

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effects of H₂TPP and HfCl₂TPP on the hydrogen desorption of HfCl₄-NaAlH₄

4.1.1 Hydrogen Desorption

The thermovolumetric apparatus was used to study the hydrogen desorption of NaAlH₄ and catalysts (HfCl₄, H₂TPP and HfCl₂TPP) doped NaAlH₄. The high pressure stainless steel reactor was heated from room temperature to 280 °C at the heating rate of 7 °C min⁻¹ via a furnace controlled by a PID temperature controller. The K-type thermocouple was placed inside the reactor to measure the temperature.

The hydrogen desorption of undoped NaAlH₄ (**S1**) occurs at about 185 °C and completes the reaction at about 260 °C with total released hydrogen of 5.5 wt% (Table 4.1 and Figure 4.1).

The hydrogen desorption of NaAlH₄ doped with 4 mol% HfCl₄ (**S2**) occurs at about 90 °C and completes the reaction at about 260 °C with total released hydrogen of 5.6 wt% (Table 4.1 and Figure 4.1).

In order to reduce the alloys formation and enhance the performance of the decomposition of HfCl₄-NaAlH₄, the effects of H₂TPP and HfCl₂TPP on the decomposition of HfCl₄-NaAlH₄ were studied. When all the components were mixed together, the hydrogen desorption of 1mol% H₂TPP-HfCl₄-NaAlH₄ (**S3**), 0.1mol% H₂TPP-HfCl₄-NaAlH₄ (**S4**), 1mol% HfCl₂TPP-HfCl₄- NaAlH₄ (**S5**) and 0.1mol% HfCl₂TPP-HfCl₄-NaAlH₄ (**S6**) occur at the temperature in range of 170-220 °C. The desorption temperature of H₂TPP and HfCl₂TPP doped on the HfCl₄-NaAlH₄ (170 °C) is higher than the desorption temperature of HfCl₄ doped NaAlH₄ (**S2**) (90 °C). It was observed that the higher amount of the doped co-catalysts decreased the amount of released hydrogen (3.0 - 4.5 wt%) and increased the temperature of desorption as shown in Table 4.1 and Figure 4.1 (**S3** – **S6**). Moreover, when all the components were mixed together, the hydrogen re-absorption cannot occur. It is probably because of the aggregation of the compounds in the system after the hydrogen desorption.

It was unexpectedly found that the 1st dehydrogenation of sample with the addition of 0.1 mol% H₂TPP as a co-catalyst after the mixing of HfCl₄-NaAlH₄ (S7), took place at 75 °C and the amount of hydrogen released reached 5.2 wt%. However, the subsequent dehydrogenation cycles occurred at higher temperature (90-150 °C) and the amount of hydrogen released is about 0.7-1.0 wt% as shown in Table 4.1 and Figure 4.2.

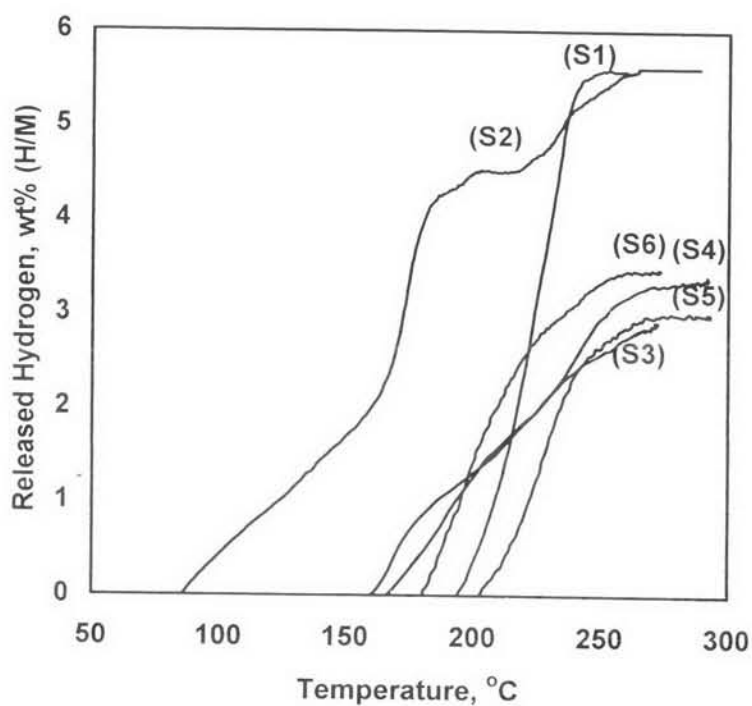
The addition of 0.01 mol% H₂TPP as a co-catalyst after the mixing of HfCl₄-NaAlH₄ (S8), it was found that the hydrogen desorption temperature in the 1st desorption and the subsequent desorption (100 °C and 132 °C respectively) are higher than those with 0.1 mol% H₂TPP (75 °C and 90 °C respectively). However, the hydrogen desorption capacity of NaAlH₄ doped with 4 mol% HfCl₄ before added 0.01 mol% H₂TPP (S8) reached 5.3 wt% and the amount of hydrogen released in the subsequent cycles is about 0.7-2.1 wt%, reported in Table 4.1 (S8) and Figure 4.3. It was observed that when the small amount of H₂TPP were doped the amount of released hydrogen in the 1st desorption and the subsequent desorption are increased to 5.3 wt% and 0.7-2.1 wt%, respectively.

From the desorption processes of undoped NaAlH₄ (S1) and doped NaAlH₄ (S2-S6), it was observed that the decomposition temperature has been shifted to higher temperature after the first cycle. It may be because, after the first desorption, the NaAlH₄ melts due to the experiment was performed at the high temperature (up to 260 °C) (higher than the melting point, 178 °C; Bogdanovic *et al.*, 2000 [9]), resulted in the agglomeration of NaAlH₄, which, in turn, causes the incomplete reabsorption of hydrogen and the need for higher temperature for decomposition. These also causes the non-reabsorption in the dehydrogenation processes of NaAlH₄ doped with the co-catalysts.

Table 4.1 Effects of HfCl_4 , H_2TPP and HfCl_2TPP doping on NaAlH_4

| Samples | Catalyst doped on NaAlH_4 (%mol) | | | Hydrogen capacity (wt%) | | Temperature of desorption in range ($^{\circ}\text{C}$) | |
|------------------|---|------------------------|---------------------------|----------------------------|-----------------------|---|-----------------------|
| | HfCl_4 | H_2TPP | HfCl_2TPP | 1 st desorption | Subsequent desorption | 1 st desorption | Subsequent desorption |
| S1 | - | - | - | 5.5 | - | 185-260 | - |
| S2 | 4 | - | - | 5.6 | 2.2-2.6 | 90-260 | 150-220 |
| S3 | 4 | 1 | - | 2.9 | - | 170-270 | - |
| S4 | 4 | 0.1 | - | 3.4 | - | 165-270 | - |
| S5 | 4 | - | 1 | 2.9 | - | 200-270 | - |
| S6 | 4 | - | 0.1 | 3.5 | - | 180-260 | - |
| S7 ^{a)} | 4 | 0.1 | - | 5.2 | 0.7-1.0 | 75-260 | 90-260 |
| S8 ^{a)} | 4 | 0.01 | - | 5.3 | 0.7-2.1 | 100-300 | 132-260 |

^{a)} mix 4mol% HfCl_4 - NaAlH_4 before added H_2TPP

Figure 4.1 Temperature program desorption from room temperature to 280 $^{\circ}\text{C}$ of S1-S6

