

CHAPTER IV

CATALYZED LiBH_4 AND MgH_2 MIXTURE FOR HYDROGEN STORAGE

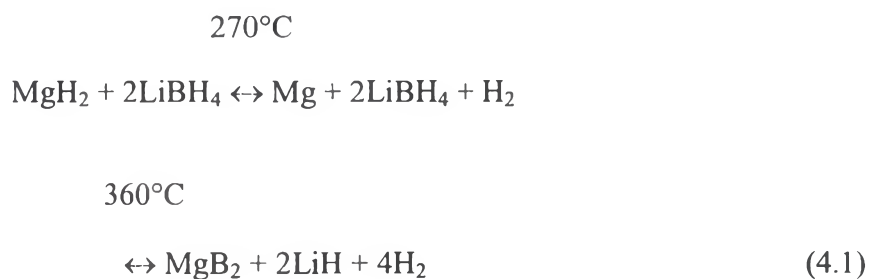
4.1 Abstract

The hydrogen desorption/absorption of the 2:1 mole ratio LiBH_4 and MgH_2 with and without a catalyst was investigated. In the case of the uncatalyzed $\text{LiBH}_4/\text{MgH}_2$ mixture, the first hydrogen desorption started at 50°C . The amount of released hydrogen was 8.6 wt% at the first hydrogen desorption and dramatically reduced to 1.8 wt% at the tenth hydrogen desorption. The decrease in the hydrogen capacity in the subsequent hydrogen desorption may be due to the irreversibility of LiBH_4 . To investigate, effects of a catalyst on the hydrogen desorption, 3 mol% of TiCl_3 , HfCl_4 , ZrCl_4 , or VCl_3 was added to the $\text{LiBH}_4/\text{MgH}_2$ mixture. The lowest hydrogen desorption temperature, 260°C , was from the sample with TiCl_3 . An amount of the catalyst also influenced the kinetics of the hydride mixture and 5 mol% seems to be an optimum amount of TiCl_3 that resulted in the lowest hydrogen desorption temperature, 240°C . In addition, the higher the amount of catalyst, the lower the amount of the released hydrogen.

4.2 Introduction

Hydrogen is considered as clean fuel for transportation applications with fuel cells as an important part to turn hydrogen to energy. To realize that, a high performance hydrogen storage system is needed in order to achieve the DOE's targets [1]. Solid-state hydrides have been widely investigated because of their high hydrogen capacity compared to its weight, safety, and reversibility property [1-2]. Unfortunately, high thermodynamic stability, low equilibrium hydrogen pressure, slow kinetics, and limited reversibility are still major hurdles [3]. These weaknesses have been overcome by adding catalysts [4-7], reacting with other metal hydrides [8-12] or reducing their particle sizes [13-18].

Theoretically, LiBH_4 has high hydrogen capacity with up to 13.5 wt% hydrogen. However, it starts to desorb hydrogen at a temperature higher than 400°C and its reversibility is still an issue. Züttle et al. [19] destabilized LiBH_4 by adding 75 wt% SiO_2 . The result shows that the hydrogen desorption started at approximately 200°C but there was still a problem with the limited reversibility even at 650°C and 150 bar hydrogen pressure. Vajo et al. [20] successfully recovered LiBH_4 by reacting MgB_2 with LiH and 3 mol% TiCl_3 to form LiBH_4 and MgH_2 . They found that the reaction enthalpy was reduced by $25 \text{ kJ (mol of hydrogen)}^{-1}$ compared to LiBH_4 and 8-10 wt% hydrogen was obtained after two cycles of hydrogen desorption. The hydrogen desorption is observed in two steps as shown in Eq. (4.1).



The hydrogen absorption under 100 bar hydrogen (Eq. (4.2)) takes place with only one step.



Bösenberg et al. [21] confirmed the two-step hydrogen desorption of the $\text{LiBH}_4/\text{MgH}_2$ mixture doped with 5 at% titanium isopropoxide. The decomposition was similar to Eq. (4.1) but hydrogen desorption temperatures were different, at 390°C and $> 400^\circ\text{C}$ for the first and second step, respectively. By focusing on the reversibility, Pinkerton et al. [22] found that the $\text{LiBH}_4/\text{MgH}_2$ mixture could be fully reversible if overpressure of hydrogen was applied during the dehydrogenation.

In this work, we report hydrogen desorption behavior of the $\text{LiBH}_4/\text{MgH}_2$ mixture milled for 1 h from its first hydrogen desorption to the tenth desorption. For

the catalyzed $\text{LiBH}_4/\text{MgH}_2$ mixture, both type and amount of a catalyst was investigated for their effects on the hydrogen desorption behavior. Information from the XRD was used to understand the hydrogen desorption/absorption and reversibility of the mixtures.

