



## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Material Properties

##### 4.1.1 Lithium amide (LiNH<sub>2</sub>)

Figure 4.1 shows the thermal desorption mass spectra (TDMS) of NH<sub>3</sub> and hydrogen emissions from LiNH<sub>2</sub>. It can clearly be noticed that the emission profiles of NH<sub>3</sub> and hydrogen take place at the same temperature around 150°C, after that the NH<sub>3</sub> emission profile distinctively increases at the temperature range of 200-300°C. The H<sub>2</sub> emission profile, on the other hand, obviously increases at temperature higher than 400°C. Moreover, the formation of NH<sub>3</sub> as a by-product during the decomposition of LiNH<sub>2</sub> is a problem, which impairs the performance of the catalyst in a polymer membrane electrolyte fuel cell and loses the storage materials itself as the constituent nitrogen disappears from the system.

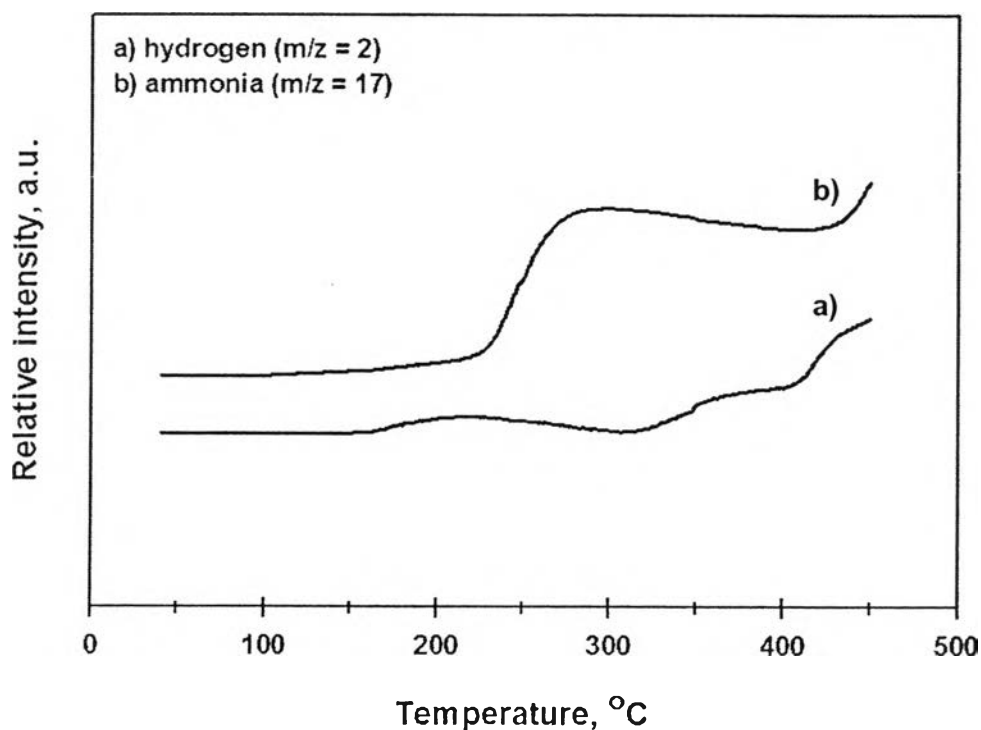


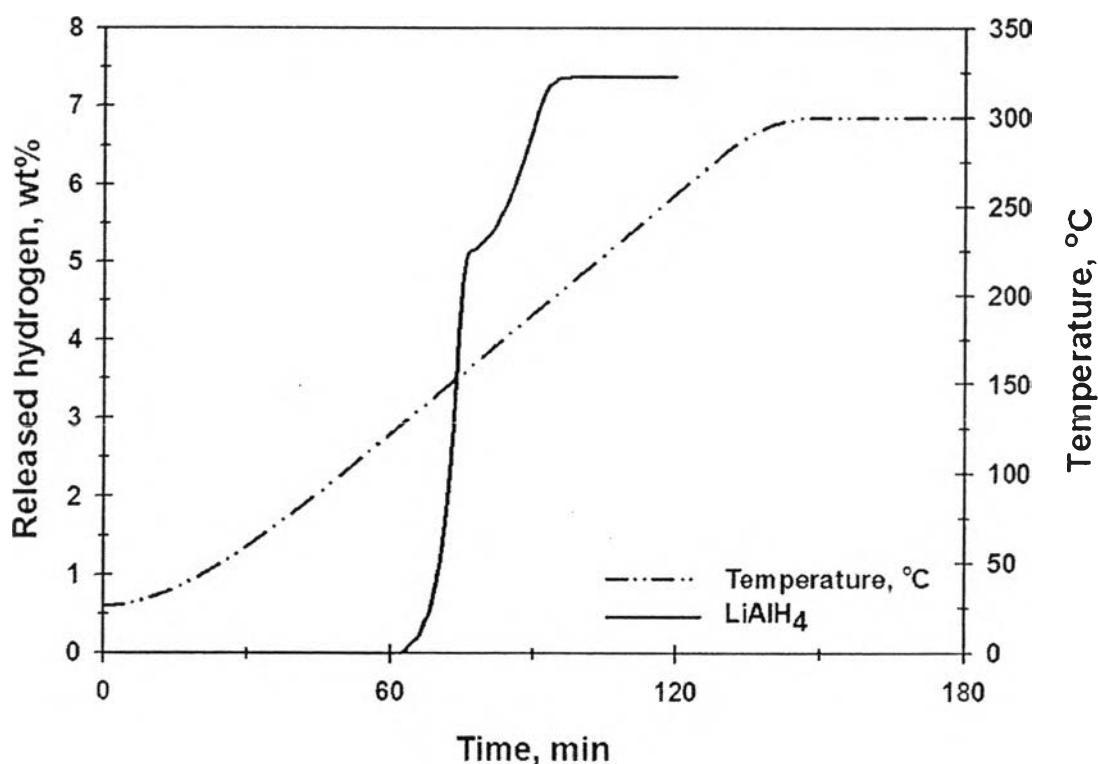
Figure 4.1 MS spectra of LiNH<sub>2</sub>: a) hydrogen (m/z = 2) and b) ammonia (m/z = 17).

#### 4.1.2 Lithium aluminum hydride (LiAlH<sub>4</sub>)

LiAlH<sub>4</sub> desorbs hydrogen about 7.4 wt% by the temperature-programmed desorption (TPD) measurement at the temperature lower than 300°C, Figure 4.2. The decomposition reaction of LiAlH<sub>4</sub> has 2 steps, by following reactions:



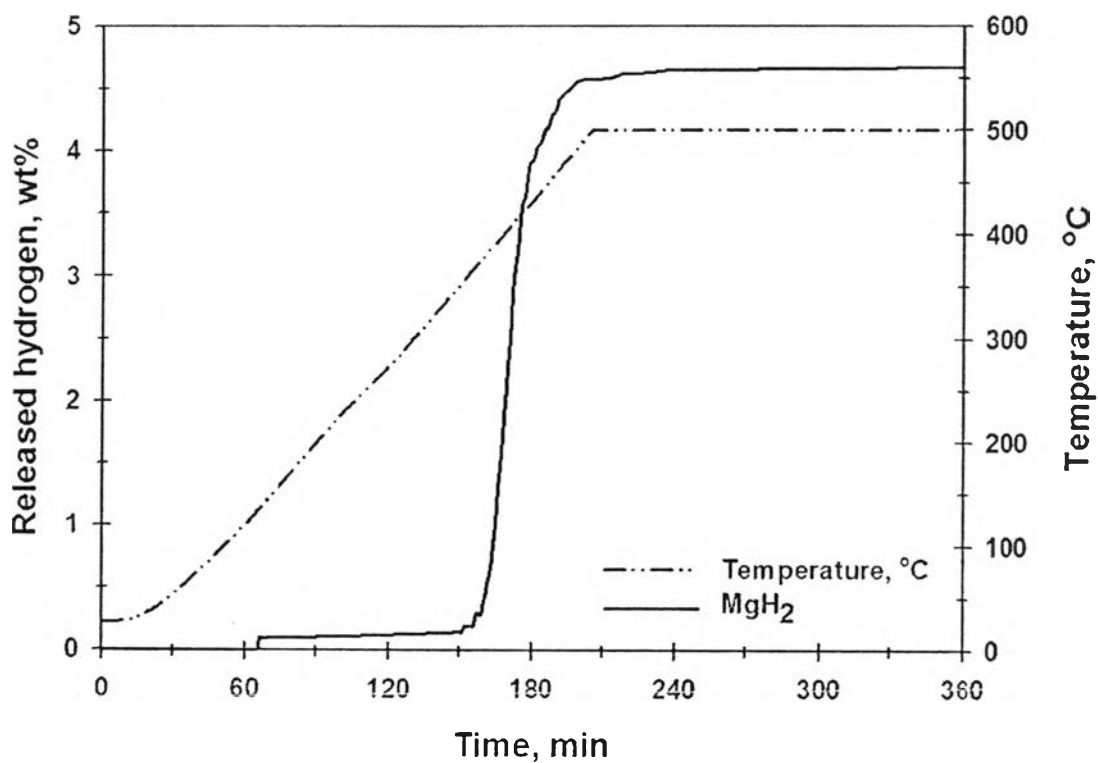
The first step, Reaction (4.1), takes place at temperature range of 125-160°C and releases 5.3 wt% hydrogen. The second step, Reaction (4.2), releases 2.1 wt% hydrogen and occurs at about 160-200°C.



**Figure 4.2** Hydrogen desorption profiles of LiAlH<sub>4</sub>.

#### 4.1.3 Magnesium hydride (MgH<sub>2</sub>)

Magnesium hydride starts to release a small amount of hydrogen at 130°C due to the increase in the temperature. Hydrogen rapidly increases up to 4.6 wt% in the temperature range of 350-500°C, Figure 4.3. The decomposition reaction of MgH<sub>2</sub> can be written as shown in Reaction (4.3).

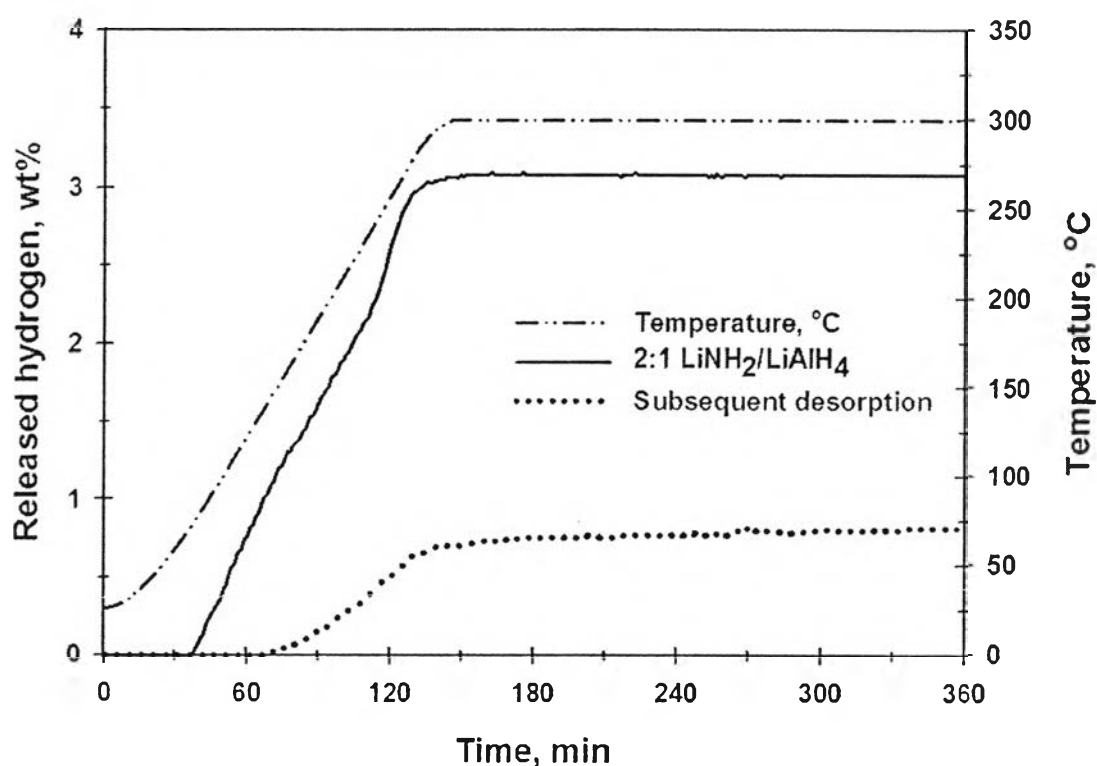


**Figure 4.3** Hydrogen desorption profiles of MgH<sub>2</sub>.

The results show that high operating temperature is needed, which is too high for practical on-board application. So many efforts have focused on Mg-based hydrides in the past few years to lower the desorption temperature and fasten the dehydrogenation in LiNH<sub>2</sub>. These can be accomplished by mixing with LiNH<sub>2</sub>, which helps reducing the stability of LiNH<sub>2</sub> and also acts as catalysts to improve the desorption/absorption kinetics.