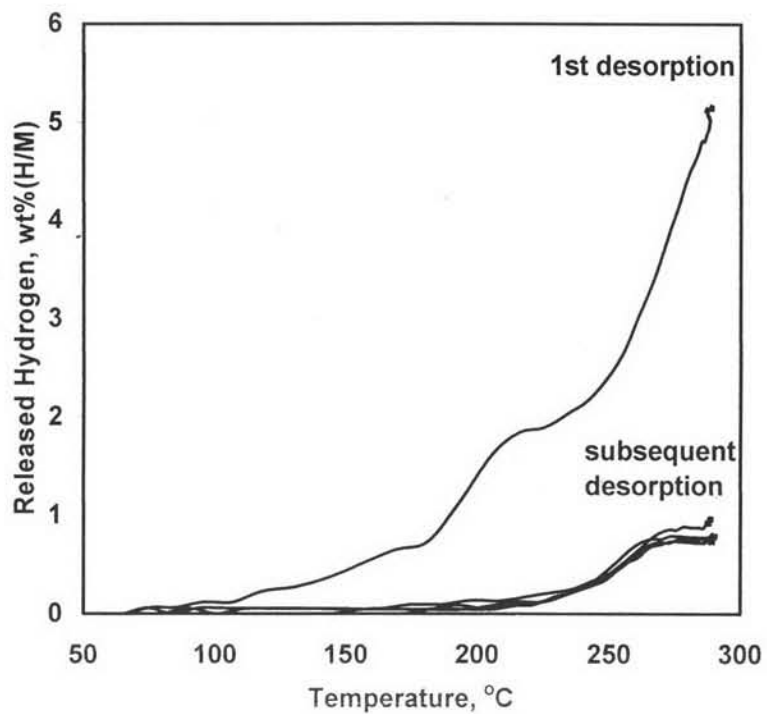


Figure 4.2 Temperature program desorption from room temperature to 280 °C of S7

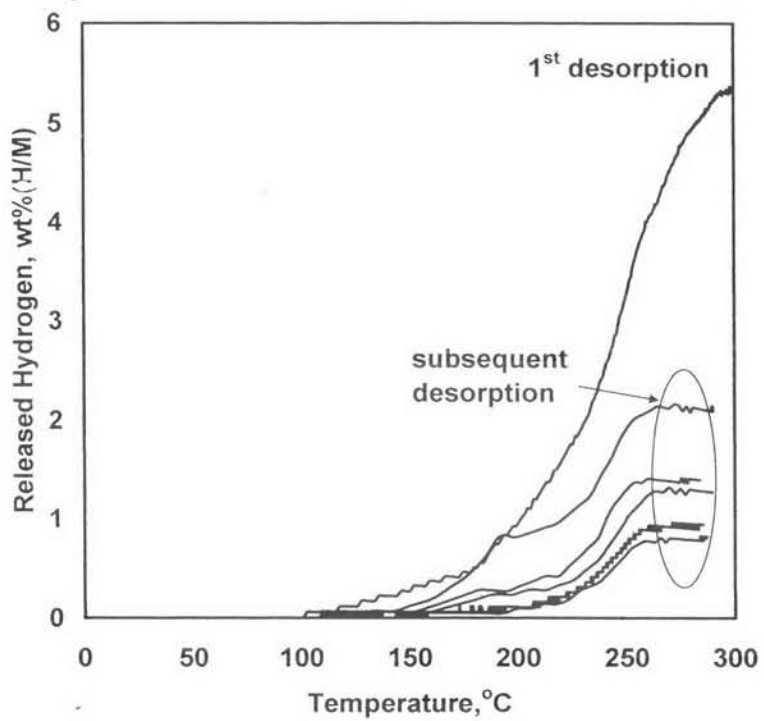


Figure 4.3 Temperature program desorption from room temperature to 280 °C of S8

In conclusion, the hydrogen desorption of $\text{HfCl}_4\text{-NaAlH}_4$ with the organic compound (H_2TPP and HfCl_2TPP), when mixed at once, take place at the temperature range of 170-220 °C, the pressure of 11MPa with 4.5 wt% (when added H_2TPP into doped NaAlH_4) and with about 3 wt% (when added HfCl_2TPP into doped NaAlH_4). The amount of the organic compound which was added to $\text{HfCl}_4\text{-NaAlH}_4$ contribute to low hydrogen desorption and the rehydrogenation cannot occur. Unexpectedly, when mixed 4mol% $\text{HfCl}_4\text{-NaAlH}_4$ before added H_2TPP , the hydrogen desorption occur at 75 °C (lower than the one without H_2TPP (90 °C)) with about 5.2 wt% hydrogen released and the subsequent desorption occur at 90 °C with about 0.7-1.0 wt% hydrogen released. Moreover, when small amount of H_2TPP (0.01 wt%) were doped, the amount of released hydrogen in the 1st desorption and the subsequent desorption are increased to 5.3 wt% and 0.7-2.1 wt%, respectively.

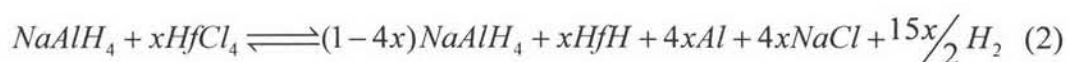
4.1.2 Characterization of H_2TPP and HfCl_2TPP on the hydrogen desorption of $\text{HfCl}_4\text{-NaAlH}_4$ by XRD

To elicit the roles of catalysts on the hydrogen desorption/absorption of NaAlH_4 , the sample was characterized by an X-ray diffractometer at room temperature over a range of diffraction angle from 2θ 20°- 80° with CuK-alpha radiation ($\lambda=1.54 \text{ \AA}$, 40 kV, 30 mA). Due to the powder samples are the air sensitive substances, before the X-ray diffraction analysis, they were covered with Kapton tape. This results in the reduction of the signal to noise ratio, and the resolution of the obtained X-ray diffraction. However, the diffraction peaks and their relative intensities are sufficient quality for qualitative analysis.

The XRD patterns of the undoped NaAlH_4 (S1) and the doped NaAlH_4 with 4mol% HfCl_4 (S2), compared with the reference pattern of NaAlH_4 (085-0374) and NaCl (088-2300), are illustrated in Figure 4.4. From the XRD patterns indicate that NaAlH_4 is a major crystalline phase and NaCl is a minor crystalline phase. The present of a small amount of NaCl in the samples may be because of the decomposition of some NaAlH_4 phases by the HfCl_4 doping, as show in equation (1).



Figure 4.4 is the XRD patterns of undoped NaAlH_4 (S1) and 4 mol% HfCl_4 doped NaAlH_4 (S2) before desorption compared to the reference patterns of NaAlH_4 (085-0374) and NaCl (088-2300). From the XRD patterns of 4 mol% HfCl_4 doped NaAlH_4 (S2) before desorption, there is no reflection peaks that could be related to Hf species (according to eq.1), even though there is a significant amount of hafnium in the samples, The absence of Hf peaks indicate that it completely converse to HfH during the doping reaction (eq. 2). The presence of HfH peaks are shown in Figure 4.6.



The XRD patterns of the catalysts doped NaAlH_4 with 4mol% HfCl_4 and H_2TPP or HfCl_2TPP (samples S3 to S6) before desorption processes are shown in Figure 4.5. The main crystalline phase detected by XRD is NaAlH_4 and a minor crystalline phase is NaCl . The XRD patterns of the catalysts doped NaAlH_4 with 4 mol% HfCl_4 and H_2TPP or HfCl_2TPP (samples S3 to S6) are pertinent to the XRD patterns of the undoped NaAlH_4 (S1) and the doped NaAlH_4 with 4 mol% HfCl_4 (S2).