4.3 Experimental

LiBH_4 (95%) and MgH_2 (90%) were purchased from Sigma-Aldrich. All handling procedures in this work were performed in a glove-box filled with purified nitrogen in order to minimize the sample contamination. A hydride mixture was prepared by mixing the as-received LiBH_4 and MgH_2 together in the mole ratio of 2:1. Then, the mixture was mechanically ball-milled in a stainless steel vial with the ball-to-powder weight ratio of 40:1 by using a Retsch ball mill (Model S100) at the speed of 300 rpm under nitrogen atmosphere for 1 h. After the sample preparation, 0.3 g of the $\text{LiBH}_4/\text{MgH}_2$ mixture was transferred into the Sievert's type reactor. The hydrogen desorption was carried out from room temperature to 450°C with the heating rate of 2°C min^{-1} and held at 450°C for 6 h. After the hydrogen desorption, the sample was compressed under 10 MPa hydrogen (99.9999%) and 350°C for 12 h. The same procedure was repeated to investigate the reversibility. The pressure change was measured and used to calculate the gravimetric capacity of hydrogen stored in the sample. 3 mol% of TiCl_3 , HfCl_4 , ZrCl_4 , or VCl_3 was added into the $\text{LiBH}_4/\text{MgH}_2$ mixture to investigate their catalytic effects. The catalytic mixtures were examined for the starting hydrogen desorption temperature by the TPDRO 1100 (ThermoFinnigan) directly connected to an MS. The sample temperature was ramped from 50 to 500°C with the heating rate of 5°C min^{-1} . The kinetics investigation as well as the hydrogen desorption capacity were performed by using the Sievert's type apparatus with the same condition as that of the $\text{LiBH}_4/\text{MgH}_2$ mixture.

For the characterization, a Rigaku X-ray diffractometer with $\text{CuK}\alpha$ radiation operated at 40 kV and 30 mA at room temperature over the range of

diffraction angles from 20° to 80° was used to identify phase transformations and crystal structures at various conditions.

4.4 Results and Discussion

4.4.1 Hydrogen Desorption/absorption of the LiBH₄/MgH₂ Mixture

The hydrogen desorption profiles of the LiBH₄/MgH₂ mixture are presented in Fig. 4.1. For the first cycle of hydrogen desorption, the mixture releases hydrogen in three steps. The first step (Fig. 4.1(a)) occurs in the temperature range of 50-380°C with 3.0 wt% hydrogen while the starts of the second and third desorption are at 380 and 450°C with the accumulated released hydrogen of 5.4 and 8.6 wt%, respectively. The results show that the mixing between LiBH₄ and MgH₂ could decrease the onset desorption temperature as compared to that of either LiBH₄ (420°C) or MgH₂ (380°C). Figs. 4.1(b) and (c) show the hydrogen desorption in the subsequent desorption. Interestingly, there are only two steps of hydrogen desorption. The first and second ones now take place at 360 and 450°C, respectively. The total amount of released hydrogen at the second hydrogen desorption is lowered to 5.4 wt%. The hydrogen desorption behavior of other hydrogen desorption resembles that of the second cycle. And the total amount of released hydrogen is reduced to 1.8 wt% at the tenth desorption. This lower amount of hydrogen in the subsequent desorption also corresponds with the report from Pinkerton et al. [22]. It should be pointed out that the hydrogen desorption profile of the first desorption (Fig. 4.1 (a)) is different from that of the subsequent desorption (Figs. 4.1(b) and (c)), especially, the first step of the first desorption, or *shoulder*, which is accounted for approximately 3.0 wt% hydrogen. It may be possible that different reactions are involved during the first and subsequent hydrogen desorption. To examine this hypothesis, the XRD patterns of mixtures obtained at different conditions are examined.