#### 4.2 Effect of $\text{LiAlH}_4$ on Hydrogen Desorption of $\text{LiNH}_2$

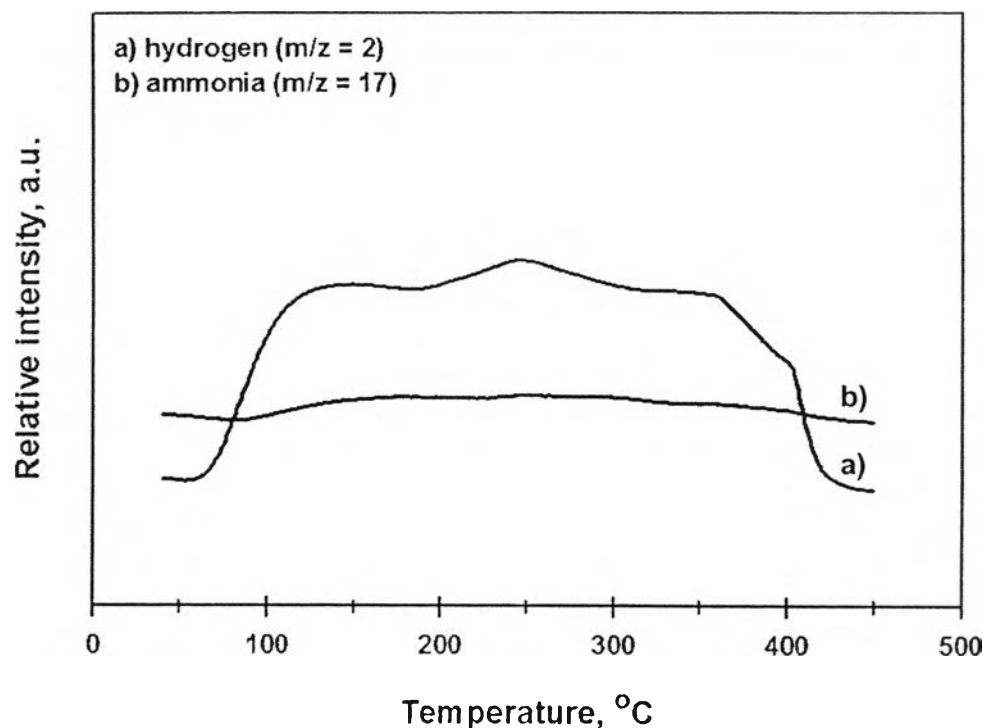
Figure 4.4 shows the TPD of the mixture of  $\text{LiNH}_2$  and  $\text{LiAlH}_4$  with 2:1 molar ratio. It was found that the mixture of 2:1  $\text{LiNH}_2/\text{LiAlH}_4$  releases hydrogen about 3.1 wt% at 65-70°C while the amount of released hydrogen in the subsequent desorption about 0.8 wt%, which is smaller than the first desorption. It is worth noting that the first decomposition seems to disappear in the subsequent desorption. In addition, the desorption temperature increases to 150°C.



**Figure 4.4** Hydrogen desorption profiles of 2:1  $\text{LiNH}_2/\text{LiAlH}_4$  and its subsequent desorption.

The thermal desorption mass spectra (TDMS) of  $\text{NH}_3$  and hydrogen emissions from the mixture of 2:1  $\text{LiNH}_2/\text{LiAlH}_4$  were also studied. It shows that the relative intensity of hydrogen starts at about 60-80°C (Figure 4.5a) as the main product from the mixture. On the other hand, not only does hydrogen release during the desorption but also  $\text{NH}_3$ . Figure 4.5b reveals the small peak of  $\text{NH}_3$  shifts from

the base line, which means the mixture has a small amount of  $\text{NH}_3$  released during the decomposition of the mixture.

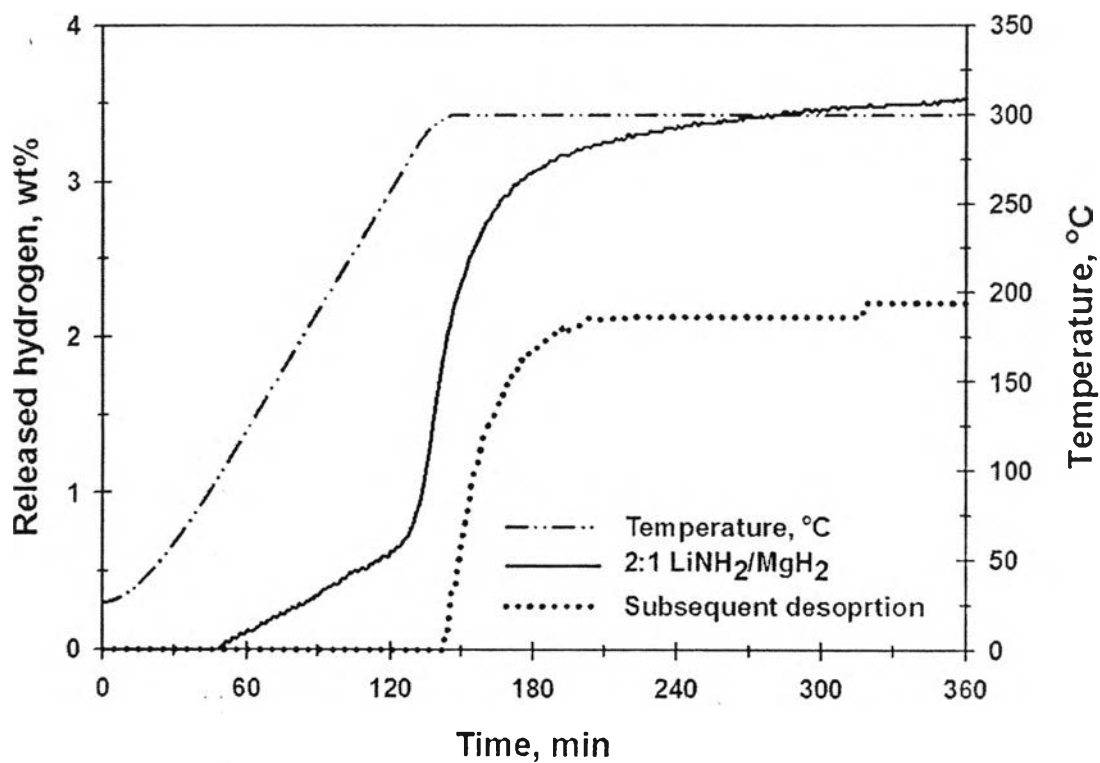


**Figure 4.5** MS spectra of 2:1  $\text{LiNH}_2/\text{LiAlH}_4$ : a) hydrogen ( $m/z = 2$ ) and b) ammonia ( $m/z = 17$ ).

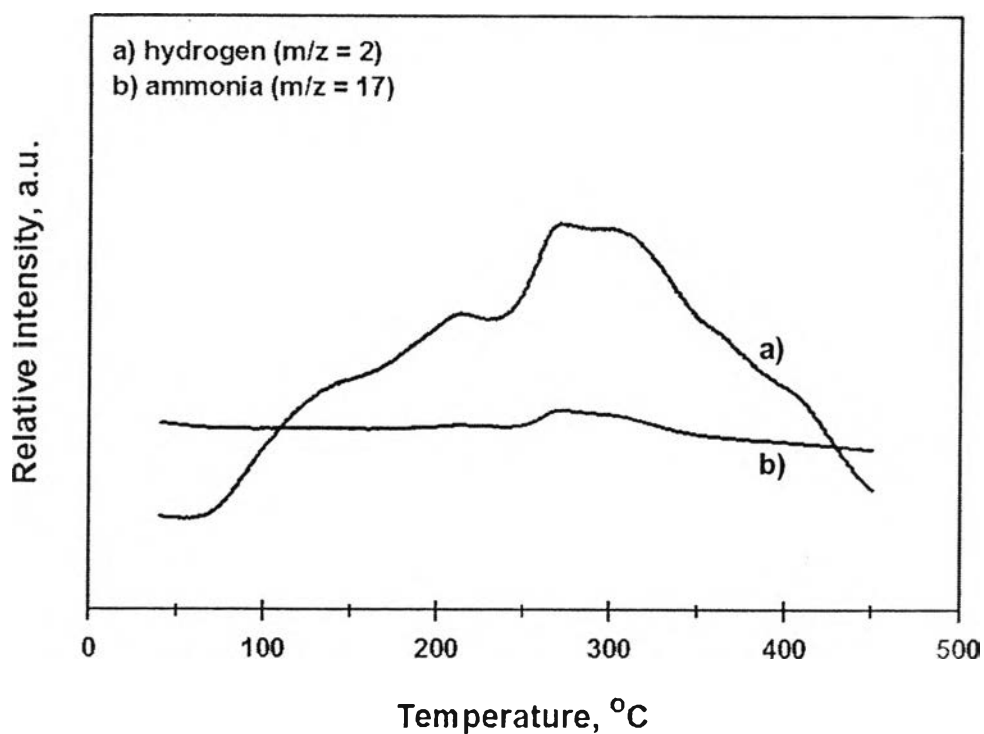
Therefore, it can be clearly seen that adding  $\text{LiAlH}_4$  can partially suppress the formation of  $\text{NH}_3$  in  $\text{LiNH}_2$  but it still has a small amount of  $\text{NH}_3$  in the mixture while the hydrogen capacity of the 2:1  $\text{LiNH}_2/\text{LiAlH}_4$  mixture is about 3.1 wt%.

### 4.3 Effect of $\text{MgH}_2$ on Hydrogen Desorption of $\text{LiNH}_2$

Figure 4.6 presents the hydrogen desorption profiles of the 2:1  $\text{LiNH}_2/\text{MgH}_2$  mixture. In the first hydrogen desorption, the mixture releases hydrogen in two steps starting at the temperature of 80-90°C with the total hydrogen of 3.6 wt% at about 300°C. However, in the subsequent desorption, the amount of released hydrogen decreases to 2.3 wt%. In addition, the desorption temperature increases to 300°C.



**Figure 4.6** Hydrogen desorption profiles of 2:1  $\text{LiNH}_2/\text{MgH}_2$  and its subsequent desorption.

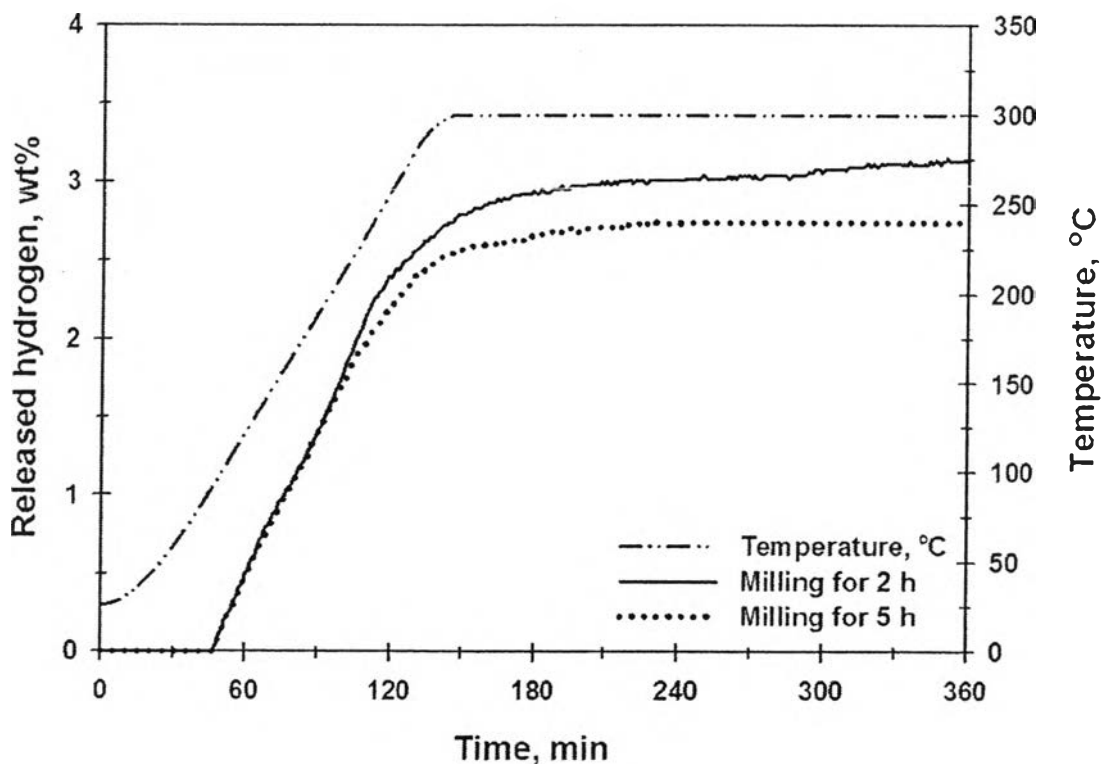


**Figure 4.7** MS spectra of 2:1  $\text{LiNH}_2/\text{MgH}_2$ : a) hydrogen ( $m/z = 2$ ) and b) ammonia ( $m/z = 17$ ).