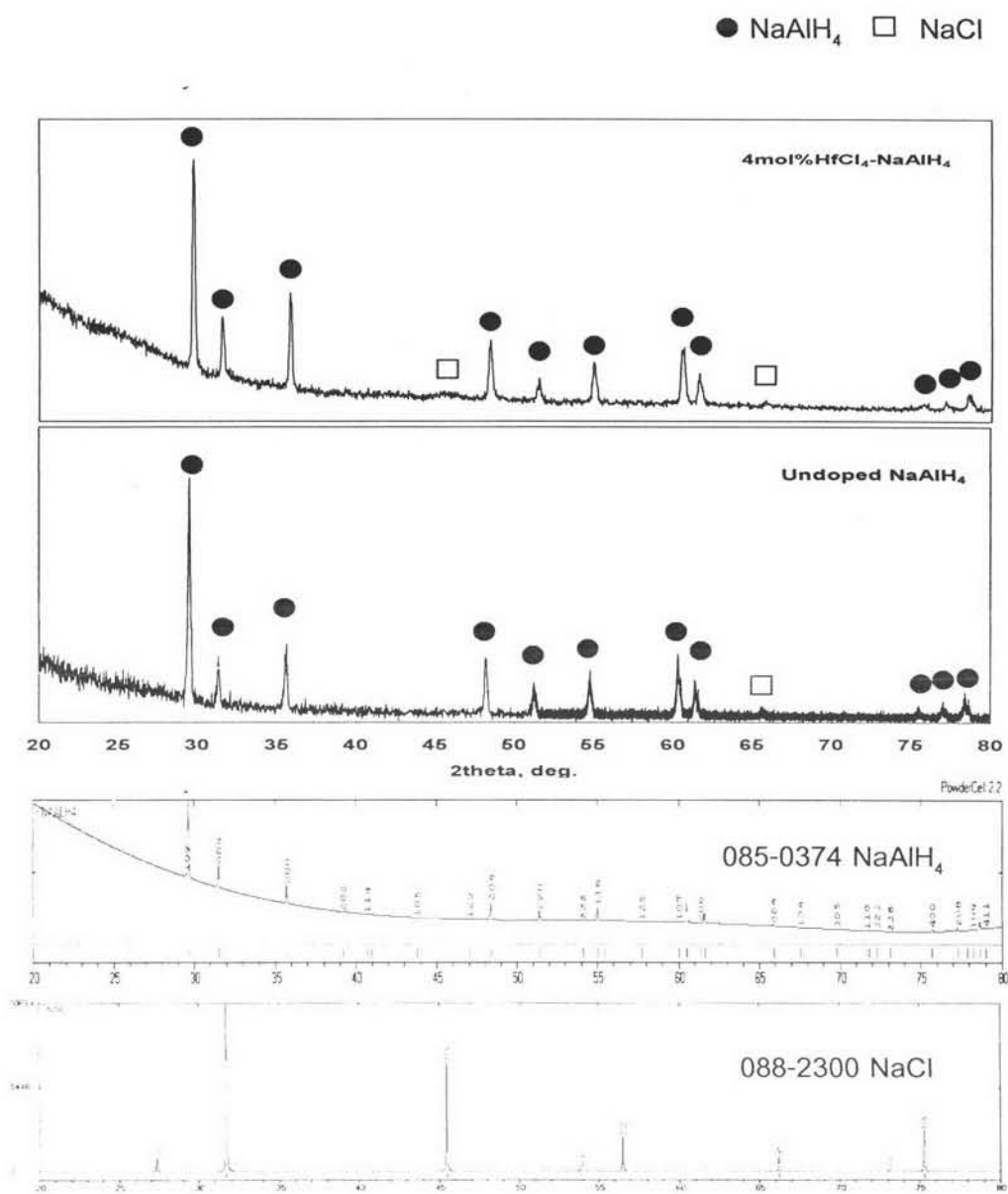


Figure 4.4 XRD patterns of undoped NaAlH₄ (S1) and 4mol%HfCl₄ doped NaAlH₄ (S2) before desorption compared to the reference patterns of NaAlH₄ (085-0374) and NaCl (088-2300)

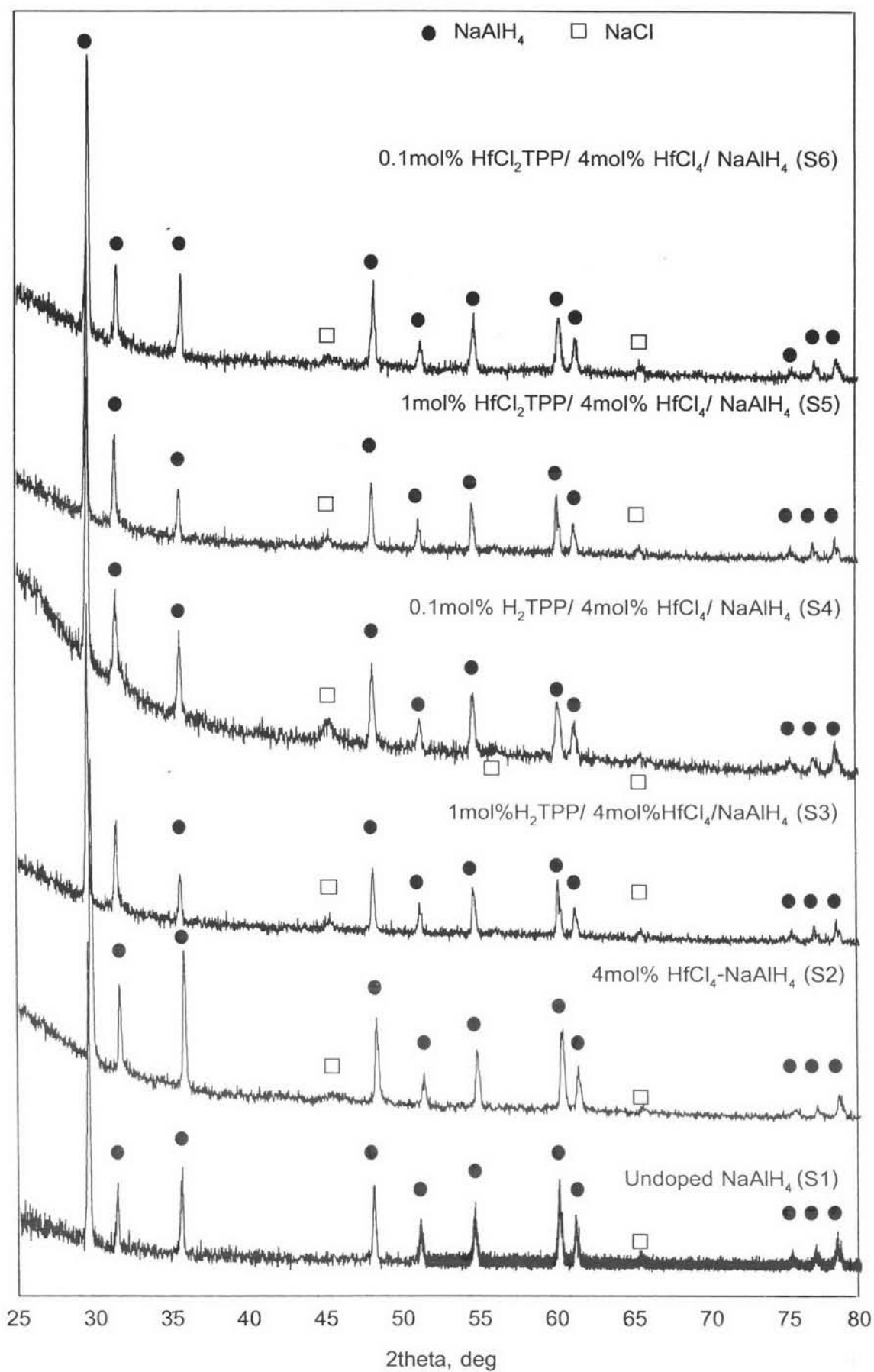


Figure 4.5 XRD patterns of samples S1 to S6 before desorption.

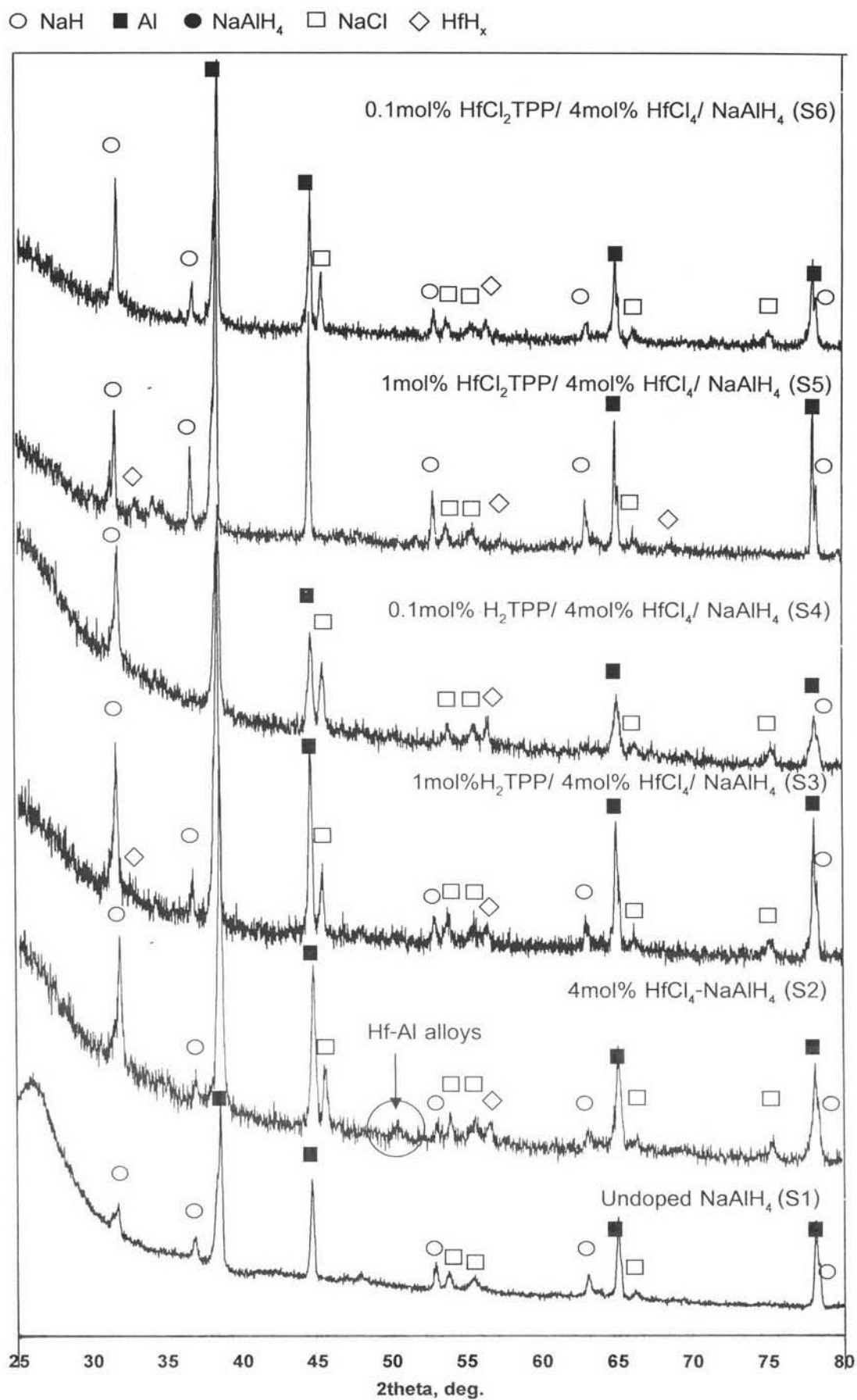
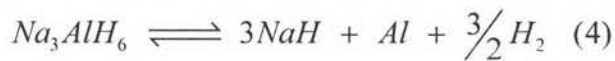
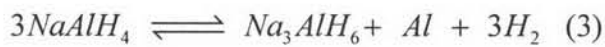