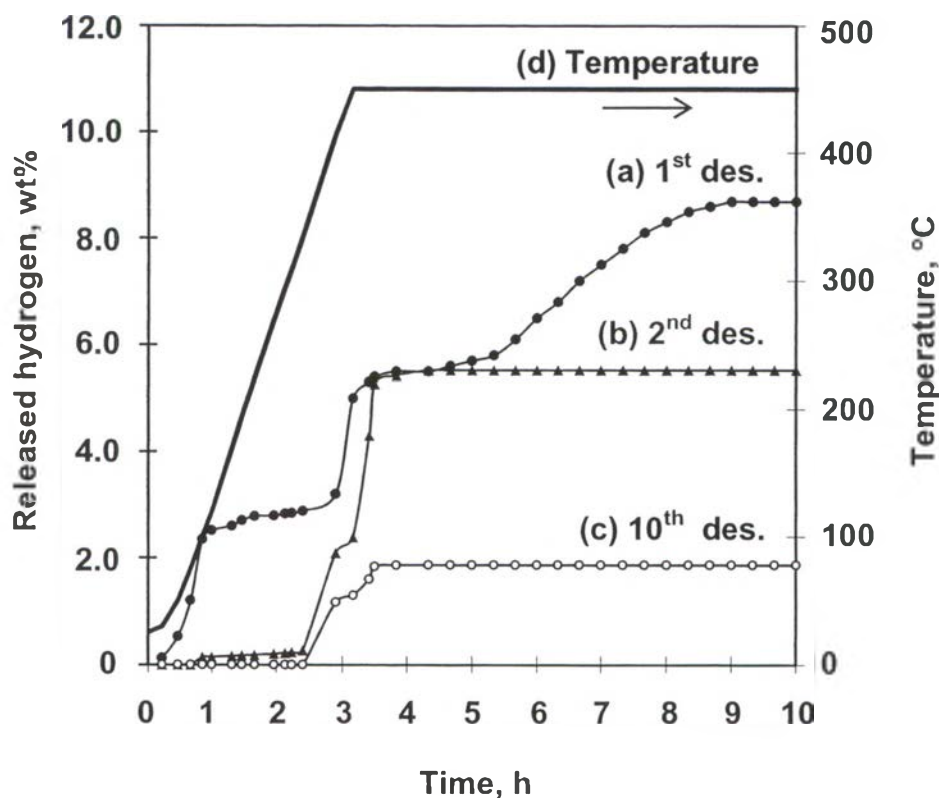
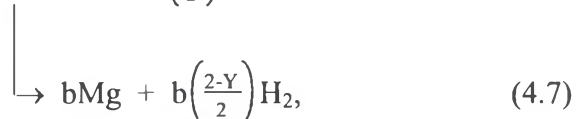
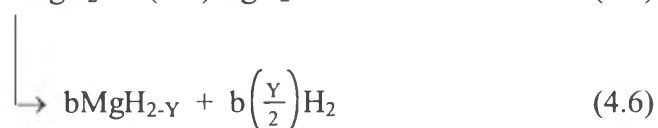
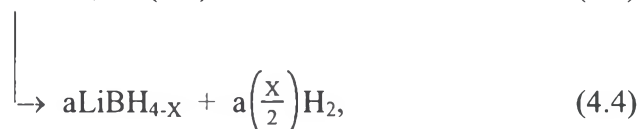


Figure 4.1 Hydrogen desorption profiles of the $\text{LiBH}_4/\text{MgH}_2$ mixture milled for 1 h: (a) the first hydrogen desorption, and the subsequent hydrogen desorptions (b) the second hydrogen desorption, (c) the tenth hydrogen desorption, and (d) hydrogen desorption temperature.

The X-ray diffraction patterns in Fig. 4.2 provide the phase transition of the $\text{LiBH}_4/\text{MgH}_2$ mixture milled for 1 h after the first hydrogen desorption at different final desorption temperatures. For the hydrogen desorption in the first step or the *shoulder*, at the temperature range of 100-300°C, no reaction between LiBH_4 and MgH_2 can be observed as only LiBH_4 , MgH_2 , and oxide compounds, which might be from the milling process, are present. It is worth mentioning that the hydrogen released in the first step may be induced from the milling process. The peak intensity of LiBH_4 is very low compared to that of MgH_2 despite the fact that there is more LiBH_4 in the mixture. Possible reasons could be from the interaction between LiBH_4 and MgH_2 , the transformation of LiBH_4 to an amorphous state after melting [13], and the formation of the LiBH_4 nanoscale particle size after the milling

process [16-17]. The proposed reactions are the partial hydrogen desorption of LiBH_4 and/or MgH_2 phases to LiBH_{4-x} and/or MgH_{2-y} phases, respectively, after the milling. When the temperature is increased to 350°C , MgH_2 and MgH_{2-y} are decomposed to Mg. At the same time, Mg reacts with a trace amount of air either from the milling process or sample preparation step to form MgO. The MgO phase is a possible reason for the decrease in the hydrogen capacity [7]. For the temperature higher than 400°C , both $\text{LiBH}_4/\text{LiBH}_{4-x}$ and $\text{MgH}_2/\text{MgH}_{2-y}$ are transformed to LiH and Mg, respectively. Simultaneously, $\text{LiBH}_4/\text{LiBH}_{4-x}$ reacts with $\text{MgH}_2/\text{MgH}_{2-y}/\text{Mg}$ to form the new phase of MgB_2 , which is suggested to be the key to the reversibility of the $\text{LiBH}_4/\text{MgH}_2$ mixture [21]. The combination between MgB_2 and LiH, in order to form MgH_2 and LiBH_4 , can also be improved if the hydrogen desorption is preformed with over pressure of hydrogen gas [21-22]. In addition, stability of the $\text{LiBH}_4/\text{MgH}_2$ mixture can be reduced because of the MgB_2 formation. The reaction between MgB_2 and LiH is also more favorable than B with LiH [23]. The remaining LiBH_4 and MgH_2 are also revealed indicating that the hydrogen desorption is not complete. That may possibly be due to the very slow hydrogen desorption kinetics of the mixture. These result in the lower total hydrogen desorption capacity from the theoretical value of 11.4 wt% to 8.6 wt%. Eqs. (4.3)-(4.11) summarize the overall reactions during the decomposition of the $\text{LiBH}_4/\text{MgH}_2$ mixture.