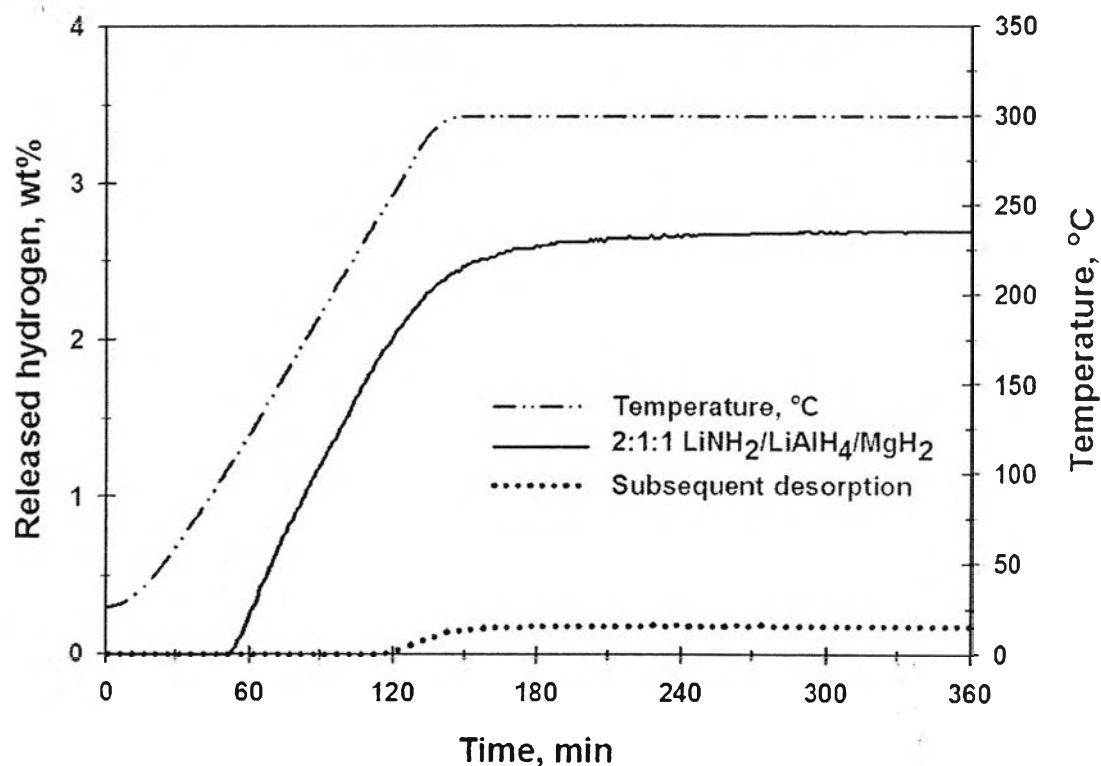
Figure 4.7 shows the TDMS of  $\text{NH}_3$  and hydrogen emissions from the mixture of 2:1  $\text{LiNH}_2/\text{MgH}_2$ . It reveals that the hydrogen releases at about  $70\text{--}80^\circ\text{C}$  (Figure 4.7a) with the main product of the decomposition of the mixture. Moreover, it was found that  $\text{NH}_3$  releases during the decomposition of the mixture as shown in Figure 4.7b at about  $250^\circ\text{C}$ .

#### 4.4 Effect of Milling Time on Hydrogen Desorption of 2:1:1 $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$

The comparison of hydrogen desorption from 2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$  milled for 2 h and 5 h is presented in Figure 4.8. It can be clearly noticed that the mixture milled for 2 h releases hydrogen about 3.2 wt% while the mixture milled for 5 h releases hydrogen about 2.7 wt%. The reason that the amount of released hydrogen from the mixture milled for 5 h is lower than the one milled for 2 h because the mixture could partially decompose during the milling.



**Figure 4.8** Hydrogen desorption profiles of 2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$ : Milled for 2 h (—) and 5 h (.....).



**Figure 4.9** Hydrogen desorption profiles of 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> milled for 5 h and its subsequent desorption.

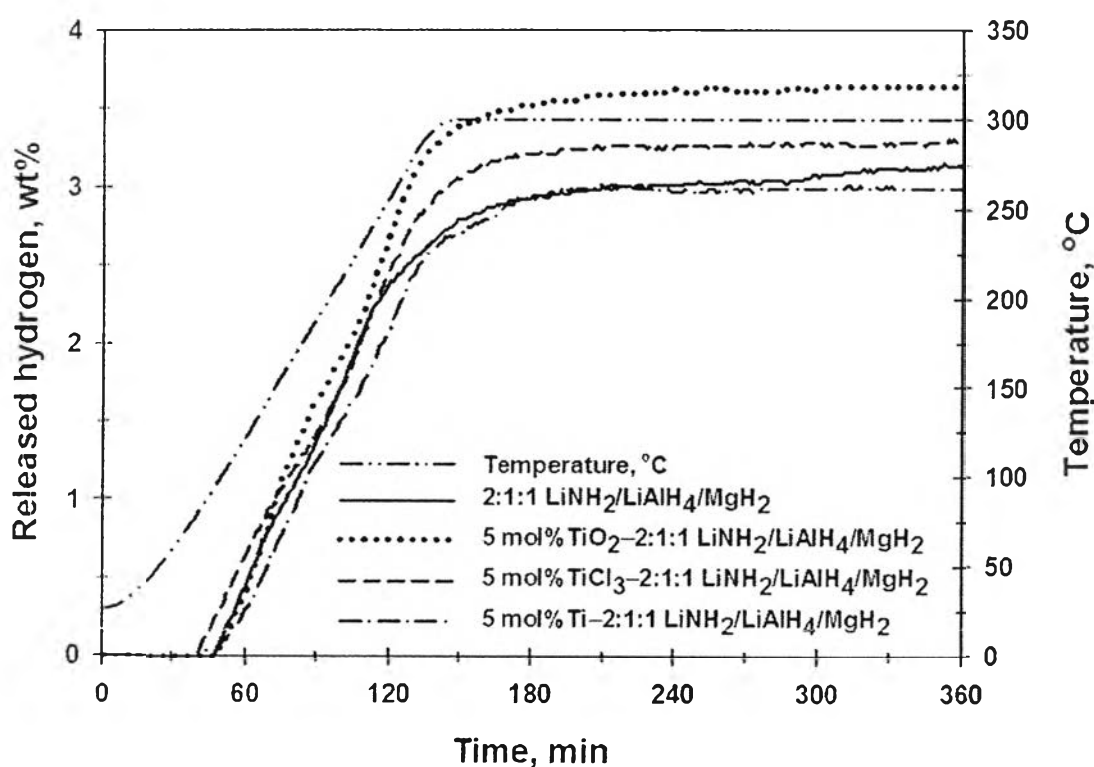
Moreover, the results shown in Figure 4.9 reveal the hydrogen desorption profile of 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> milled for 5 h and its subsequent desorption. The mixture can re-absorb hydrogen while the mixture milled for 2 h can not. This indicates that the homogeneity of the mixture could influence the reversibility. In addition, from the figure, it is worth noting that the first decomposition disappears in the subsequent desorption.



## 4.5 Effect of Catalysts on Hydrogen Desorption of 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub>

### 4.5.1 Effect of Catalysts

To study the effect of catalyst types on hydrogen desorption of 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub>, Ti and Ti compounds (TiO<sub>2</sub> and TiCl<sub>3</sub>) are used. Figure 4.10 shows the temperature programmed desorption of 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> doped with 5 mol% TiO<sub>2</sub>, TiCl<sub>3</sub> and Ti compared to the undoped mixture milled for 2 h.



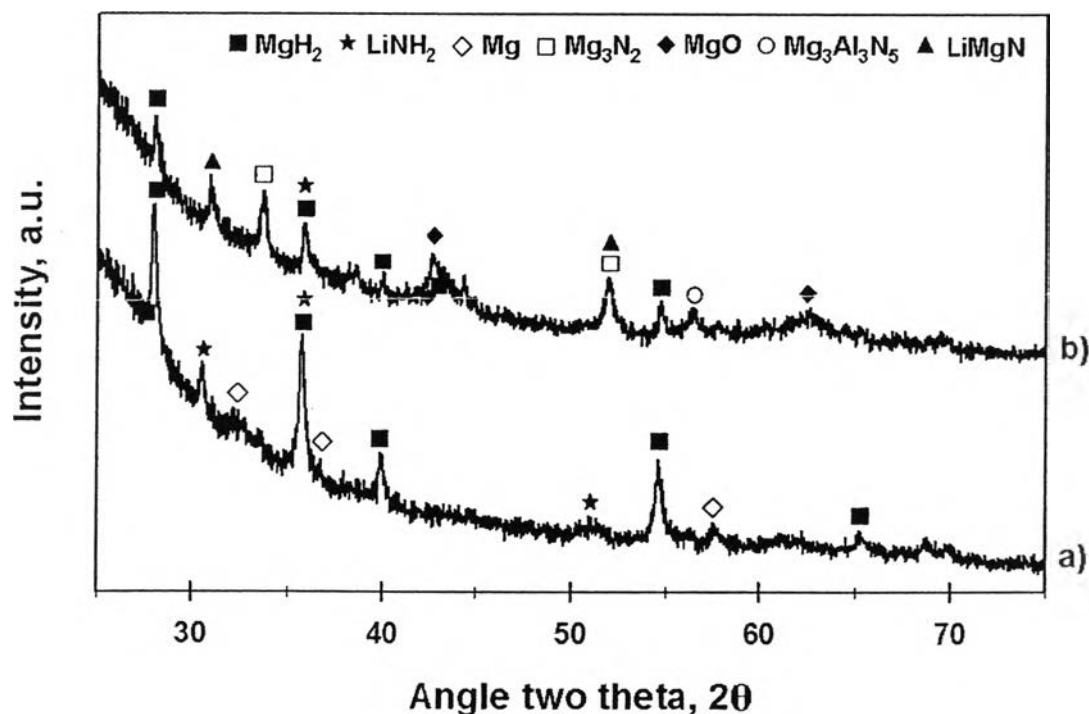
**Figure 4.10** Hydrogen desorption profiles of 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> (—), 5 mol%TiO<sub>2</sub>-2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> (.....), 5 mol%TiCl<sub>3</sub>-2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> (— —), and 5 mol%Ti-2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> (— ·).

Figure 4.10 clearly reveals that the catalysts enhance the kinetics of the hydrogen desorption. The mixture doped with TiO<sub>2</sub> shows a higher amount of hydrogen desorption, 3.7 wt% at 300°C, than the mixtures doped with TiCl<sub>3</sub>, Ti, and undoped one, which are 3.3, 3.0, and 3.2 wt%, respectively. In addition, doping with TiO<sub>2</sub> increases the amount of hydrogen desorption while doping with TiCl<sub>3</sub> increases

the amount of hydrogen desorption and desorption kinetics. In contrast, adding Ti does not show any significant improvement from the undoped sample.

#### 4.5.2 Reversibility of $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$

To study the reversibility and stability of hydrogen desorption-absorption of  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$  mixtures, all samples are dehydrogenated from room temperature to  $300^\circ\text{C}$  with the heating rate of  $2^\circ\text{C min}^{-1}$ . The first dehydrogenation of 2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$  mixture releases about 3.2 wt% hydrogen. After the first desorption, the sample was re-absorbed under 1,200 psi of hydrogen atmosphere at  $200^\circ\text{C}$  for 12 h. It was found that the 2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$  mixture milled for 2 h is not able to re-absorb hydrogen (data is not shown) while the addition of  $\text{TiO}_2$ ,  $\text{TiCl}_3$ , and Ti resulted in the reversibility of the mixture of 2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$ .