Figure 4.6 XRD patterns of samples S1 to S6 after desorption

Figure 4.6 shows the XRD patterns of **S1** to **S6** after the desorption processes. The diffraction peaks of NaH, Al and NaCl were presented in **S1**. The increase in the intensity and narrow peak of aluminum shows the formation of aluminum crystallites. The desorption of undoped NaAlH₄ resulted in the conversion of the NaAlH₄ to NaH and Al. The decomposition of Sodium alanate (NaAlH₄) was represented in the two equations. The proposed decomposition mechanism is a series of reactions that show a simple progress from starting material (NaAlH₄) to the intermediate (Na₃AlH₆) according to eq.3 and from intermediate to the final products (NaH and Al) according to eq.4.



Furthermore, it was observed the peak of HfH_x in the patterns of HfCl₄-NaAlH₄ doped with H₂TPP or HfCl₂TPP (**S2-S6**) (see Figure 4.6(**S2-S6**)). The appearance of HfH_x peaks at 2θ ≈ 55.53° show in XRD patterns of **S2**, **S3**, **S4**, **S6** and at 2θ ≈ 33.15°, 38.60°, 55.53° and 66.29° show in XRD patterns of **S5**. Peak identification using reference XRD pattern database (JCPDS-International Centre for Diffraction Data) suggests that they would be the diffraction of HfH_{1.98} (2θ ≈ 33.05°, 36.2°, 52.91°, 63.99°, and 78.14°), HfH_{1.628} (2θ ≈ 33.05°, 38.46°, 55.55° and 66.30°) and HfH_{1.5} (2θ ≈ 33.04°, 34.25°, and 36.45°). Therefore, this indicates the possibility of the HfH_x formation during the hydrogen desorption. As illustrated in Figure 4.7, the XRD pattern of sample **S5** compared with the XRD pattern of HfH_{1.98}, HfH_{1.628} and HfH_{1.5}. The HfH_x formation could form by the decomposition reaction of HfH₄ as following in eq. 5.



It was observed the peak at 2θ ~ 50.5° in the XRD patterns of **S2** (Figure 4.6). Suttisawat and co-workers [30] suggest that the formation of Hf-Al alloys shows XRD diffraction peaks at 2θ ~ 41.5° and 50.48°. However, there is no peaks at 2θ ~ 50.5° in the XRD patterns of **S3-S6** (sample of HfCl₄-NaAlH₄ doped with H₂TPP or HfCl₂TPP).

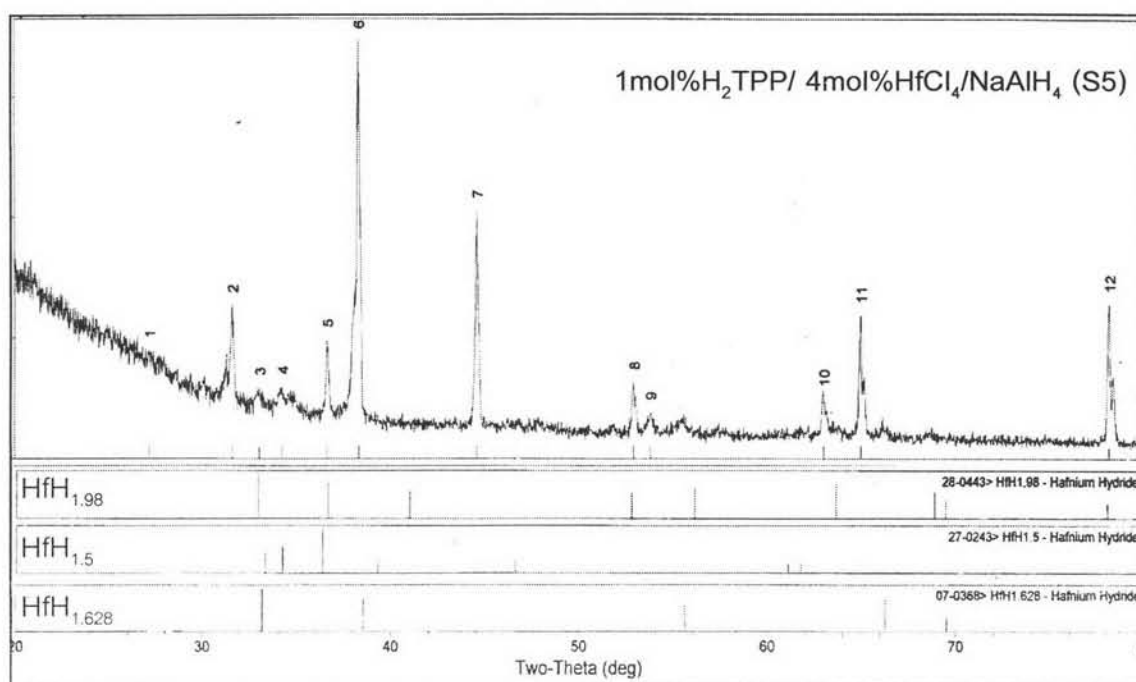


Figure 4.7 XRD pattern of sample S5 compared with the XRD pattern of $\text{HfH}_{1.98}$, $\text{HfH}_{1.628}$ and $\text{HfH}_{1.5}$.

The results which were obtained in this section could be concluded that after milling, NaAlH_4 doped with HfCl_4 and H_2TPP or HfCl_2TPP give the phases of NaAlH_4 and NaCl . After the hydrogen desorption, the doped NaAlH_4 decomposed to NaH , Al , NaCl and HfH_x .

From the results above, the hydrogen re-absorption processes cannot occur when all the components were mixed together. Then, the procedure of sample preparation was changed by mixed NaAlH_4 with 4 mol% HfCl_4 by milling for 10 minutes before adding 0.1 mol% H_2TPP and then milled for further 5 minutes. Figure 4.8 shows the XRD patterns of the mix 4 mol% HfCl_4 - NaAlH_4 before added 0.1 mol% H_2TPP (S7). The XRD patterns of the sample before desorbed shows NaAlH_4 crystalline phase. After the desorption of sample S7, it was observed the diffraction patterns of NaH , Al , NaCl and small peaks of HfH_x . This XRD patterns of sample S7 after desorption shows the complete dehydrogenation reaction of NaAlH_4 . The XRD patterns of sample S7 after re-

absorption, it was clearly observed the diffraction peaks of Na_3AlH_6 in the sample. From these results, it can be concluded that the re-absorption reaction of NaAlH_4 doped with 4 mol% HfCl_4 and 0.1 mol% H_2TPP does not complete and affect to decrease the amount of hydrogen released in the subsequent desorption cycles.