At temperature lower than 350°C :



where a, b are the amount of decomposed metal hydride in mole, $a, b \leq 1$; and x, y are the amount of decomposed hydrogen in mole, $x \leq 4, y \leq 2$.

At temperature higher than 400°C :

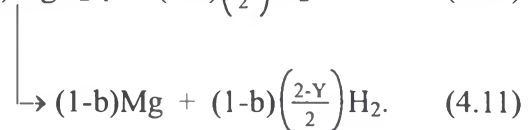
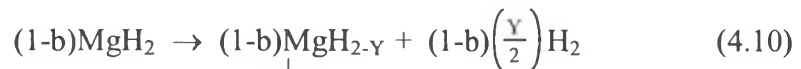
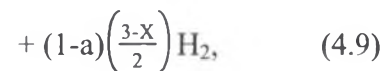
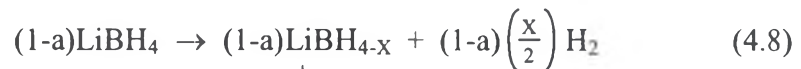


Fig. 4.3 shows the X-ray diffraction patterns of the $\text{LiBH}_4/\text{MgH}_2$ mixture milled for 1 h before and after the hydrogen desorption/absorption. After the milling process (Fig. 3(a)), no new phase is detected other than the oxide compounds. It reveals that no reaction between the two metal hydrides during the ball milling process. Fig. 3(b) confirms that the reversible reaction of the desorbed $\text{LiBH}_4/\text{MgH}_2$ mixture is possible to a certain extent. Fig. 3(c) further substantiates that after the hydrogen absorption both LiBH_4 and MgH_2 are recovered even after the tenth hydrogen desorption although the quantity of LiBH_4 is lower than MgH_2 . However, there are unconverted phases of MgO and MgB_2 indicating that only Mg combines with LiH to form MgH_2 and Li-compounds. It is not MgB_2 that reacts with LiH to form MgH_2 and LiBH_4 . The result is consistent with the previous study [22]. So it implies that only MgH_2 is reversible. This is the explanation why hydrogen capacity of the $\text{LiBH}_4/\text{MgH}_2$ mixture gradually decreases from 8.6 wt% at the first hydrogen desorption to 1.8 wt% at the tenth hydrogen desorption.