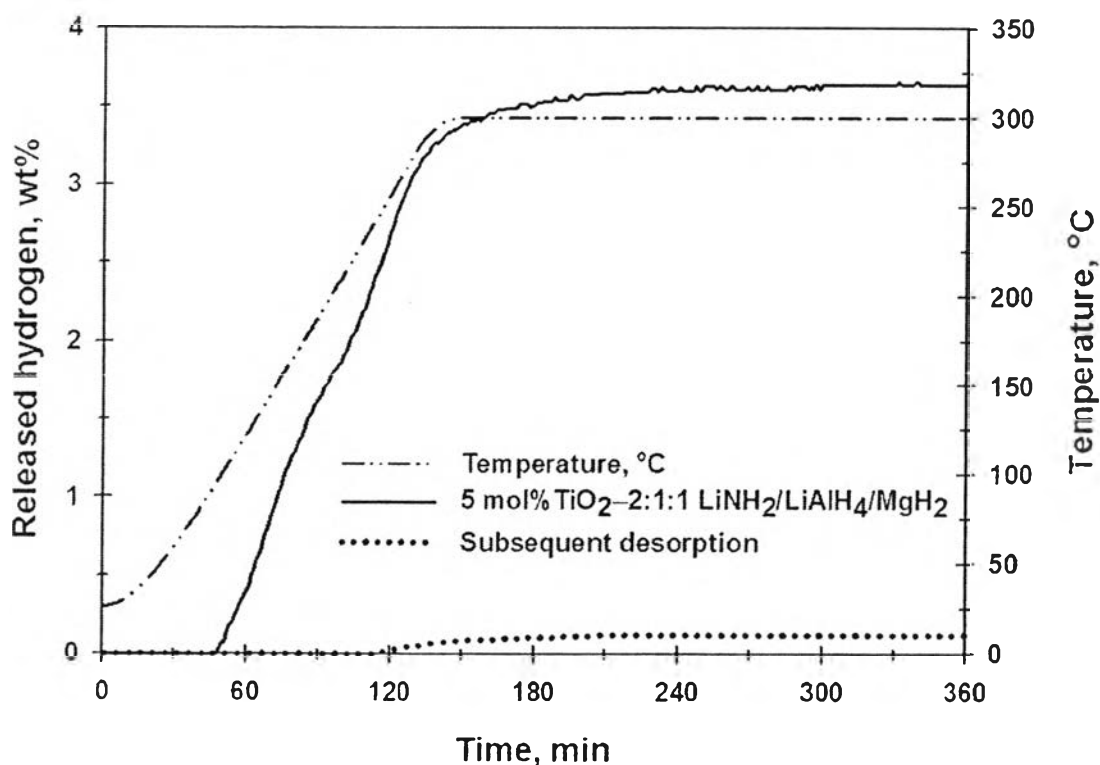


**Figure 4.11** XRD patterns of 2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$ : a) after milling for 2 h, b) after hydrogen desorption.

Figure 4.11 shows the XRD patterns of 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub>. The result presents a high intensity of LiNH<sub>2</sub>, MgH<sub>2</sub>, and Mg after milling (Figure 4.11a). After hydrogen desorption (Figure 4.11b), a new phase of Mg<sub>3</sub>N, MgO, LiMgN, and Mg<sub>3</sub>Al<sub>3</sub>N<sub>5</sub> appears in the mixture, meaning the interaction of LiNH<sub>2</sub>, LiAlH<sub>4</sub>, and MgH<sub>2</sub>. The presence of MgO could be an impurity in the mixture. Although the XRD patterns of the re-absorbed sample is not shown, it is not different from the XRD patterns after the hydrogen desorption.

#### 4.5.2.1 5 mol%TiO<sub>2</sub>-2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub>

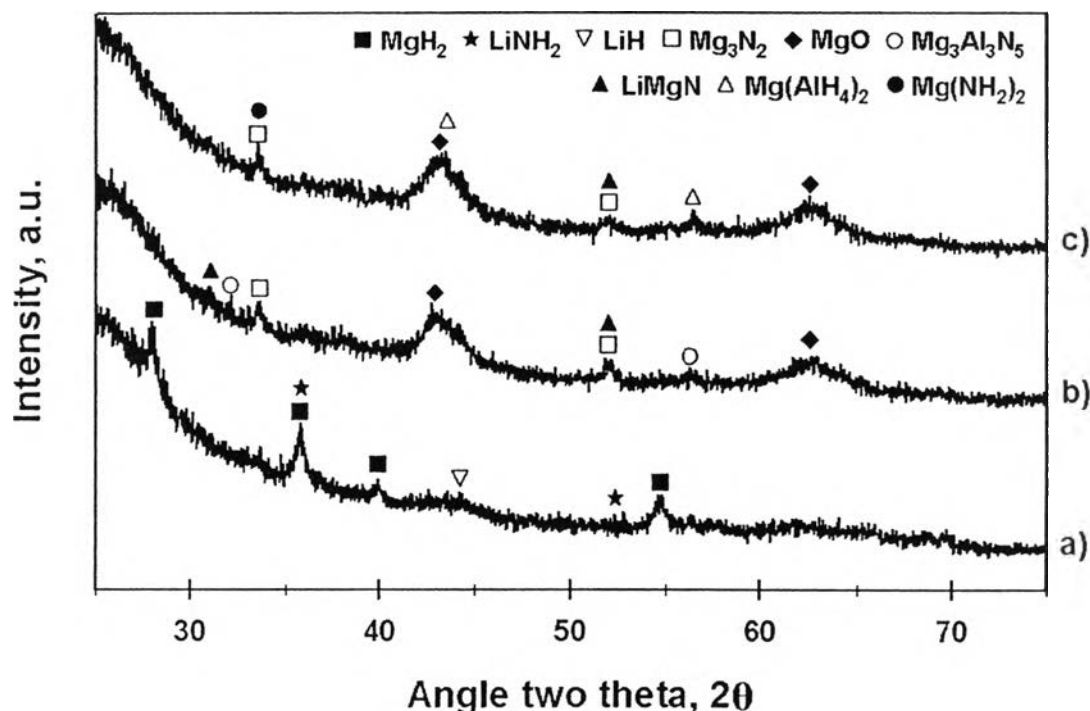
Figure 4.12 presents the reversibility of the 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> mixture doped with TiO<sub>2</sub>. The results show that the first dehydrogenation of the mixture starts at around 90°C and reaches 3.7 wt% hydrogen at 300°C.



**Figure 4.12** Hydrogen desorption profiles of 5 mol%TiO<sub>2</sub>-2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> and its subsequent desorption.

After the first desorption, the sample was re-absorbed under 1,200 psi of hydrogen atmosphere at 200°C for 12 h. The amount of released

hydrogen drops to 0.13 wt% for the subsequent desorption (dotted line), as shown in Figure 4.12. Moreover, the decomposition temperature is shifted from 90°C to 240°C.



**Figure 4.13** XRD patterns of 5 mol%TiO<sub>2</sub>-2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub>: a) after milling for 2 h, b) after hydrogen desorption, and c) after hydrogen re-absorption.

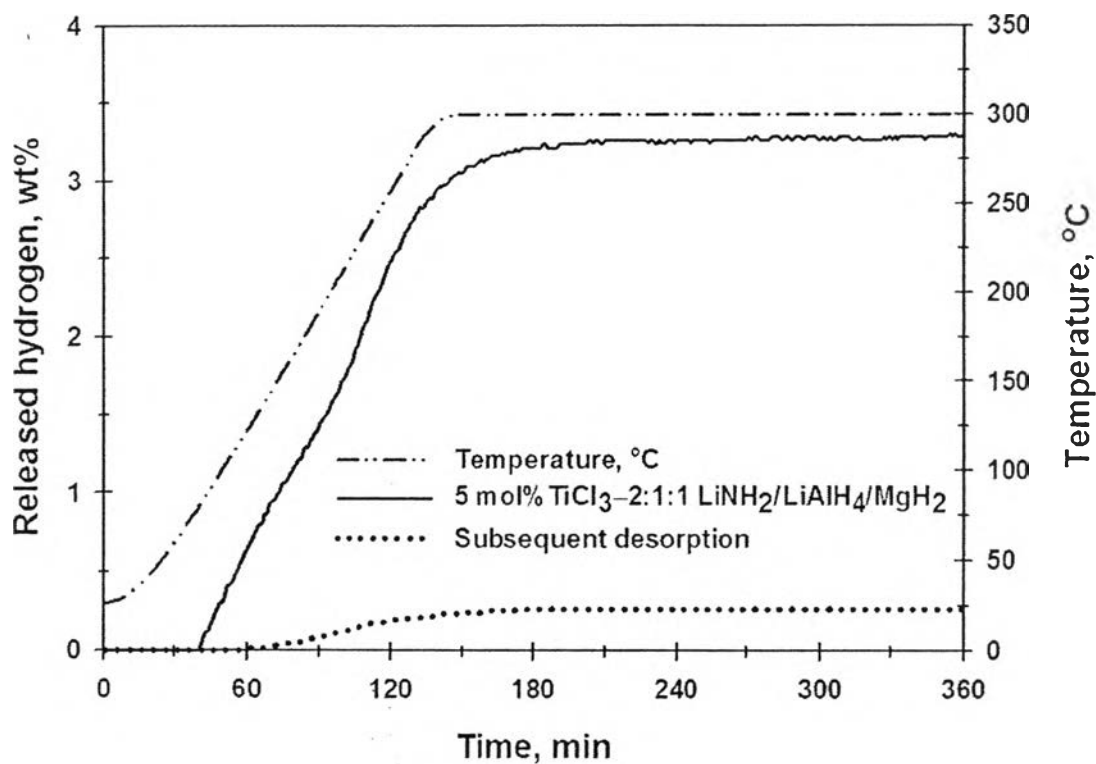
The XRD analysis results are used to study the phase transformation of the LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> mixture. The XRD patterns of 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> doped with TiO<sub>2</sub> is shown in Figure 4.13. The result shows that after milling, LiH peaks appear, indicating the decomposition of LiAlH<sub>4</sub>. The peaks of MgH<sub>2</sub> and LiNH<sub>2</sub> are observed after the milling (Figure 4.13a), which means the mixture consists of MgH<sub>2</sub>, LiNH<sub>2</sub>, and LiH before the hydrogen desorption. After the desorption, the products consist of MgO, Mg<sub>3</sub>N<sub>2</sub>, LiMgN, and Mg<sub>3</sub>Al<sub>3</sub>N<sub>5</sub> (Figure 4.13b). In addition, the starting materials do not remain in the mixture after the desorption. For the re-absorbed hydrogen (Figure 4.13c), the peak of MgO is observed. That may be from the reaction between MgH<sub>2</sub> and LiOH, which are impurities present in commercial LiNH<sub>2</sub> (Palumbo *et al.*, 2008). The peak of

$\text{Mg}_3\text{Al}_3\text{N}_5$  disappears indicating that it may transform to another phase by re-absorbing with hydrogen. Small peaks of  $\text{Mg}(\text{AlH}_4)_2$  and  $\text{Mg}(\text{NH}_2)_2$  appear in the re-absorbed products, which are the reversible phases in the mixture.

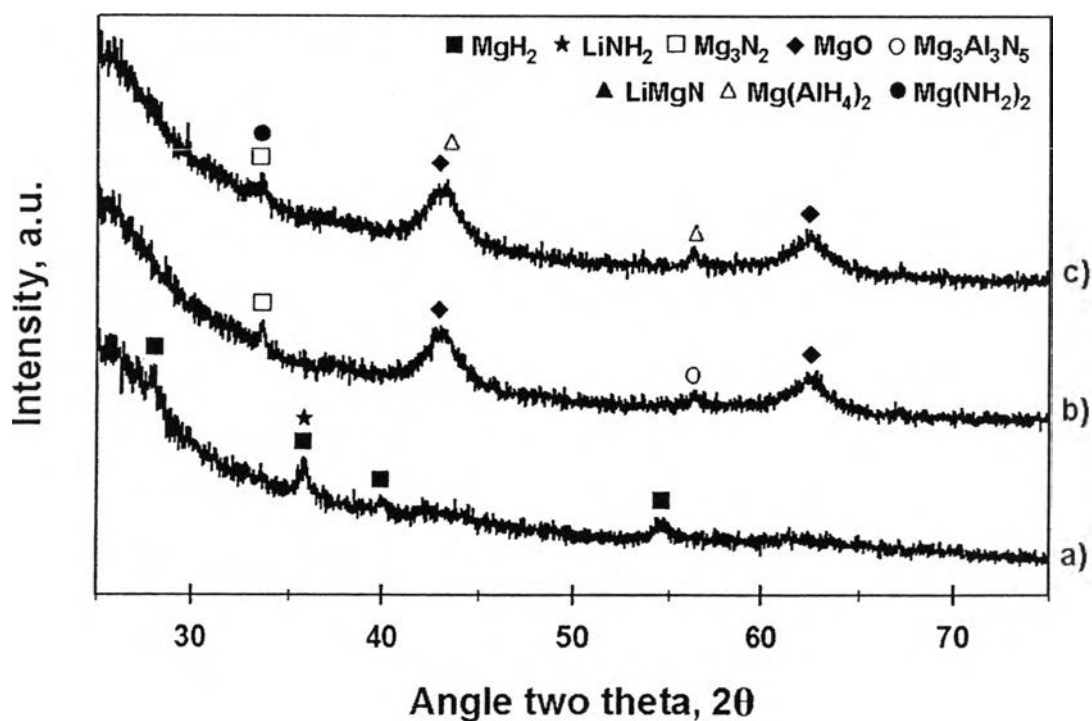
#### 4.5.2.2 5 mol% $\text{TiCl}_3$ -2:1:1 $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$

The reversibility of 2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$  mixture doped with  $\text{TiCl}_3$  is presented in Figure 4.14. It was found that hydrogen releases at around  $80^\circ\text{C}$  and achieves 3.3 wt% hydrogen at  $300^\circ\text{C}$ . After the first desorption, the sample was re-absorbed under 1,200 psi of hydrogen atmosphere at  $200^\circ\text{C}$  for 12 h. For subsequent desorption (dotted line), the amount of released hydrogen decreases to 0.27 wt% as shown in the figure. In addition, the decomposition temperature increases to  $125^\circ\text{C}$ .