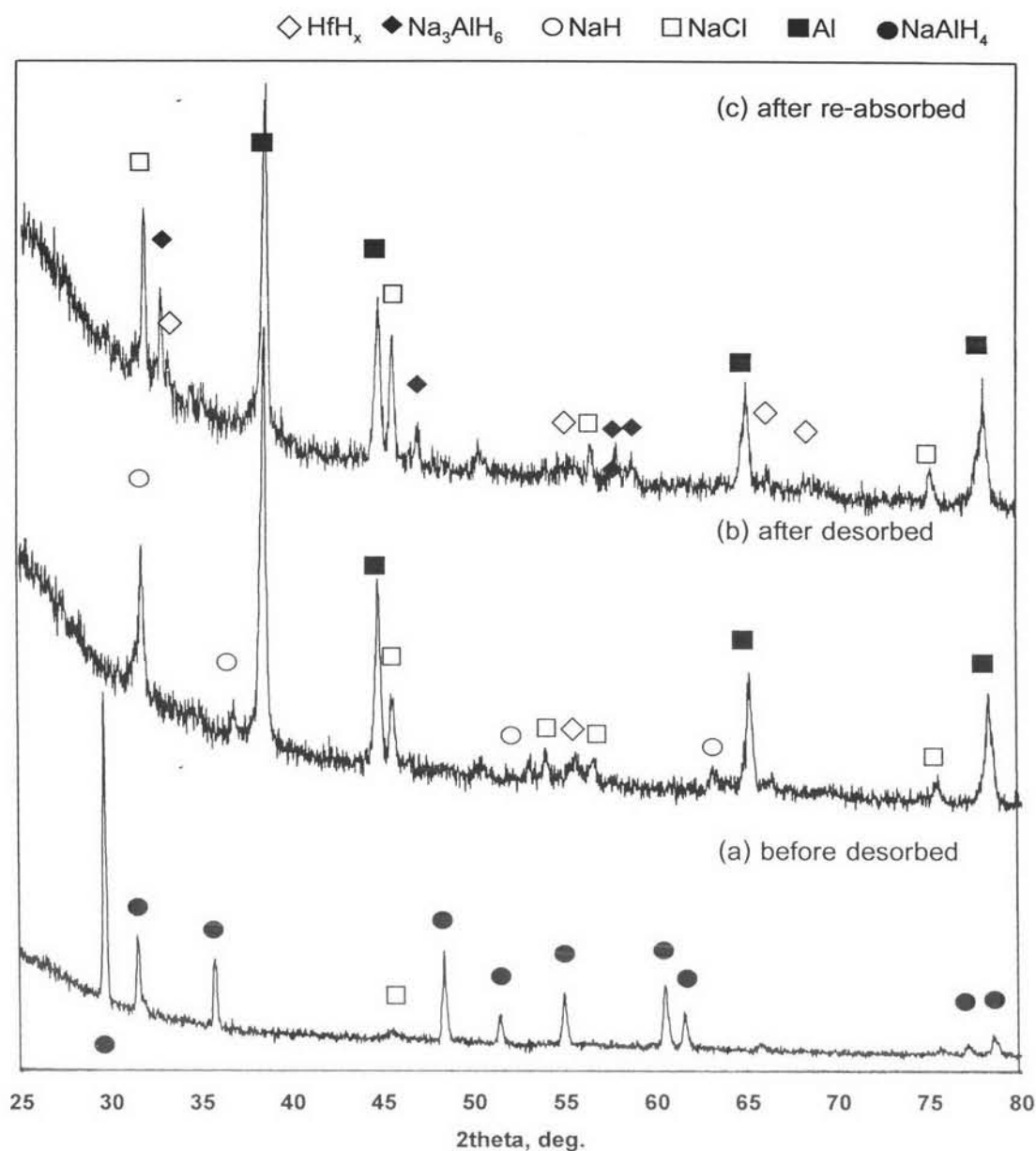


Figure 4.8 XRD patterns of samples S7 (the mix 4 mol% HfCl_4 - NaAlH_4 before added 0.1 mol% H_2TPP) ; (a) before desorbed, (b) after desorbed and (c) after re-absorbed.

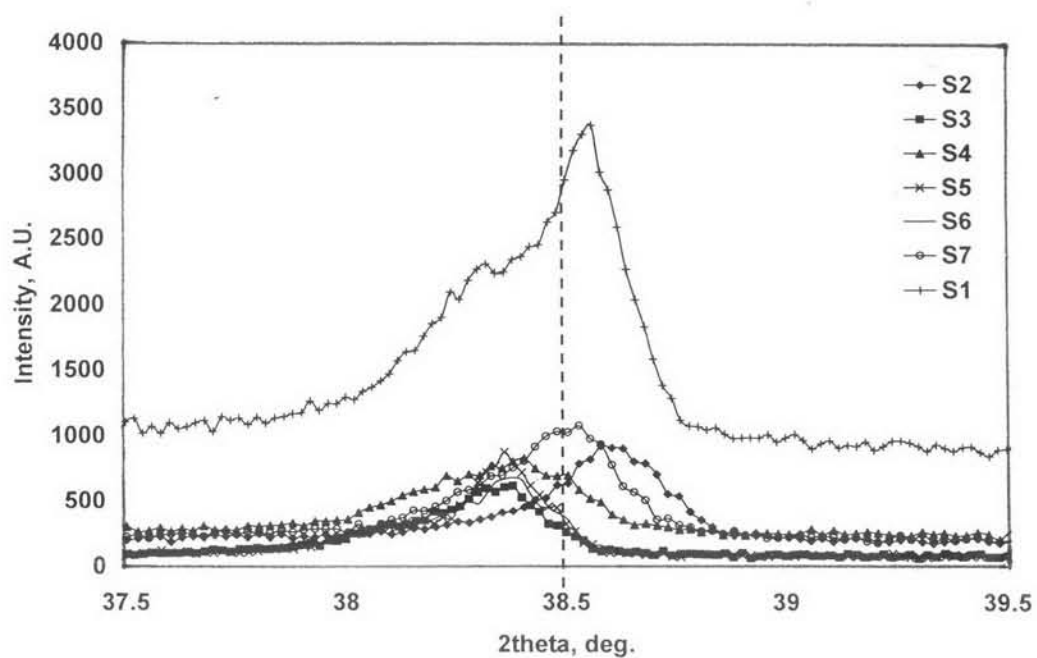
4.1.2.1 Aluminum reflection in XRD patterns of NaAlH_4 doped with HfCl_4 and porphyrins (S1-S7).

Consideration of the asymmetrical broadening of the main Al peaks at 2θ about 38.5° which are presented in S1-S7 (Figure 4.9) in order to investigate an intermetallic compound formation. The presence of the asymmetry is actually a shoulder which might be assigned to the presence of another crystalline phase (Bogdanovic, 2003 [11]). From bogdanovic work, The Al reflections show a clear asymmetry on the side of higher 2θ values. Because the Ti-Al alloy has the main diffraction peaks at 38.5° . The broad shoulders appear suggest that a crystalline Al-Ti alloy has formed during the phase transformation processes [11]. Suttisawat and co-workers [30] suggest that the formation of Hf-Al alloys shows XRD diffraction peaks at $2\theta \sim 41.5^\circ$ and 50.48° . The formation of Al_3Hf intermetallic compound is a stable compound that would decrease the activity of the catalyst. It would affect the reformation to NaAlH_4 and reduce the amount of Al metallic to absorb hydrogen.

Figure 4.9 shows Al reflections at $2\theta \sim 38.5^\circ$ of S1 to S7. S1 is an undoped NaAlH_4 while S2-S7 contained Hf species in the samples. The Al reflections positions compared with Al reflections of the reference Al patterns 085-1327 are in Table 4.2. The Al reflections of S1 to S7 present at $2\theta = 38.56^\circ, 38.58^\circ, 38.38^\circ, 38.41^\circ, 38.36^\circ, 38.38^\circ$ and 38.53° , respectively. It was observed that the Al reflections peaks of 4 mol% HfCl_4 - NaAlH_4 (S2) shifted about $+0.1^\circ 2\theta$. In contrast, the Al reflections peaks of S3-S6, which H_2TPP or HfCl_2TPP were added at once, shifted about $-0.1^\circ 2\theta$. The Al reflections peaks of S7 which 0.1 mol% H_2TPP was added after mixed 4 mol% HfCl_4 - NaAlH_4 does not shifted. Furthermore, the asymmetric peak and the broad shoulders on the side of higher 2θ values are no observed. Consideration the whole XRD patterns of samples which H_2TPP and HfCl_2TPP were added, there is no reflections peaks at $2\theta = 41.5^\circ$ and 50.48° . These results suggest that the formation of Hf-Al alloys does not occur in the hydrogen desorption processes of HfCl_4 - NaAlH_4 which H_2TPP or HfCl_2TPP were added.