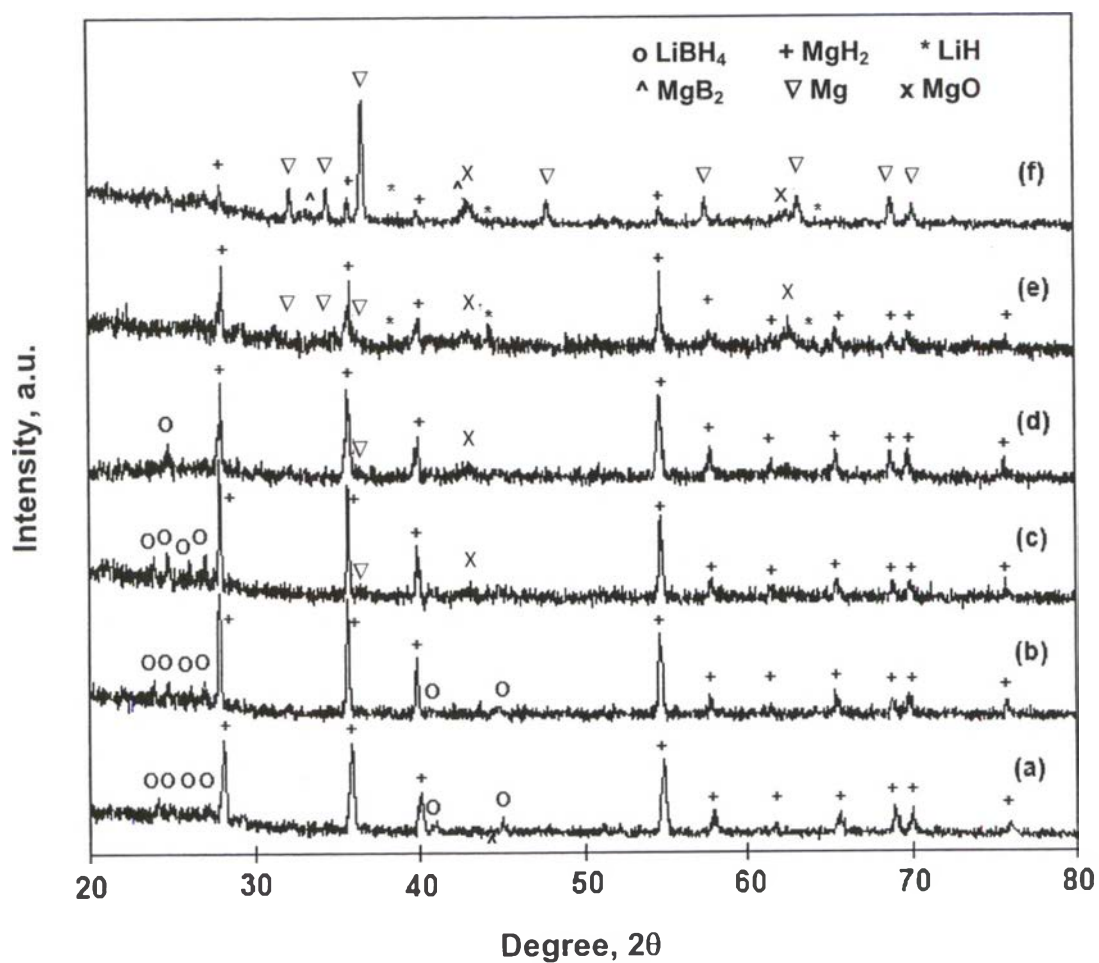


Figure 4.2 X-ray diffraction patterns of the $\text{LiBH}_4/\text{MgH}_2$ mixture milled for 1 h after the first hydrogen desorption at: (a) 100°C, (b) 200°C, (c) 300°C, (d) 350°C, (e) 400°C, and (f) 450°C.

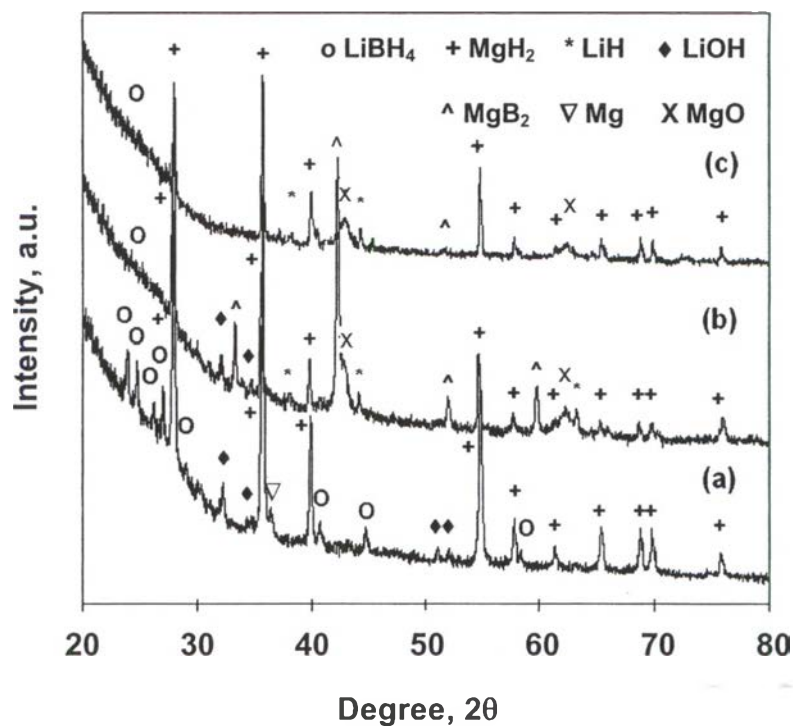


Figure 4.3 X-ray diffraction patterns of the $\text{LiBH}_4/\text{MgH}_2$ mixture: (a) after milling for 1 h, (b) after the first hydrogen absorption, and (c) after the tenth hydrogen absorption.

From Fig. 4.1, there is a difference in the hydrogen desorption profiles between the first and subsequent hydrogen desorption. So to shed some light on this issue, the phase transition of the $\text{LiBH}_4/\text{MgH}_2$ mixture milled for 1 h after the second hydrogen desorption at various temperatures was investigated and the result is reported in Fig. 4.4. It clearly confirms that the phases at the second hydrogen desorption are similar to that of the first one. The observed phases of LiH, MgO and MgB_2 at 350°C as well as 450°C are resulted from the incomplete first hydrogen absorption. It is not from the reaction between $\text{LiBH}_4/\text{LiBH}_{4-x}$ and $\text{MgH}_2/\text{MgH}_{2-y}$.

