₂

It is well known that catalysts are an important factor that affects the desorption temperature of metal hydrides and complex metal hydrides [4]. This work further substantiates

the effects of a catalyst on the desorption behaviors of $\text{Mg}(\text{BH}_4)_2$.

The hydrogen desorption profiles of 16 wt% Nb_2O_5 - $\text{Mg}(\text{BH}_4)_2$ with 2 and 5 h ball milling times are presented in Fig. 5. The samples release hydrogen in two steps as the uncatalyzed sample. For 16 wt% Nb_2O_5 - $\text{Mg}(\text{BH}_4)_2$ ball milled for 2 h (Fig. 5a), it starts to decompose at 31 °C. The first step desorption releases 3.20 wt% hydrogen and takes place at 236 °C, while the start of the second desorption is at 308 °C with 1.40 wt% hydrogen and the total amount of desorbed hydrogen about 4.86 wt%. 16 wt% Nb_2O_5 - $\text{Mg}(\text{BH}_4)_2$ ball milled for 5 h (Fig. 5b) shows the first desorption step at 241 °C and releases 2.79 wt% hydrogen, whereas the second step occurs at 307 °C with 1.49 wt% hydrogen and the total desorbed hydrogen of 4.73 wt%. The results suggest that Nb_2O_5 improves the desorption behaviors of $\text{Mg}(\text{BH}_4)_2$, which is to decrease the desorption temperature at the second step from 374 °C (uncatalyzed) to 308 °C and 307 °C for 16 wt% Nb_2O_5 - $\text{Mg}(\text{BH}_4)_2$ ball milled for 2 and 5 h, respectively. The result also supports that the ball milling time of 2 h is sufficient to prepare $\text{Mg}(\text{BH}_4)_2$ with the percent of Nb_2O_5 . Therefore, the addition of Nb_2O_5 contributes to fast hydrogen desorption with a significant decrease of desorption temperature about 65 °C, which is in agreement with that reported by Friedrichs *et al.*, (2006) [10].

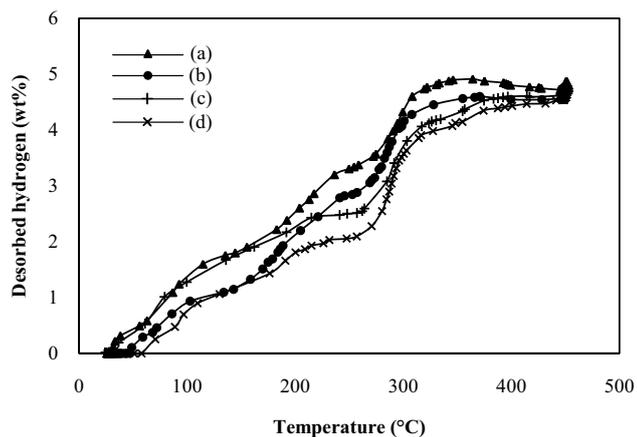


Fig. 5 Hydrogen desorption profiles of 16wt% Nb_2O_5 - $\text{Mg}(\text{BH}_4)_2$ milled for 2 h (a) and 5 h (b) and hydrogen desorption profiles of the $\text{LiBH}_4/\text{MgCl}_2$ mixture milled for 2 h (c) and 5 h (d)

TiO_2 is one of the titanium catalysts that can improve the performance of metal hydride, and Fig. 6 shows the hydrogen desorption profiles of 16 wt% TiO_2 - $\text{Mg}(\text{BH}_4)_2$ with 2 and 5 h ball milling times. Hydrogen desorbs in two steps same as the uncatalyzed sample. 16 wt% TiO_2 - $\text{Mg}(\text{BH}_4)_2$ ball milled for 2 h (Fig. 6a) starts to decompose at 41 °C, and the first desorption step occurs at 246 °C and releases about 3.25 wt% hydrogen. The second step releases 1.74 wt% hydrogen at 303 °C with the total hydrogen of 5.27 wt%. 16 wt% TiO_2 - $\text{Mg}(\text{BH}_4)_2$ ball milled for 5 h (Fig. 6b) shows similar hydrogen desorption profile to the one ball milled for 2 h. It starts to desorb at 41°C and the first desorption step appears at 249 °C with 3.10 wt% hydrogen. The second step releases 1.75 wt%

hydrogen at 307 °C and provides the total hydrogen capacity of 5.03 wt%. The results indicate that TiO_2 improves the desorption behaviors of $\text{Mg}(\text{BH}_4)_2$, which is to decrease the desorption temperature at the second step about 71 °C and 67 °C for the samples ball milled for 2 h and 5 h, respectively.

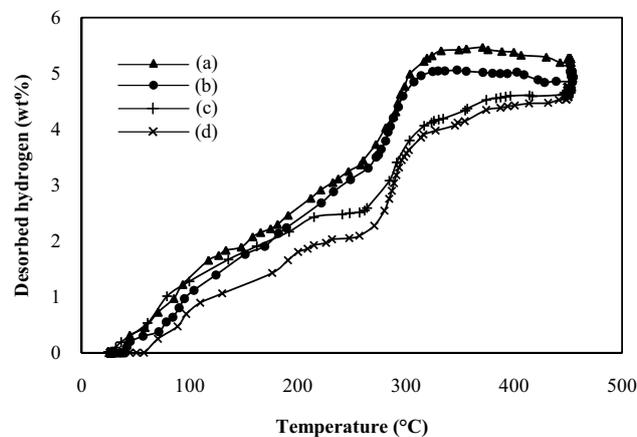


Fig. 6 Hydrogen desorption profiles of 16wt% TiO_2 - $\text{Mg}(\text{BH}_4)_2$ milled for 2 h (a) and 5 h (b) and hydrogen desorption profiles of the $\text{LiBH}_4/\text{MgCl}_2$ mixture milled for 2 h (c) and 5 h (d)

From the amount of desorbed hydrogen, it was found that the sample with 16 wt% TiO_2 releases higher amount of hydrogen than the undoped and 16 wt% Nb_2O_5 doped samples and also decreases the hydrogen desorption temperature of the hydride in the second step decomposition.

IV. CONCLUSIONS

In this research, the method to prepare $\text{Mg}(\text{BH}_4)_2$, the desorption behaviors and desorption temperature of $\text{Mg}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2$ doping with catalysts (Nb_2O_5 and TiO_2) were investigated. Ball-milling technique for 2 h is adequate for the synthesis of $\text{Mg}(\text{BH}_4)_2$ by mixing LiBH_4 with MgCl_2 at 2:1 molar ratio. The hydrogen desorption profiles of the $\text{Mg}(\text{BH}_4)_2$ showed two steps of hydrogen released. The first desorption step occurs at 214 °C and releases about 2.43 wt% hydrogen. The second step releases 2.10 wt% hydrogen and takes place at 374 °C, with a total amount of desorbed hydrogen about 4.78 wt% hydrogen. $\text{Mg}(\text{BH}_4)_2$ doped with Nb_2O_5 , 16wt%, showed a good desorption behaviors that is the second desorption temperature is decreased by 66 °C as compared with the uncatalyzed sample. Furthermore, doping with 16 wt% TiO_2 , not only exhibits the best desorption behaviors, but also shows the good hydrogen desorption capacity, 5.23 wt% hydrogen, and the second desorption temperature is decreased by 71 °C when compared with the undoped sample. However, the absorption of dehydrogenated samples mixed with the catalysts cannot re-absorb hydrogen under H_2 pressure 9.5 MPa at 350 °C.

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