Figure 4.15 shows the XRD patterns of 2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$  doped with  $\text{TiCl}_3$ .  $\text{MgH}_2$  and  $\text{LiNH}_2$  are present a very low relative intensity after the milling (Figure 4.15a), and they disappear after the hydrogen desorption by heating up from room temperature to  $300^\circ\text{C}$  (Figure 4.15b). The mixture after the desorption consists of  $\text{MgO}$ ,  $\text{Mg}_3\text{N}_2$ , and  $\text{Mg}_3\text{Al}_3\text{N}_5$ . The peak of  $\text{MgO}$  may be from a product from the reaction between  $\text{MgH}_2$  and  $\text{LiOH}$ , the impurity of  $\text{LiNH}_2$ . After the hydrogen re-absorption (Figure 4.15c), the phase of  $\text{Mg}(\text{AlH}_4)_2$  and  $\text{Mg}(\text{NH}_2)_2$  can be observed and considered as the reversible phases of the mixture.



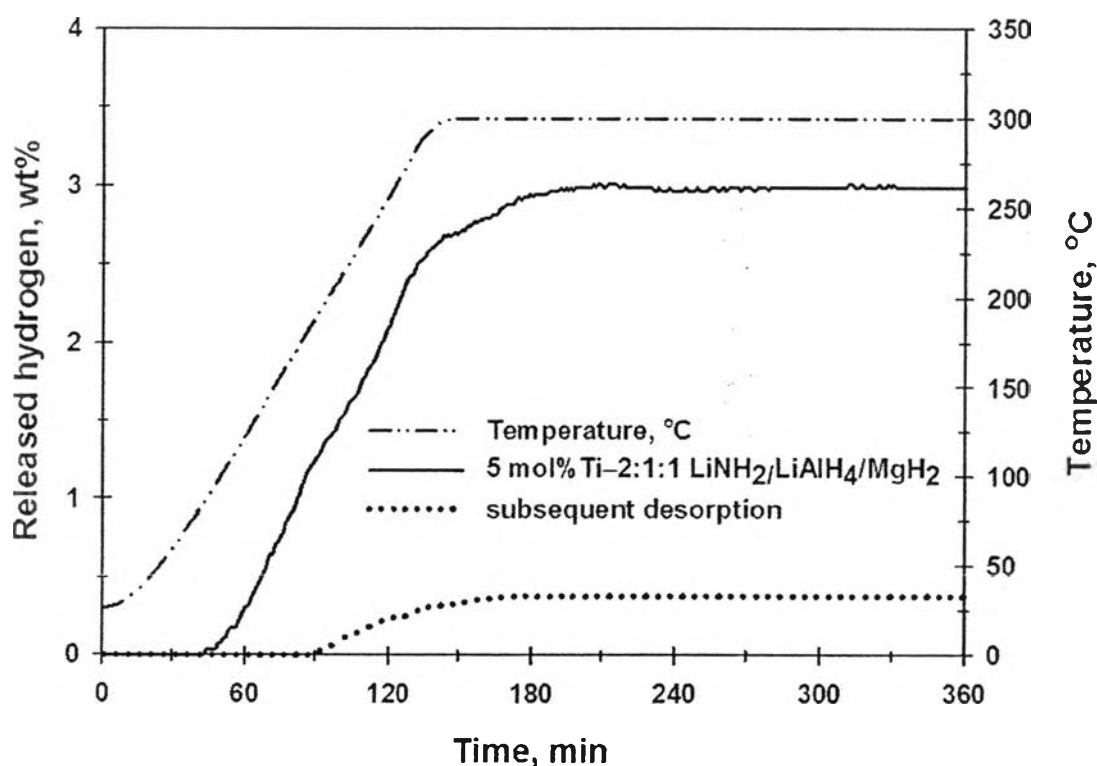
**Figure 4.14** Hydrogen desorption profiles of 5 mol%TiCl<sub>3</sub>-2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> and its subsequent desorption.



**Figure 4.15** XRD patterns of 5 mol%TiCl<sub>3</sub>-2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub>: a) after milling for 2 h, b) after hydrogen desorption, and c) after hydrogen re-absorption.

#### 4.5.2.3 5 mol%Ti-2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub>

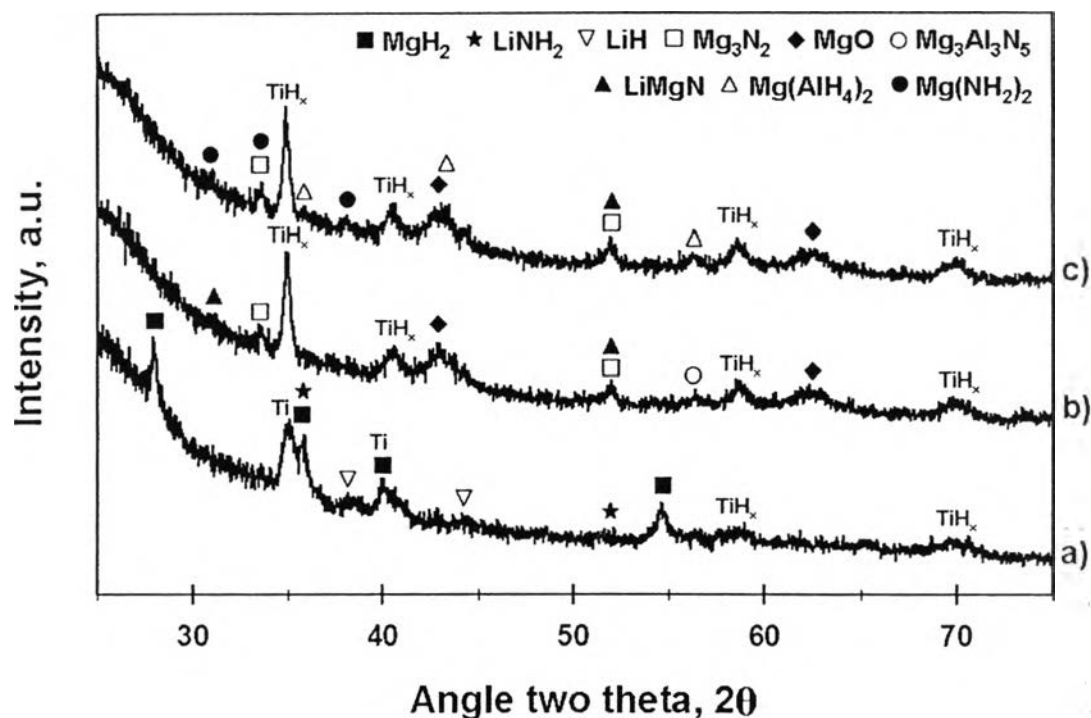
Figure 4.16 presents the reversibility of the 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> mixture doped with Ti. The result shows that the mixture releases hydrogen at around 90°C with the total hydrogen of 3.0 wt% at 300°C. After the first desorption, the sample was re-absorbed under 1,200 psi of hydrogen atmosphere at 200°C for 12 h. However, in the subsequent desorption, the amount of released hydrogen decreases to 0.38 wt% (dotted line). In addition, the decomposition temperature is shifted from 80°C to 180°C.



**Figure 4.16** Hydrogen desorption profiles of 5 mol%Ti-2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> and its subsequent desorption.

The XRD patterns of 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> doped with Ti is presented in Figure 4.17. The peak of MgH<sub>2</sub>, LiNH<sub>2</sub>, LiH, Ti, and TiH<sub>x</sub> can be observed after the milling (Figure 4.17a). Thus, the presence of LiH in the mixture implies the decomposition of LiAlH<sub>4</sub>. In addition, Ti and TiH<sub>x</sub> are also observed in the mixture. This may be due to the role of Ti in the mixture and hydrogen partially

reacts with Ti due to the milling. Figure (4.17b) shows the peak of MgO, LiMgN, Mg<sub>3</sub>N<sub>2</sub>, Mg<sub>3</sub>Al<sub>3</sub>N<sub>5</sub>, and TiH<sub>x</sub> after the hydrogen desorption.

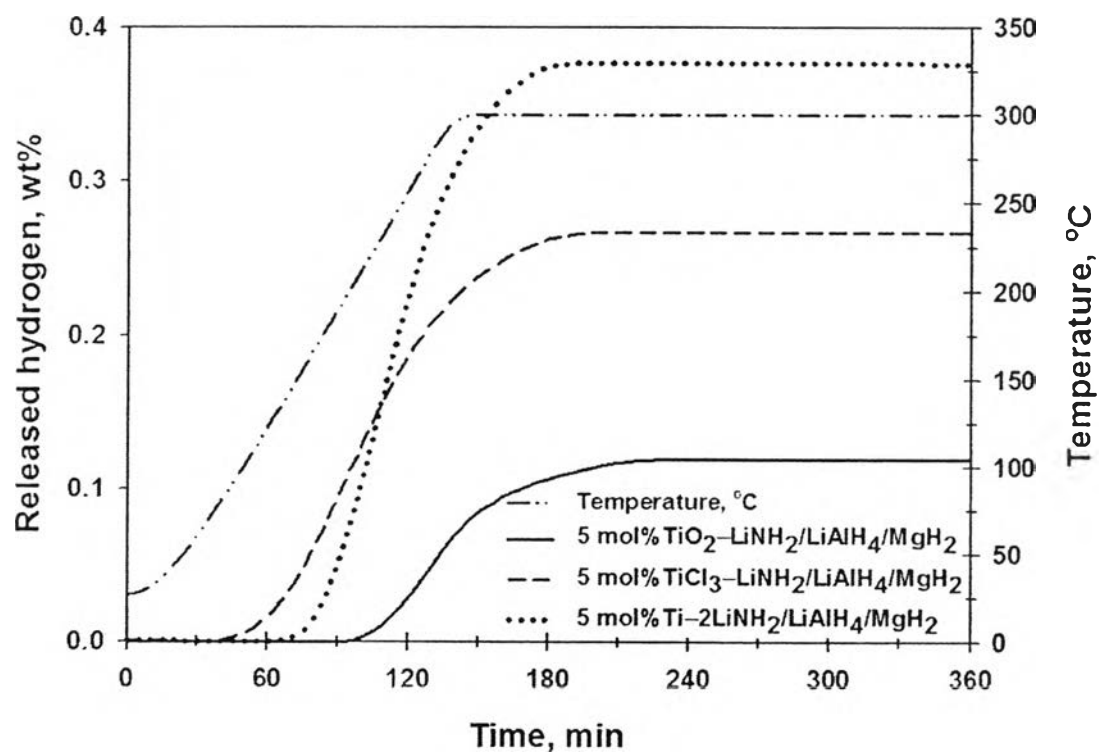


**Figure 4.17** XRD patterns of 5 mol%Ti-2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub>: a) after milling for 2 h, b) after hydrogen desorption, and c) after hydrogen re-absorption.

In the case of the H<sub>2</sub> re-absorption, small peaks of Mg(AlH<sub>4</sub>)<sub>2</sub> and Mg(NH<sub>2</sub>)<sub>2</sub> appear in the re-absorbed products, which are the reversible phases in the mixture. Moreover, the XRD confirms the formation of TiH<sub>1<x<2</sub> in the mixture after the H<sub>2</sub> desorption. This result suggests that a role of Ti on the H<sub>2</sub> re-absorption of the mixture would be to assist the H<sub>2</sub> dissociation in the system. Although it is not reported here, the XRD analysis of doped TiO<sub>2</sub> or TiCl<sub>3</sub> in 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> does not indicate the state of Ti in the mixtures.



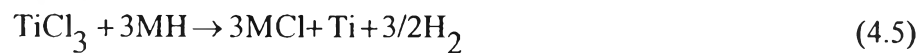
In addition, Figure 4.18 shows the reversibility of 2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$  doped with  $\text{TiO}_2$ ,  $\text{TiCl}_3$ , and Ti. It clearly reveals that the sample doped with Ti can re-absorb hydrogen 0.38 wt%, which is higher than that doped  $\text{TiCl}_3$  and  $\text{TiO}_2$ , 0.27 wt% and 0.13 wt%, respectively. However, the amount of hydrogen re-absorbed is very small compared to the first desorption of each mixture.



**Figure 4.18** Hydrogen desorption profiles in the subsequent cycles of 5 mol%  $\text{TiO}_2$ -2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$  (—), 5 mol%  $\text{TiCl}_3$ -2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$  (- -), and 5 mol% Ti-2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$  (.....)

#### 4.6 Roles of TiO<sub>2</sub>, TiCl<sub>3</sub>, and Ti on the LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> mixture

In the milling process, the mixture doped with TiO<sub>2</sub> and TiCl<sub>3</sub> partially releases hydrogen during the milling because the structure of the metal hydrides in the mixture is distorted. Moreover, TiO<sub>2</sub> and TiCl<sub>3</sub> in the mixture are reduced by the metal hydrides and transformed to Ti-neutral as shown in Reactions (4.4) and (4.5). And this result could be the reason that the LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> mixture doped with TiO<sub>2</sub> and TiCl<sub>3</sub> has the higher amount of released hydrogen than the undoped mixture.