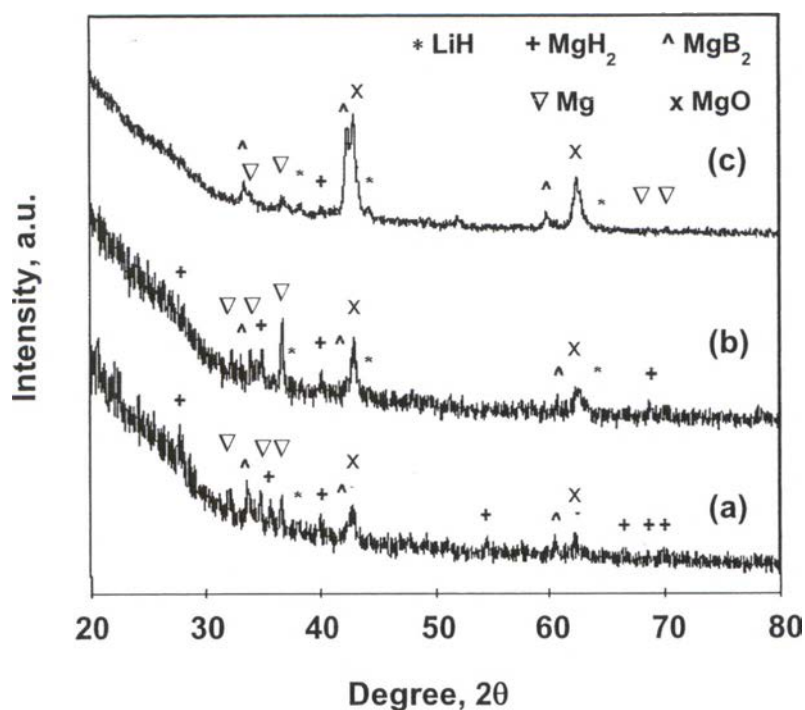


Figure 4.4 X-ray diffraction patterns of the $\text{LiBH}_4/\text{MgH}_2$ mixture milled for 1 h after the second cycle of hydrogen desorption at: (a) 350°C , (b) 400°C , and (c) 450°C .

4.4.2 Hydrogen Desorption/absorption of the Catalyzed $\text{LiBH}_4/\text{MgH}_2$ Mixture

TPDRO/MS profiles of the $\text{LiBH}_4/\text{MgH}_2$ mixture both uncatalyzed and catalyzed with 3 mol% TiCl_3 , HfCl_4 , ZrCl_4 , or VCl_3 are shown in Fig. 4.5. All samples release hydrogen in two steps at different temperatures. Corresponding with the hydrogen desorption of the $\text{LiBH}_4/\text{MgH}_2$ mixture, the first step is attributed to the decomposition of mainly MgH_2 followed by the reaction between metal hydrides to form the final products of LiH , MgB_2 , and Mg . Generally, hydrogen intensity in all catalyzed samples seems to be higher than that of the uncatalyzed one. With the presence of VCl_3 in the $\text{LiBH}_4/\text{MgH}_2$ mixture, its TPDRO/MS profile is slightly different from that of the mixture without VCl_3 . Only a slight shift in the first and second desorption can be observed. The lowest hydrogen desorption temperature can be obtained from the $\text{TiCl}_3\text{-LiBH}_4/\text{MgH}_2$ and $\text{HfCl}_4\text{-LiBH}_4/\text{MgH}_2$ mixtures. The

starting hydrogen desorption temperatures of the two mixtures are the same at about 260°C, which is shifted by at least 90°C relative to that of the $\text{LiBH}_4/\text{MgH}_2$ mixture, at 350°C (Fig. 4.5(e)). In term of hydrogen intensity, the $\text{TiCl}_3\text{-LiBH}_4/\text{MgH}_2$ mixture provides higher intensity than the $\text{HfCl}_4\text{-LiBH}_4/\text{MgH}_2$ mixture, especially, in the second step. So the $\text{TiCl}_3\text{-LiBH}_4/\text{MgH}_2$ mixture is further used to investigate the effects of the catalyst amount.