Table 4.2 The Al reflections position of S1 to S7 compared with Al reflections 085-1327.

| Main peak position | 2θ ($^{\circ}$) | | | | | | | |
|--------------------|--------------------------|-------|-------|-------|-------|-------|-------|-------|
| | Al 085-1327 | S1 | S2 | S3 | S4 | S5 | S6 | S7 |
| 1 | 38.47 | 38.56 | 38.58 | 38.38 | 38.41 | 38.36 | 38.38 | 38.53 |
| 2 | 44.73 | 44.70 | 44.87 | 44.62 | 44.67 | 44.64 | 44.64 | 44.75 |
| 3 | 65.10 | 65.06 | 65.28 | 64.98 | 65.08 | 64.98 | 65.00 | 65.11 |

Figure 4.9 X-ray powder diffraction patterns of NaAlH_4 doped with HfCl_4 and porphyrin (S1-S7) observe at aluminium reflection.

4.1.3 The proposed decomposition mechanism

The decomposition mechanisms of NaAlH_4 doped with HfCl_4 have been proposed by monitoring the reaction at 80°C , 120°C , 180°C , 220°C and 250°C . The sample of NaAlH_4 doped with HfCl_4 was heated in a thermovolumetric apparatus at room temperature to 80°C , 120°C , 180°C , 220°C and 250°C and then describe the mechanism base on the XRD analysis. These events are marked by circles in Figure 4.10. The hydrogen evolution taking place at the same time was recorded. The heating was stop and small samples were removed to the XRD measurement. In parallel, the undoped NaAlH_4 was performed in the same procedure. These events are marked by rectangles in Figure 4.10.

4.1.3.1 *The decomposition mechanism of NaAlH_4 undoped .*

Table 4.3 shows the hydrogen desorption at different temperature stages of the undoped NaAlH_4 and 4 mol% HfCl_4 - NaAlH_4 . The hydrogen desorption was not detected when the undoped NaAlH_4 was heated to 80°C , 120°C and 180°C . The hydrogen desorption of undoped NaAlH_4 starts at 196°C (see Figure 4.10). At 220°C , the undoped NaAlH_4 shows about 2.9 wt% hydrogen released. It is 78.1% decomposed from NaAlH_4 . The undoped NaAlH_4 completely desorbed at 250°C with 5.5 wt%. The hydrogen desorption of NaAlH_4 doped with 4 mol% HfCl_4 occurs at about 75°C (see Figure 4.10). When 4 mol% HfCl_4 - NaAlH_4 was heated to 80°C , it is 13.5% decomposed from NaAlH_4 with 0.2 wt% hydrogen released. At 120°C and 180°C , it is 23.8% and 94.6% decomposed from NaAlH_4 with 0.9 wt% and 3.5 wt% hydrogen released, respectively. The 2nd dehydrogenation step occurs at the temperature over 180°C . It is 4.5 wt% hydrogen released at 220°C and complete at 250°C with 5.5 wt% hydrogen.

The XRD diffraction patterns of the undoped NaAlH_4 (Figure 4.11(b)) when heated to 120°C , the main crystalline phase of NaAlH_4 was observed in the dehydrogenated sample. After desorbed to 196°C , the crystalline phase detected at this stage is NaAlH_4 , follow by Na_3AlH_6 and Al (Figure 4.11(c)).The XRD indicates that the first dehydrogenation of NaAlH_4 start at the temperature over 180°C . This correspond to the desorption temperature program in Figure 4.10, show that it starts

desorption at 196 °C. The dehydrogenation after 250 °C, NaH could be detected as a new phase by XRD, also the Al peaks but no diffraction peaks of NaAlH₄. This suggests that the complete dehydrogenation occurs at this stage.

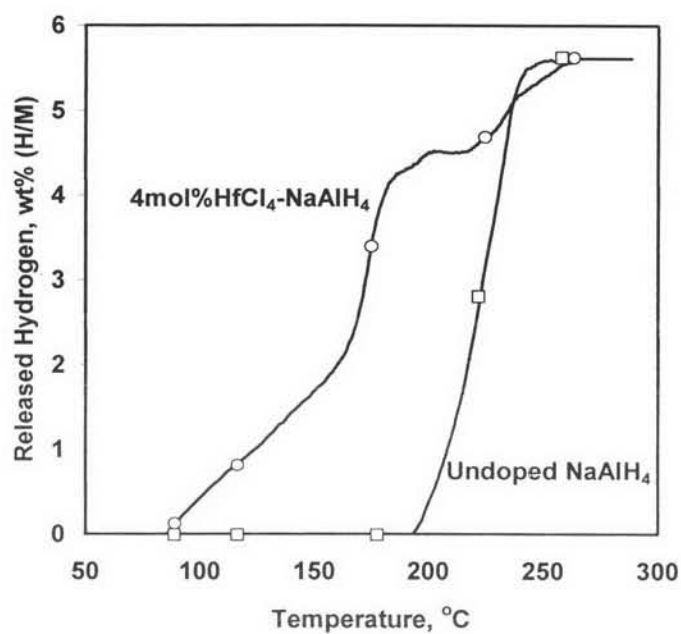


Figure 4.10 Dehydrogenation of NaAlH₄ and NaAlH₄ doped with HfCl₄

Table 4.3 Hydrogen desorption at different temperature stages.

| Desorption temperature (°C) | Undoped NaAlH ₄ | | 4mol% HfCl ₄ – NaAlH ₄ | |
|-----------------------------|----------------------------|--|--|--|
| | Released hydrogen (wt%) | Decomposed from NaAlH ₄ (%) | Released hydrogen (wt%) | Decomposed from NaAlH ₄ (%) |
| 80 | - | - | 0.2 | 13.5 |
| 120 | - | - | 0.9 | 23.8 |
| 180 | - | - | 3.5 | 94.6 |
| 220 | 2.9 | 78.4 | 4.5 | 44.5 |
| 250 | 5.5 | 100.0 | 5.5 | 100.0 |