Where M = Metal.

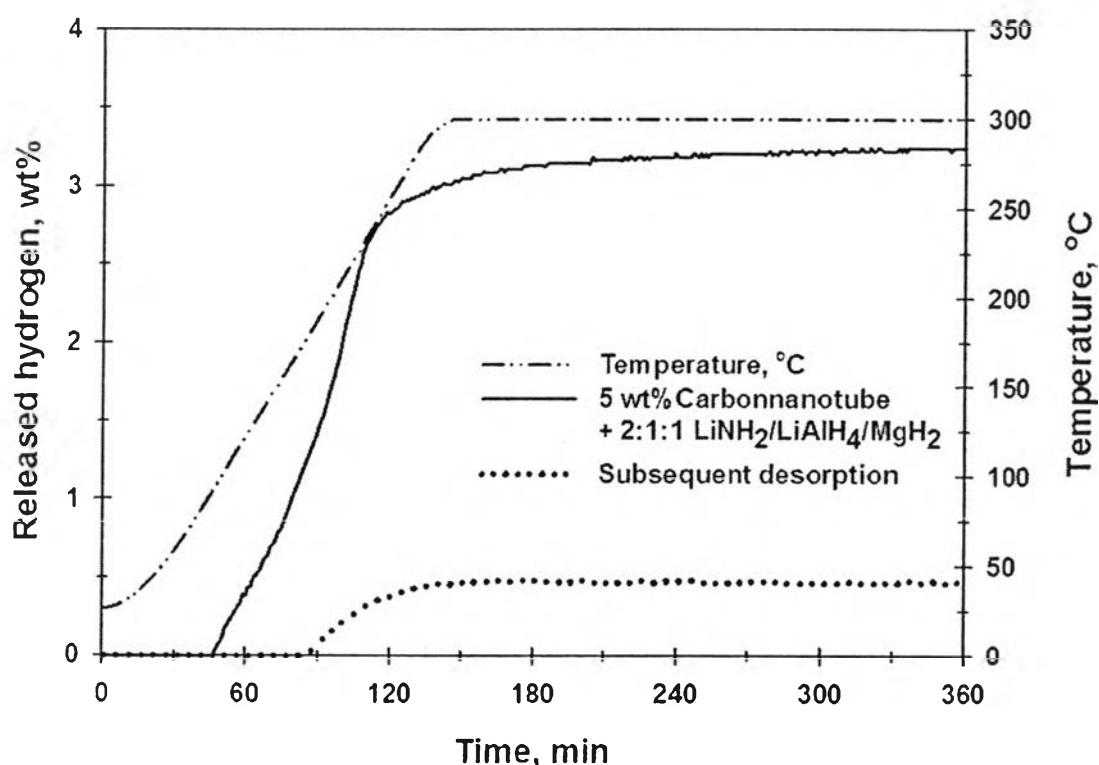
However, after the decomposition, both catalysts, TiO<sub>2</sub> and TiCl<sub>3</sub>, can form M<sub>2</sub>O and MCl as shown in Reactions (4.4) and (4.5). M<sub>2</sub>O and MCl cannot decompose further and remain in the mixture as stable materials (Isobe *et al.*, 2005). The presence of M<sub>2</sub>O and MCl affects on the reversibility of the mixture because they cannot re-absorb hydrogen and increases the weight of the mixture in the hydrogen desorption calculation.

In the case of the mixture doped with Ti, it also partially releases hydrogen during the milling process and Ti in the mixture can absorb hydrogen to form TiH<sub>x</sub> at low temperature. TiH<sub>x</sub> is very stable and needs a desorption temperature higher than 600°C (Zaluski *et al.*, 1999). As a results, the amount of released hydrogen from the first desorption is lower than the other samples doped with the other two dopants and the undoped mixtures.

## 4.7 Effect of Carbon nanotube on Hydrogen Desorption of 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub>

### 4.7.1 5 wt% Carbon nanotube + 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub>

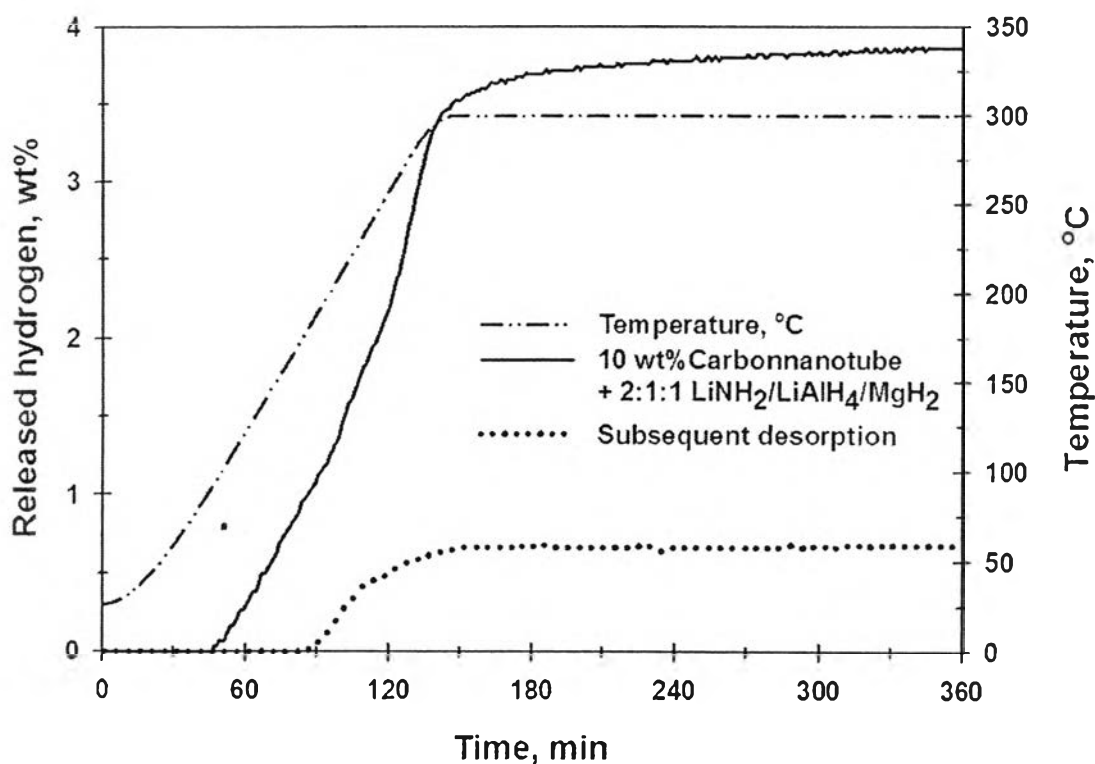
Figure 4.19 presents the TPD of the 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> sample doped with 5 wt% carbon nanotube. The results reveal that the amount of hydrogen rapidly increases in the temperature range of 90-250°C and then increases to 3.3 wt% at 300°C. In the case of hydrogen re-absorption, only 0.5 wt% hydrogen can be obtained. In addition, the desorption temperature increases to 175°C.



**Figure 4.19** Hydrogen desorption profiles of 5 wt% carbon nanotube + 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> and its subsequent desorption.

### 4.7.2 10 wt% Carbon nanotube + 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub>

The TPD of 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> doped with 10 wt% carbon nanotube is shown in Figure 4.20. The results show that hydrogen starts to release at about 90°C. After that, the amount of hydrogen increases in the temperature range of 90-300°C, and then it reaches 3.8 wt% at 300°C.



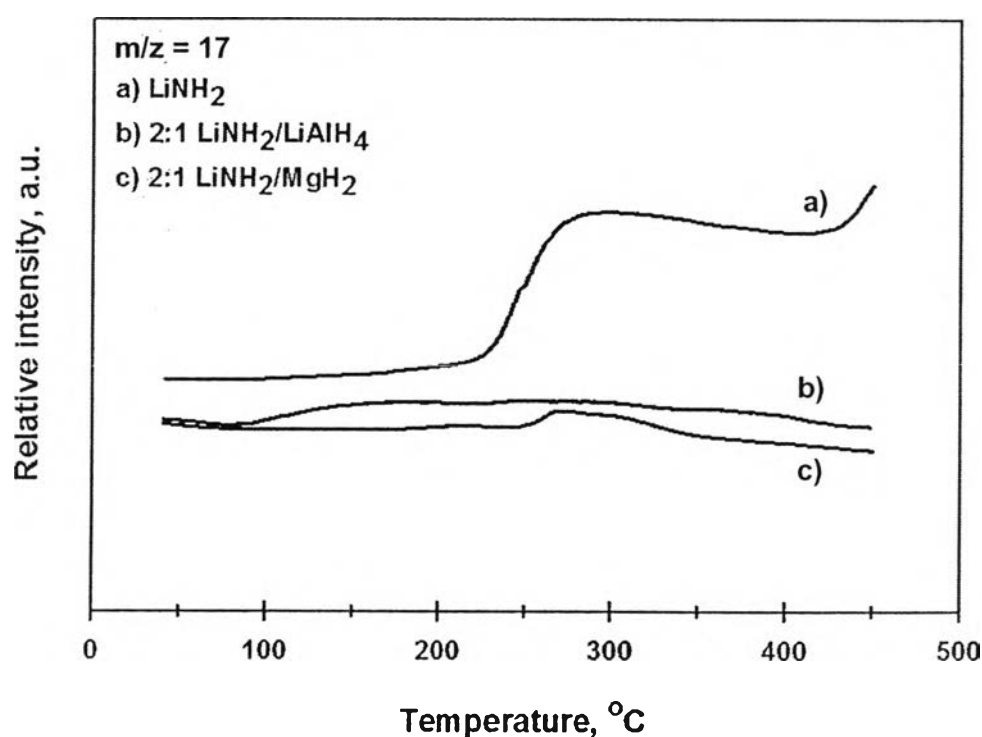
**Figure 4.20** Hydrogen desorption profiles of 10 wt% carbon nanotube + 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> and its subsequent desorption.

In the case of hydrogen re-absorption, the subsequent desorption has about 0.7 wt% hydrogen (dotted line), which is higher than that added with 5 wt% carbon nanotube. That may be due to the higher amount of carbon nanotube could prevent the agglomeration of the hydrides at a greater extent. However, the amount of hydrogen in the subsequent desorption is smaller than the first desorption. In addition, the decomposition temperature increases to 175°C.

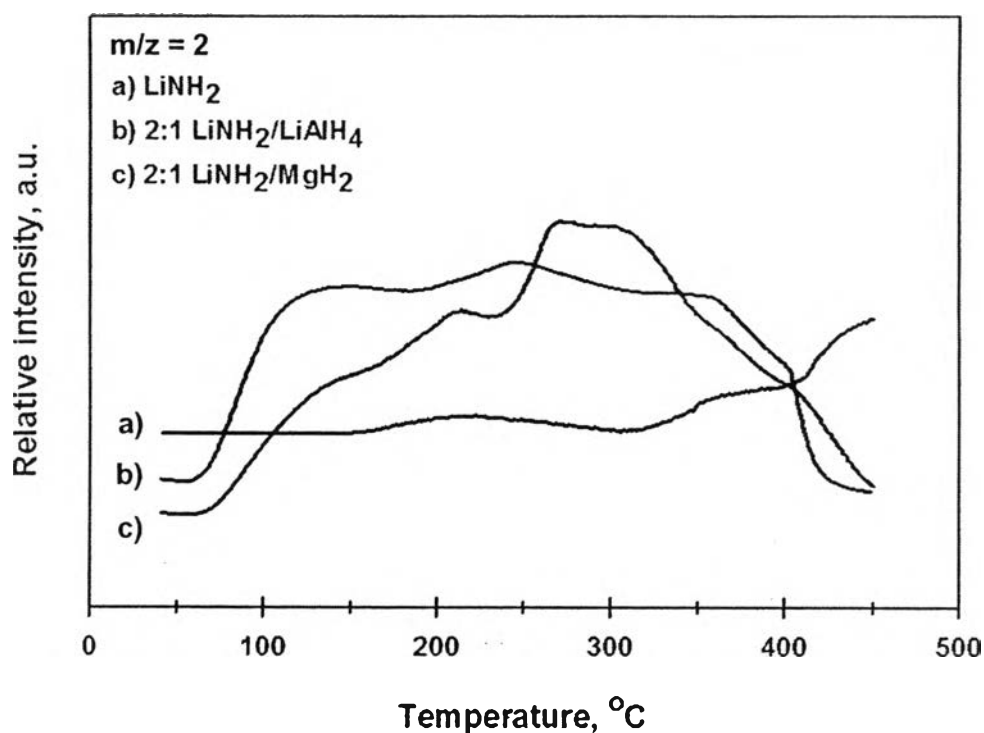
## 4.8 TPD and MS of 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub>

### 4.8.1 Effect of adding LiAlH<sub>4</sub> or MgH<sub>2</sub> on LiNH<sub>2</sub>

Figure 4.21 shows the TDMS of NH<sub>3</sub> emission from LiNH<sub>2</sub>, 2:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>, and 2:1 LiNH<sub>2</sub>/MgH<sub>2</sub> milling for 2 h. The result indicates that the emission profile of NH<sub>3</sub> ammonia ( $m/z = 17$ ) in neat LiNH<sub>2</sub> (Figure 4.21a) takes place around 150°C, after that the NH<sub>3</sub> emission profile distinctively increases at the temperature range of 200-300°C. For the 2:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub> sample (Figure 4.21b), NH<sub>3</sub> emits in the temperature range of 90-250°C and the intensity of NH<sub>3</sub> is much lower than that in neat LiNH<sub>2</sub>. For the 2:1 LiNH<sub>2</sub>/MgH<sub>2</sub> sample (Figure 4.21c), the NH<sub>3</sub> releases between 190-270°C with a significant peak at 270°C. However, its intensity is much lower than that neat LiNH<sub>2</sub>.