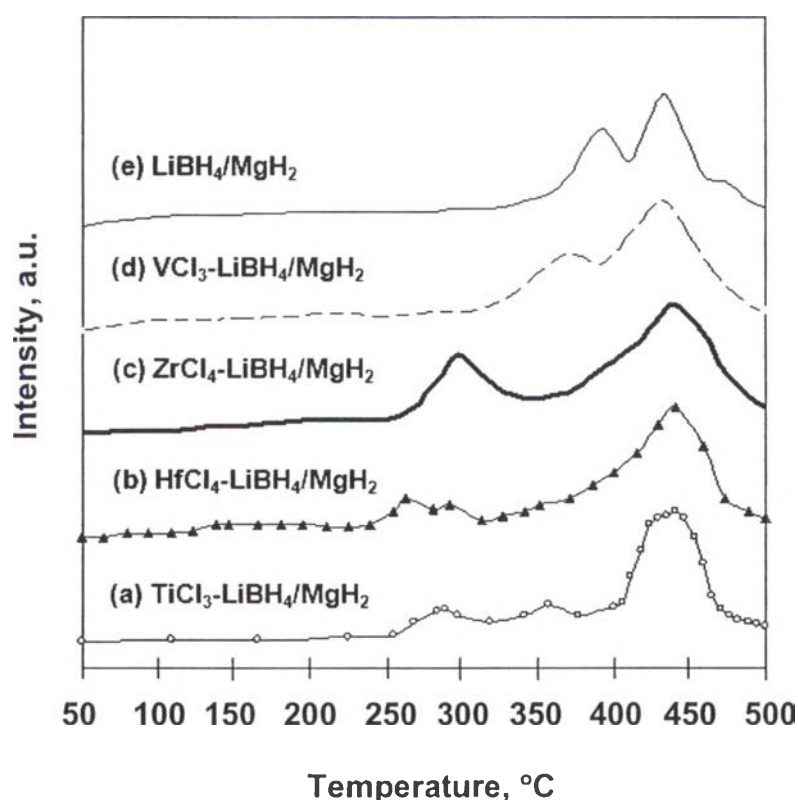


Figure 4.5 TPDRO/MS profiles of: (a) $\text{TiCl}_3\text{-LiBH}_4/\text{MgH}_2$, (b) $\text{HfCl}_4\text{-LiBH}_4/\text{MgH}_2$, (c) $\text{ZrCl}_4\text{-LiBH}_4/\text{MgH}_2$, (d) $\text{VCl}_3\text{-LiBH}_4/\text{MgH}_2$, and (e) $\text{LiBH}_4/\text{MgH}_2$.

Hydrogen evolved from the decomposition of 1, 3, 5, and 7 mol% TiCl_3 in the $\text{LiBH}_4/\text{MgH}_2$ mixture is shown and compared with that of the uncatalyzed mixture in Fig. 4.6. Again, the two steps of hydrogen desorption are obtained regarding the amount of TiCl_3 added. A distinct difference is that the higher the amount of TiCl_3 , the broader the temperature difference between the first and second hydrogen desorption temperature. The lowest starting hydrogen desorption

temperature (240°C) is with the sample added with 5 and 7 mol%. From the results, there may be an optimum amount of TiCl_3 that results in the lowest desorption temperature. If the hydrogen intensity information can be used to indicate how much hydrogen evolved from the decomposition, it is then clear that the amount of TiCl_3 plays an importation on that. To further elucidate roles of the amount of TiCl_3 on the kinetics and hydrogen storage capacity of the $\text{LiBH}_4/\text{MgH}_2$ mixture, the decomposition of the mixture was studied and the results are shown in Fig. 4.7.

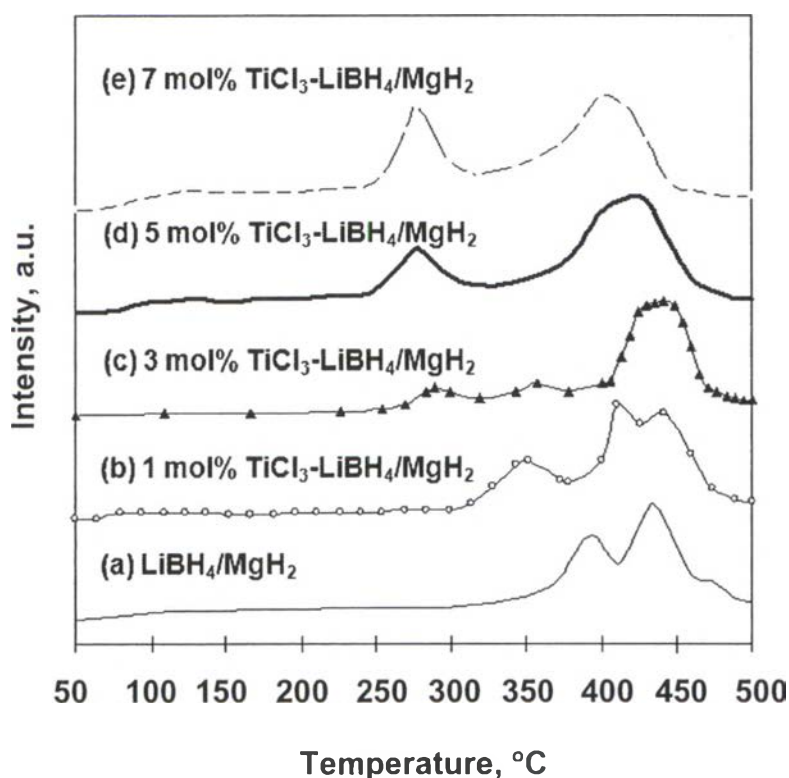


Figure 4.6 TPDRO/MS profiles of the TiCl_3 - $\text{LiBH}_4/\text{MgH}_2$ mixture with different amounts of TiCl_3 : (a) $\text{LiBH}_4/\text{MgH}_2$ (b) 1 mol%, (c) 3 mol%, (d) 5 mol%, and (e) 7 mol%- $\text{LiBH}_4/\text{MgH}_2$.