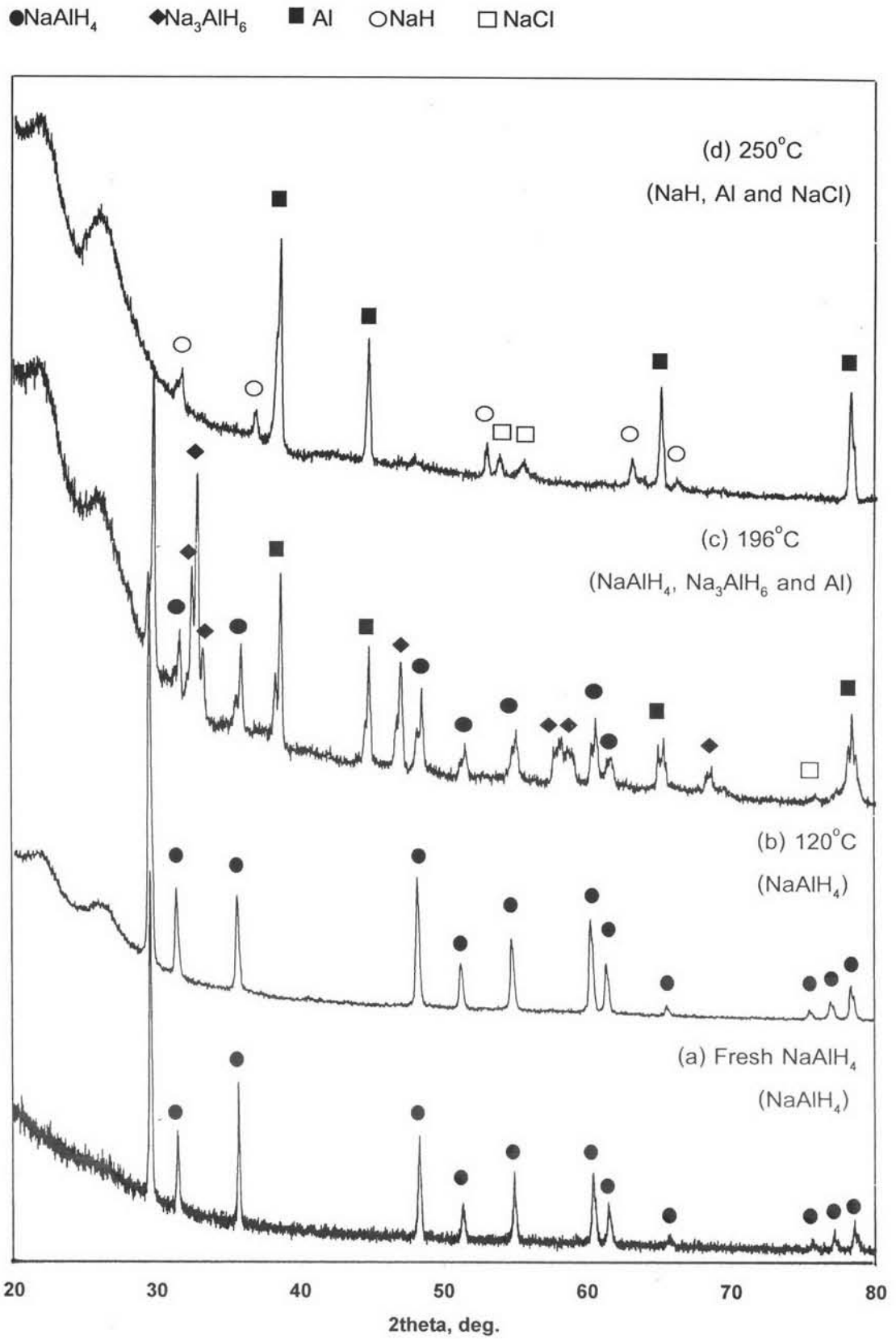


Figure 4.11 XRD patterns of undoped NaAlH_4 at different desorption temperature.

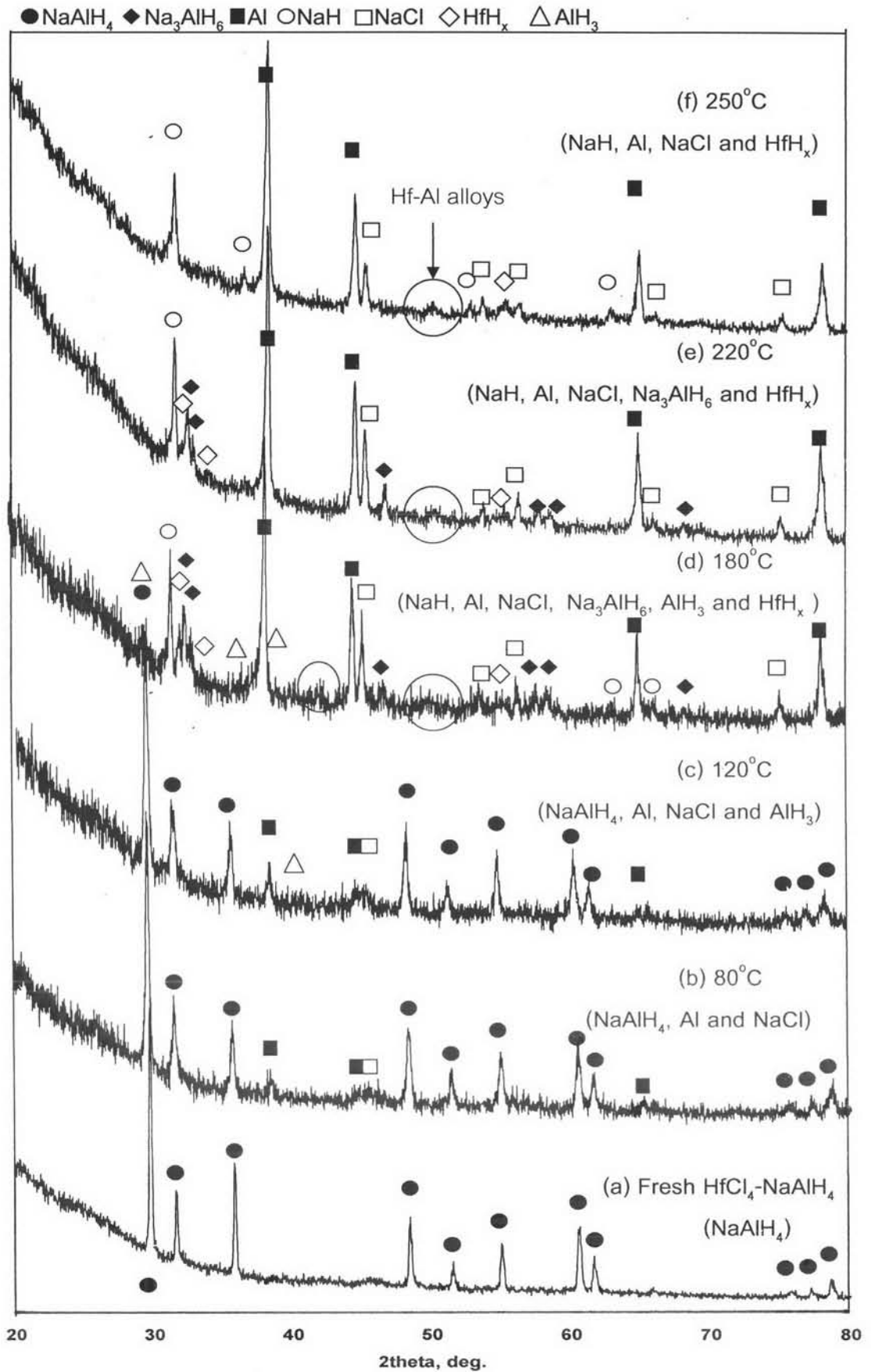


Figure 4.12 XRD patterns of 4mol%HfCl₄-NaAlH₄ at different desorption temperature.

4.1.3.2 The decomposition mechanism of NaAlH_4 doped with HfCl_4 .

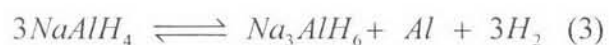
The dehydrogenation of HfCl_4 - NaAlH_4 begins at 75 °C (Figure 4.10). The hydrogen desorbed about 0.2 wt% at 80 °C (Table 4.3). It is equal to 13.5 wt% decomposed from NaAlH_4 . The main crystalline phase detected by XRD at this stage is NaAlH_4 and Al (Figure 4.12(b)). Although a finely dispersed Hf(0) is expected to form in the reduction reaction (eq.1), but no peaks corresponding to hafnium(0) seen in Figure 4.12(b).



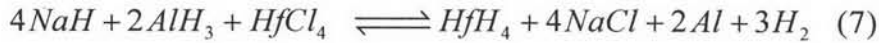
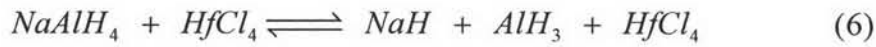
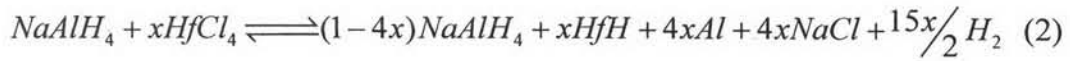
The XRD pattern of the hydrogen desorption of HfCl_4 - NaAlH_4 at 120 °C (Figure 4.12(c)) is similar to the one at 80 °C (Figure 4.12(b)). At 180 °C, HfCl_4 - NaAlH_4 decomposed 94.6 wt% and the amount of released hydrogen is 3.5 wt% (Table 4.3). The sample detected after dehydrogenation at 180 °C by XRD present the crystalline phase of NaH, Al, NaCl and Na_3AlH_6 (Figure 4.12(d)). This correspond to the first dehydrogenation step of NaAlH_4 (eq.3). The formation of NaH is shown in eq.6.



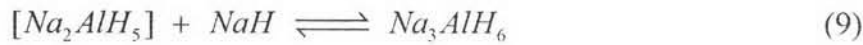
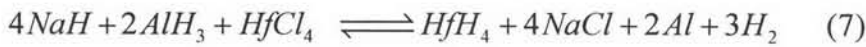
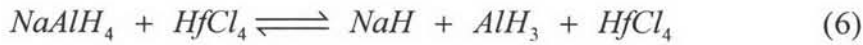
The two phases decomposition of sodium alanate (NaAlH_4) was represented in the two equations. The proposed decomposition mechanism is a series of reactions that show a simple progress from a starting material (NaAlH_4) to the intermediate (Na_3AlH_6) according to eq.3 and from the intermediate to the final products (NaH and Al) according to eq.4.