**Figure 4.21** MS spectra of ammonia ( $m/z = 17$ ): a) LiNH<sub>2</sub>, b) 2:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>, and c) 2:1 LiNH<sub>2</sub>/MgH<sub>2</sub>.



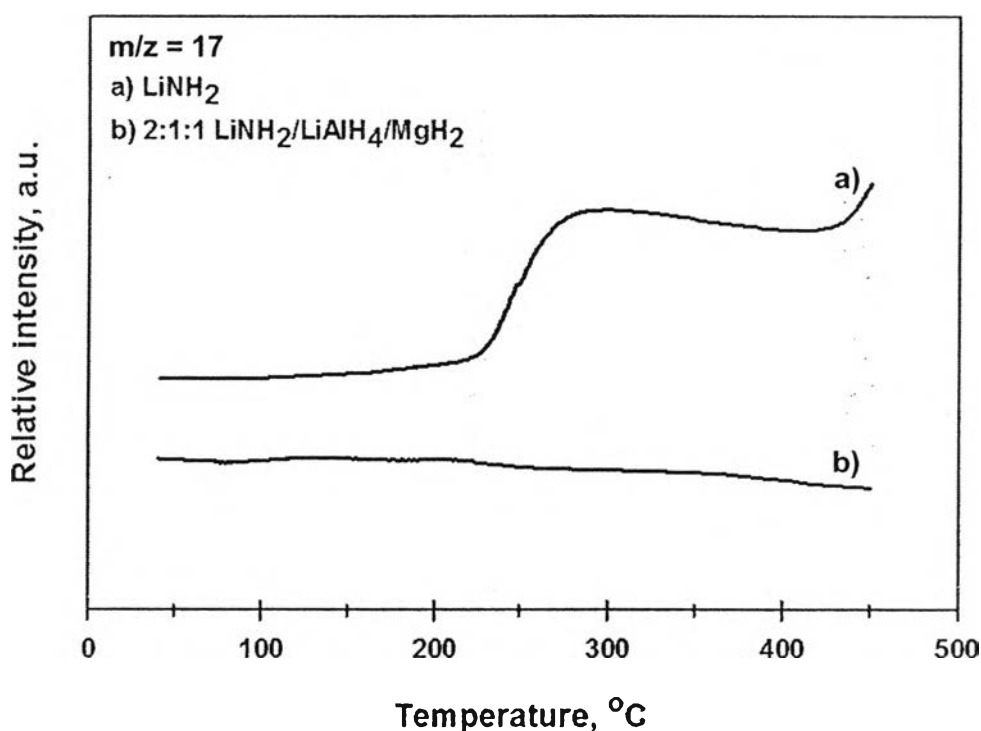
**Figure 4.22** MS spectra of hydrogen ( $m/z = 2$ ): a)  $\text{LiNH}_2$ , b) 2:1  $\text{LiNH}_2/\text{LiAlH}_4$ , and c) 2:1  $\text{LiNH}_2/\text{MgH}_2$ .

Figure 4.22 presents the TDMS of hydrogen emission from  $\text{LiNH}_2$ , 2:1  $\text{LiNH}_2/\text{LiAlH}_4$ , and 2:1  $\text{LiNH}_2/\text{MgH}_2$  milled for 2 h. The hydrogen emission profile of neat  $\text{LiNH}_2$  (Figure 4.22a) releases around  $150^\circ\text{C}$  and obviously increases at temperature higher than  $400^\circ\text{C}$ . For the 2:1  $\text{LiNH}_2/\text{LiAlH}_4$  sample (Figure 4.22b), the results indicate that hydrogen releases in the temperature range of  $80\text{--}250^\circ\text{C}$  and the intensity of hydrogen emission profile is much higher than that in neat  $\text{LiNH}_2$ . For the 2:1  $\text{LiNH}_2/\text{MgH}_2$  sample (Figure 4.22c), the hydrogen releases in temperature range of  $80\text{--}270^\circ\text{C}$  with a significant peak at  $270^\circ\text{C}$ . Moreover, its hydrogen intensity is much higher than that neat  $\text{LiNH}_2$ .

In addition, results from both Figures 4.21-4.22 show that adding  $\text{LiAlH}_4$  or  $\text{MgH}_2$  decreases the temperature and intensity of  $\text{NH}_3$  emission from  $\text{LiNH}_2$  while it does not significantly affect the temperature of the hydrogen emission. The addition of  $\text{LiAlH}_4$  and  $\text{MgH}_2$  does not only decrease the  $\text{NH}_3$  emission, but it also increases the hydrogen desorption from  $\text{LiNH}_2$ .

#### 4.8.2 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub>

Figure 4.23 shows the TDMS of NH<sub>3</sub> emission from 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> milled for 2 h compared to neat LiNH<sub>2</sub>. The result indicates that no NH<sub>3</sub> is detected from 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> (Figure 4.23b) while a neat LiNH<sub>2</sub> (Figure 4.23a) releases NH<sub>3</sub> around 150°C, after that the NH<sub>3</sub> emission profile distinctively increases at the temperature range of 200-300°C. Moreover, the intensity of NH<sub>3</sub> from 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> is much lower than that from neat LiNH<sub>2</sub> as shown in Figure 4.23.

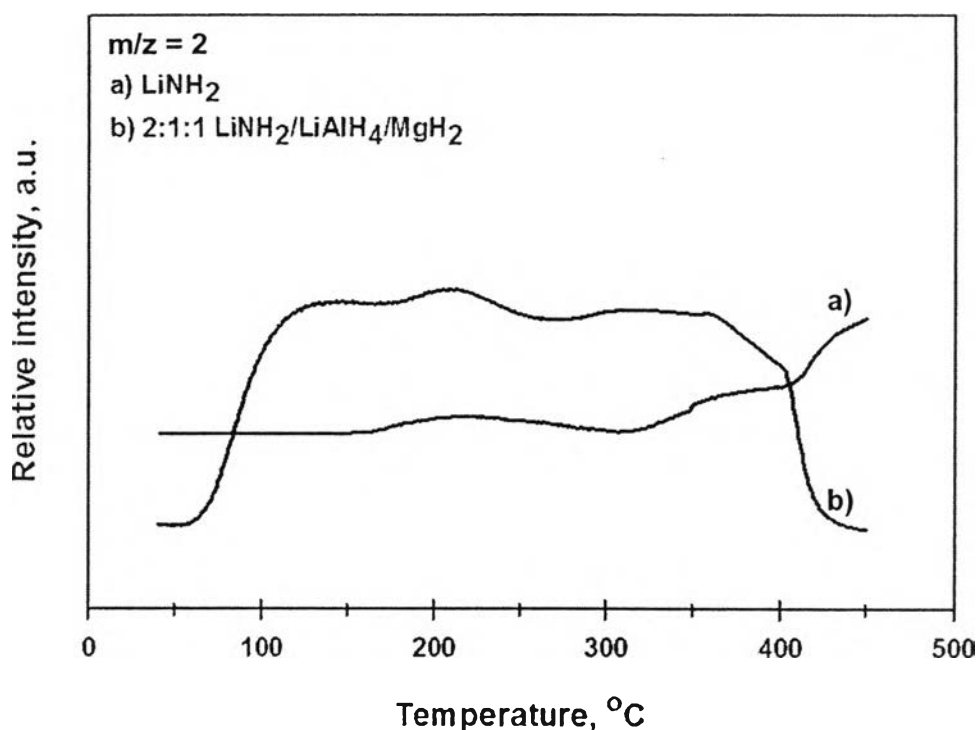


**Figure 4.23** MS spectra of ammonia ( $m/z = 17$ ): a) LiNH<sub>2</sub> and b) 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub>

The TDMS of hydrogen emission from 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> milled for 2 h is presented in Figure 4.24b. It reveals that hydrogen releases at temperature 80°C and its intensity is higher than that from neat LiNH<sub>2</sub> which releases hydrogen at temperature around 150°C and obviously increases at temperature higher than 400°C.

In addition, it is worth mentioning that adding LiNH<sub>2</sub> with MgH<sub>2</sub> or LiAlH<sub>4</sub> accelerates the decomposition of the hydriding by lowering the onset

desorption temperature from 80°C to 250°C. Moreover, adding  $\text{LiAlH}_4$  and  $\text{MgH}_2$  can suppress the formation of  $\text{NH}_3$  in the mixture.



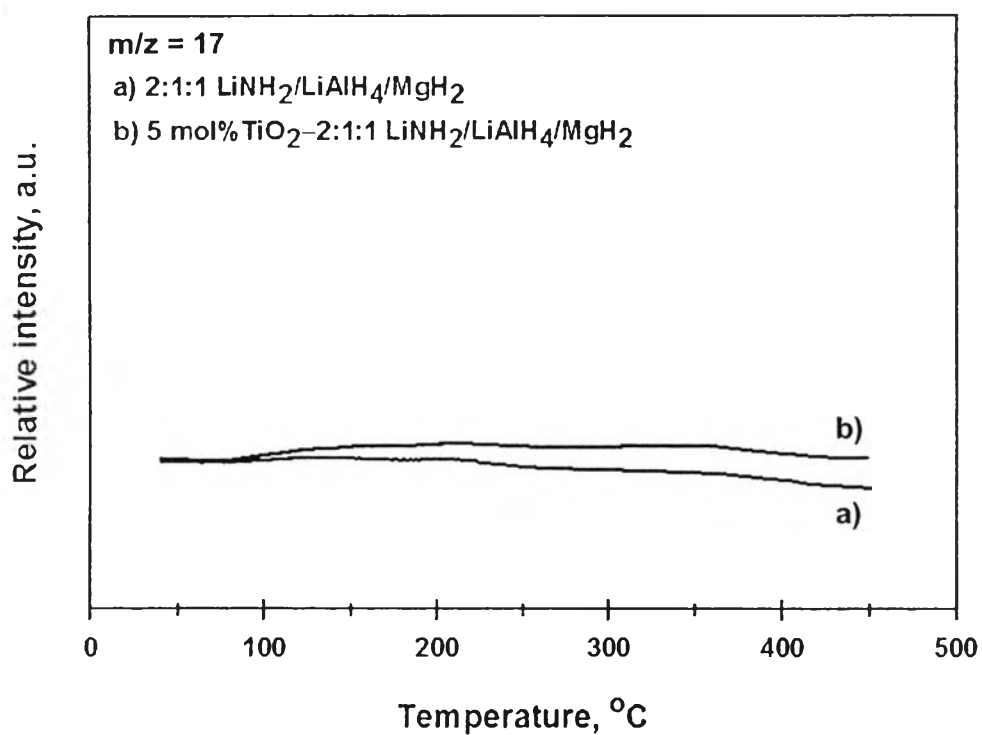
**Figure 4.24** MS spectra of hydrogen ( $m/z = 2$ ): a)  $\text{LiNH}_2$  and b) 2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$