From Fig. 4.7, it is obvious that the amount of TiCl_3 affects the kinetics of the $\text{LiBH}_4/\text{MgH}_2$ desorption. First, TiCl_3 reduces the *shoulder* of the uncatalyzed mixture. Among the tested amounts of TiCl_3 , using 3-7 mol% TiCl_3 results in a higher initial hydrogen desorption rates than using 1 mol%. The fastest

hydrogen desorption is from the sample with 5 and 7 mol% $\text{TiCl}_3\text{-LiBH}_4/\text{MgH}_2$ mixtures. In term of hydrogen desorption capacity, the higher the amount of the catalyst, the lower the hydrogen desorption capacity. This is also consistent with literature [3].

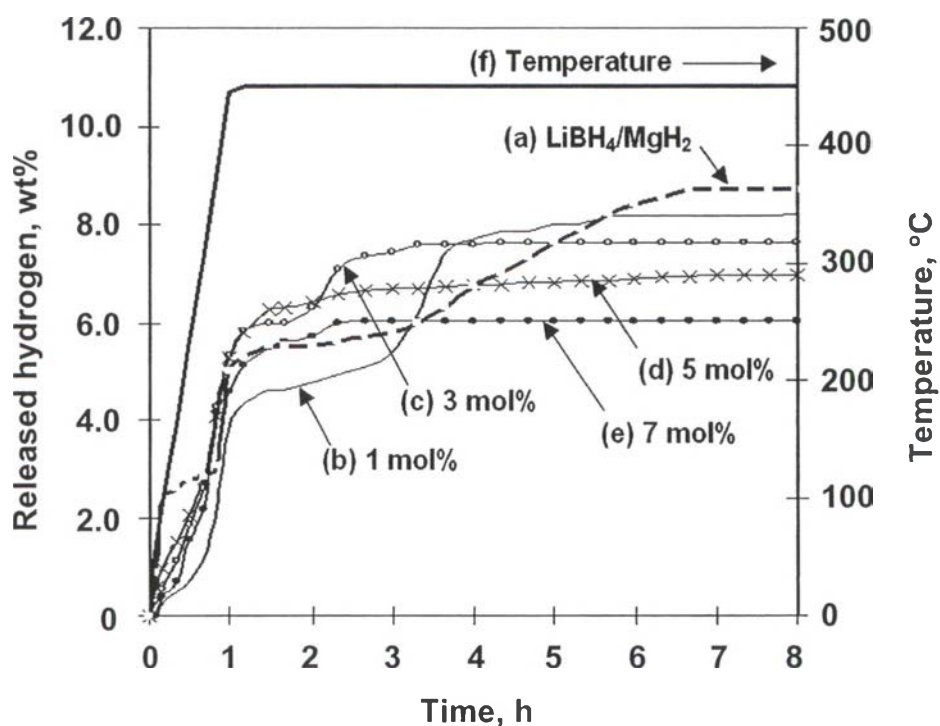


Figure 4.7 Kinetic investigations at a constant hydrogen desorption temperature, 450°C , of the $\text{TiCl}_3\text{-LiBH}_4/\text{MgH}_2$ mixture with different amounts of TiCl_3 : (a) $\text{LiBH}_4/\text{MgH}_2$, (b) 1 mol%, (c) 3 mol%, (d) 5 mol%, (e) 7 mol% $\text{-LiBH}_4/\text{MgH}_2$, and (f) hydrogen desorption temperature.

4.5 Conclusions

The hydrogen desorption of the 2:1 mole ratio of $\text{LiBH}_4/\text{MgH}_2$ was investigated and found to consist of two steps. The first step involved the hydrogen desorption of LiBH_4 and MgH_2 to LiBH_{4-x} and $\text{MgH}_{2-y}/\text{Mg}$, respectively. That was followed by the reaction between the desorbed metal hydrides, with Mg as a major product and a trace amount of MgB_2 , and LiH. The reversible hydrogen capacity after the tenth hydrogen desorption was reduced to 1.8 wt% because only MgH_2 could be recovered. The hydrogen desorption temperature and kinetics could be improved by the milling process and adding an appropriate type and amount of the catalyst. The best catalyzed- $\text{LiBH}_4/\text{MgH}_2$ mixture from this work was 5 mol% TiCl_3 - $\text{LiBH}_4/\text{MgH}_2$ mixture.

4.6 Acknowledgements

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