#### 4.8.3 Effect of Ti compounds on 2:1:1 $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$

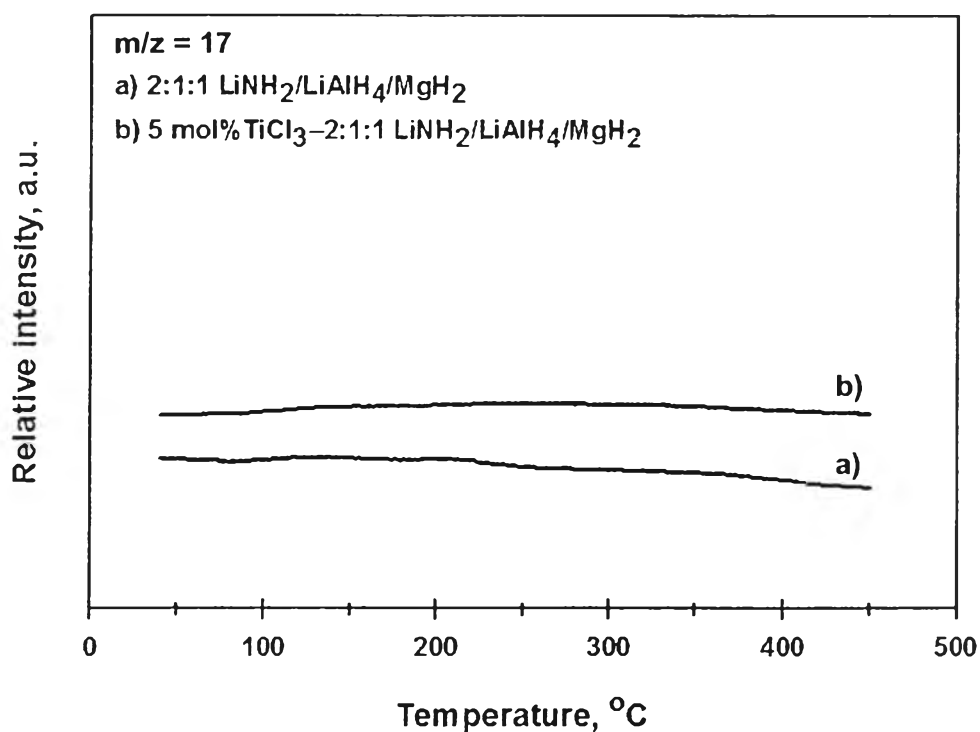
Figures 4.25, 4.26, and 4.27 show the TDMS of  $\text{NH}_3$  emission from 2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$  doped with  $\text{TiO}_2$ ,  $\text{TiCl}_3$ , and Ti, respectively. The emission profiles show almost the same results, which indicates that a very small amount of  $\text{NH}_3$  is released from doped Ti and Ti compounds ( $\text{TiO}_2$  and  $\text{TiCl}_3$ ) in 2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$  compared to the undoped one. It could be noticed that  $\text{TiO}_2$ ,  $\text{TiCl}_3$ , and Ti suppress the emission of  $\text{NH}_3$  in the doped mixtures. Moreover, the intensity of  $\text{NH}_3$  in the doped mixtures is also much lower than that in neat  $\text{LiNH}_2$ .

Comparison of TDMS of hydrogen emission between the doped samples and undoped (Figures 4.28, 4.29, and 4.30) shows that hydrogen releases at 80°C and the intensity of hydrogen emissions are the same. This means that there is no significant difference in the dehydrating of doped samples.

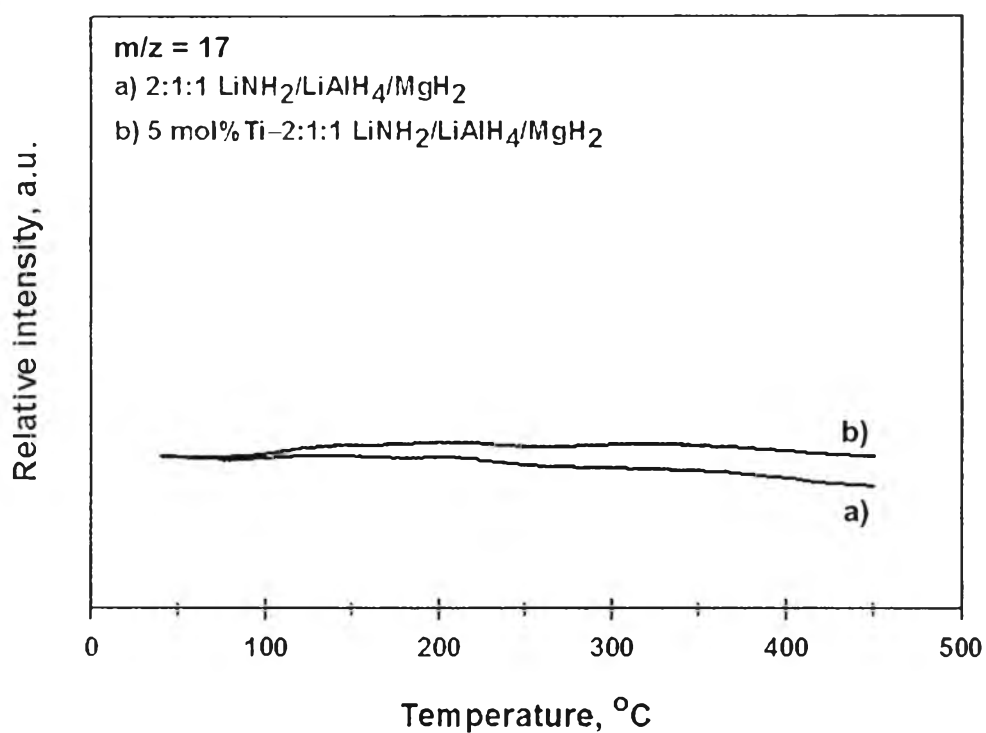




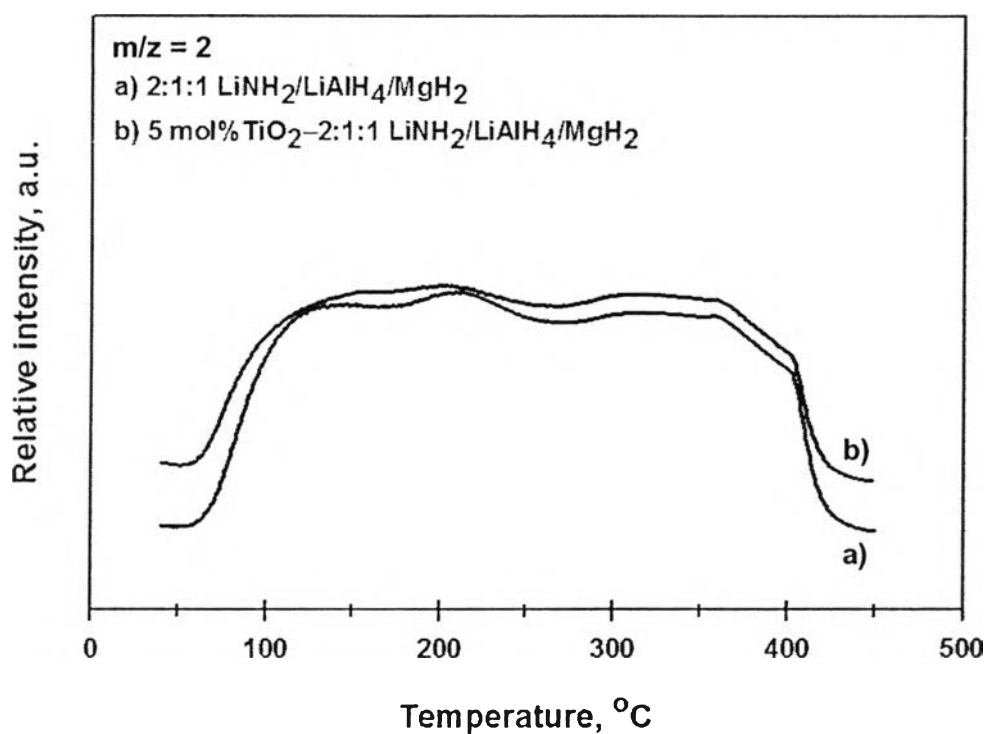
**Figure 4.25** MS spectra of ammonia ( $m/z = 17$ ): a) 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> and b) 5 mol%TiO<sub>2</sub>-2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub>



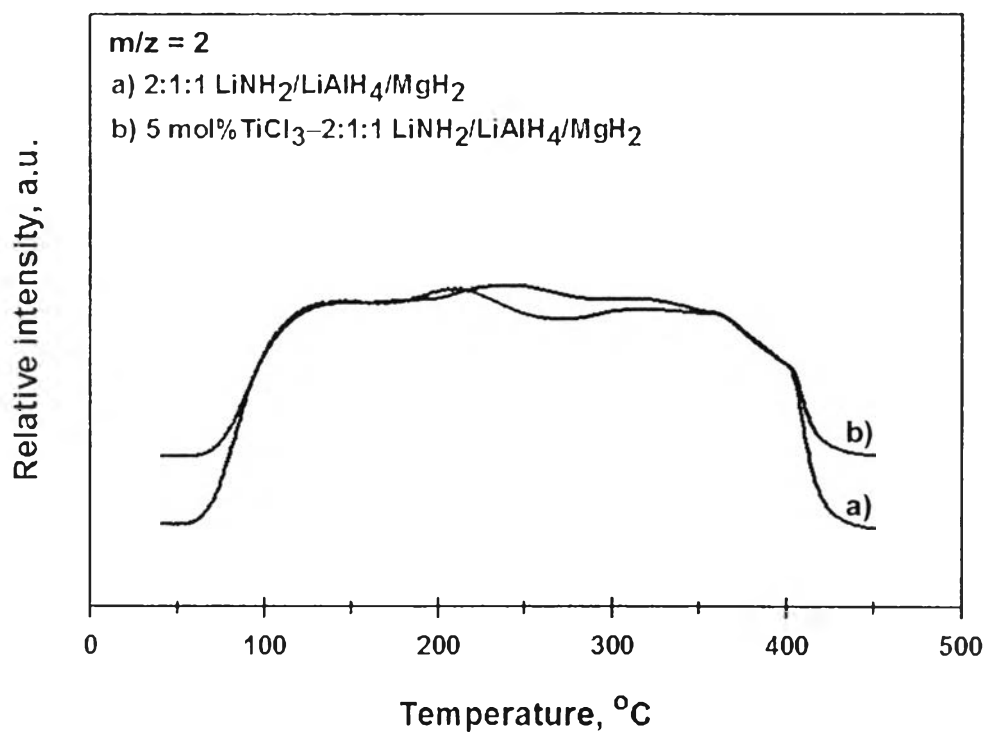
**Figure 4.26** MS spectra of ammonia ( $m/z = 17$ ): a) 2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub> and b) 5 mol%TiCl<sub>3</sub>-2:1:1 LiNH<sub>2</sub>/LiAlH<sub>4</sub>/MgH<sub>2</sub>



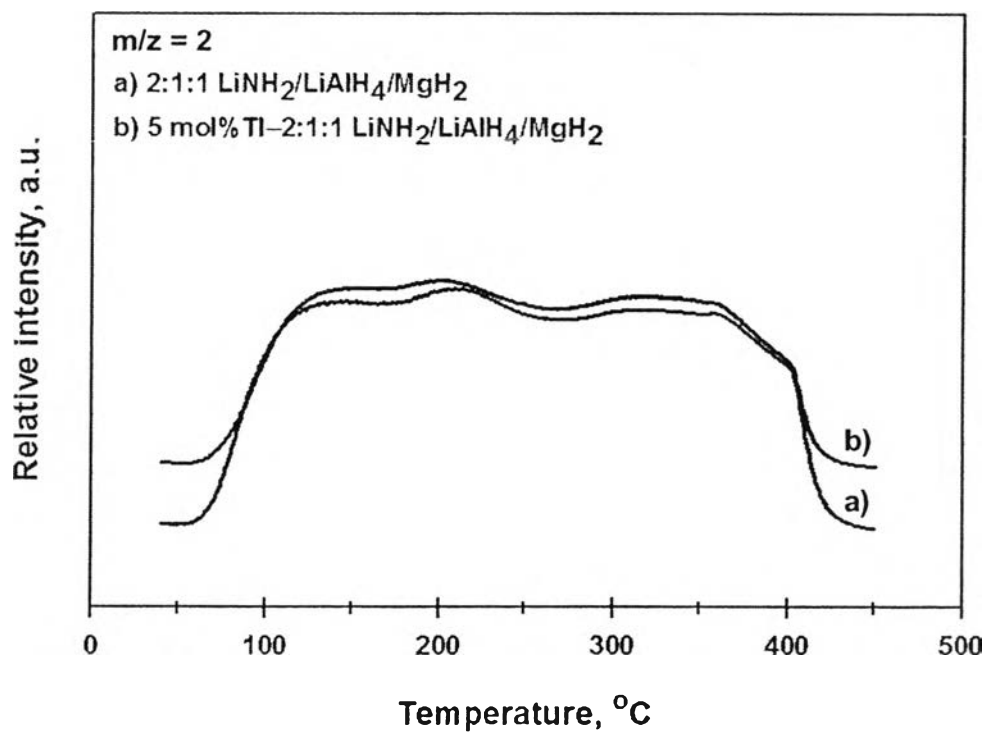
**Figure 4.27** MS spectra of ammonia ( $m/z = 17$ ): a) 2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$  and b) 5 mol%Ti-2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$



**Figure 4.28** MS spectra of hydrogen ( $m/z = 2$ ): a) 2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$  and b) 5 mol% $\text{TiO}_2$ -2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$



**Figure 4.29** MS spectra of hydrogen ( $m/z = 2$ ): a) 2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$  and b) 5 mol%  $\text{TiCl}_3$ -2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$



**Figure 4.30** MS spectra of hydrogen ( $m/z = 2$ ): a) 2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$  and b) 5 mol%  $\text{Ti}$ -2:1:1  $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$