There are the reflections at $2\theta = 33.3^\circ$, 38.4° , and 55.5° which can be assigned to the phase of HfH_x , where $0 < x < 2.0$. HfH_4 , which was obtained from the doping reaction of HfCl_4 - NaAlH_4 according to eq.2, 6 and 7, would decompose to give HfH_x (eq.5).



Moreover, there are the reflections at $2\theta = 29.8^\circ$, 36.8° , and 39.3° which can be assigned to the phase of AlH_3 . The AlH_3 formation could be as follow in eq. 6. The proposed mechanism of $NaAlH_4$ doped with $HfCl_4$ is as the following:



$NaAlH_4$ doped with $HfCl_4$ became NaH and AlH_3 (eq.6). This decomposition process has been based on the analysis of decomposition temperature of various complexes metal hydride materials. Then, NaH can react with AlH_3 and $HfCl_4$ to give HfH_4 , Al , $NaCl$ and H_2 (eq.7). The NaH can also react with $NaAlH_4$ to give $[Na_2AlH_5]$ as an intermediate (eq.8). This intermediate further react with NaH to obtain Na_3AlH_6 (eq.9). In addition, NaH can react with AlH_3 to obtain Na_3AlH_6 (eq.10) [4].

At $220^\circ C$, the $HfCl_4$ - $NaAlH_4$ decomposed 44.5 wt% in the 2nd step of dehydrogenation and the amount of released hydrogen is 4.5 wt% (Table 4.3). The sample detected by XRD after the dehydrogenation present the crystalline phase of NaH , Al , $NaCl$, Na_3AlH_6 , and HfH_x , where $0 < x < 2$, (Figure 4.12(e)) but the phase of AlH_3 does not exist. It could be assumed that $NaAlH_4$ change to Na_3AlH_6 , NaH and $NaCl$ (eq.6-10). As shown in eq. 7 above, it was assumed that HfH_4 decompose to HfH_x (eq.5). It occurs in the same reaction as the dehydrogenation reaction at $180^\circ C$.

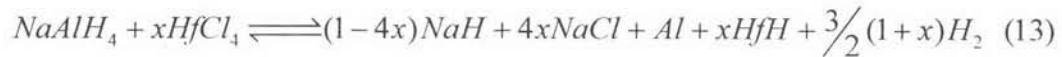
At $250^\circ C$, the $HfCl_4$ - $NaAlH_4$ dehydrogenation reaction completely decomposed and the amount of released hydrogen is 5.5 wt% (Table 4.3). The sample detected by XRD after dehydrogenation by XRD shows the crystalline phase of NaH , Al , $NaCl$ and HfH_x where

$0 < x < 2$ (Figure 4.12(f)). The phase of Na_3AlH_6 is not observed. NaH and Al, which were obtained from the dehydrogenation of Na_3AlH_6 , are the final products of NaAlH_4 dehydrogenation reaction. The equation already mentioned above in eq.4.

Moreover, it was observed the small broad peaks at $2\theta = 41.72^\circ$ and 50.74° in the XRD patterns Figure 4.12(d) and at $2\theta = 50.74^\circ$ in Figure 4.12 (e)-(f). Suttisawat and co-workers [30] suggest that the formation of Hf-Al alloys shows XRD diffraction peaks at $2\theta \sim 41.5^\circ$ and 50.48° (Figure 4.12(d)-(f)). The formation of Hf-Al alloys is proposed in the following equation (eq.11 and 12).

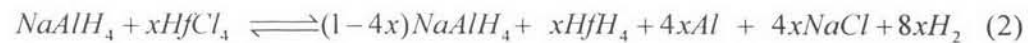


The summary reaction of the dehydrogenation reaction of NaAlH_4 doped with HfCl_4 shows in the following equation (eq.13).

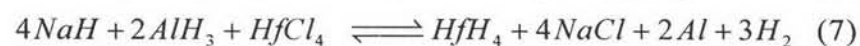
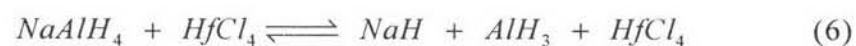


4.1.3.3 *The decomposition mechanism of NaAlH_4 doped with HfCl_4 and H_2TPP or HfCl_2TPP as a co-catalyst.*

From the mechanism proposed for the hydrogen desorption processes of NaAlH_4 doped with HfCl_4 , the decomposition reaction of $\text{HfCl}_4\text{-NaAlH}_4$ when H_2TPP or HfCl_2TPP were added, occur in the similar reaction as when doped with HfCl_4 . The dehydrogenation mechanism of $\text{HfCl}_4\text{-NaAlH}_4$ doped with H_2TPP would start with the reaction between NaAlH_4 and HfCl_4 to give NaAlH_4 , Al, NaCl, HfH_4 and H_2 according to eq.2.



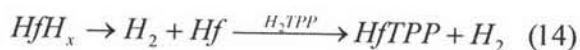
NaAlH_4 would decompose in two steps to produce NaH, NaCl and Al. It was represented in two equations (eq.6 and 7)



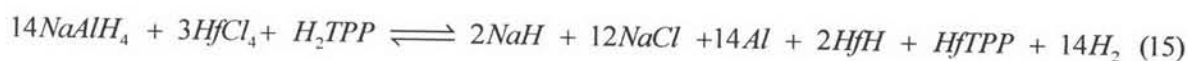
It was assumed that HfH_4 (from eq.7) decompose to HfH_x and H_2 (eq.5).



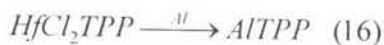
HfH_x could further decompose to give Hf and this Hf would react with H_2TPP as shown in eq.14



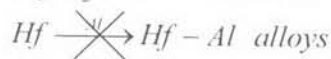
The summation of the reaction is showing in eq.15



The reaction mechanism of HfCl_4 - NaAlH_4 , which HfCl_2TPP was added, occur in the same mechanism. But the reaction of HfCl_4 - NaAlH_4 , which HfCl_2TPP was added, will produce AITPP by the reaction of Al crystallite and HfCl_2TPP (eq.16). The reaction in equation 17 present the hydrogen desorption of HfCl_4 - NaAlH_4 doped with HfCl_2TPP .



Hf-Al alloys was not detected in the sample which H_2TPP or HfCl_2TPP were added. The reaction between HfCl_4 and porphyrins is shown in eq. 14 and 16.



Because of the formation of the high stable compounds (HfTPP and AITPP) in the system when which H_2TPP or HfCl_2TPP were added into HfCl_4 - NaAlH_4 , the hydrogen desorption occur at higher temperature (170-260°C). The amount of hydrogen released is reduced because some of hydrogen atoms could react with Hf to produce HfH_x compound.

With this proposed decomposition mechanism for sodium alanate, we propose a rehydrogenation mechanism. Data from the literature reports of hydrogen adsorption on aluminum surfaces facilitates the discussion here. Decomposition of AlH_3 to Al and three H atoms is the preferred decomposition mode of alane on aluminum surfaces at low hydrogen coverage [28]. Moreover, the predominate cracking product of the alane is H atom, not H_2 [28-29]. This corresponds with our proposed decomposition mechanism. Hydrogen cycled alanates present bulk aluminum in the reaction matrix. This bulk aluminum assist the decomposition of the alanates. The rehydrogenation process, however, requires high pressure hydrogen gas, a condition that encourages the formation and desorption of alanates from the super-saturated bulk aluminum surface [28]. The mass spectrum of gaseous species formed from more than one hydrogen mono-layer adsorbed onto aluminum surfaces shows both hydrogen and alane AlH_x ($x=2,3$) desorb at around $50^\circ C$ [29]. According to the principle of microscopic reversibility, if alanates decompose through alanates, then alanates rehydrogenate through alanates. This rehydrogenation mechanism could be as follow:



The high pressure hydrogen creates the conditions for alane desorption as described [28-29]. The alane then migrates to NaH and reacts, forming both of the alanates first Na_3AlH_6 and then $NaAlH_4$. However, the alane peaks cannot be identified because its reflection is in the same range as $NaAlH_4$ peaks (see Figure 4.15).

4.2 Effects of copper-chromium oxide (CuCrO_4) and Ni as a co-catalyst on the hydrogen desorption of $\text{HfCl}_4\text{-NaAlH}_4$

4.2.1 Hydrogen desorption

Copper chromium oxide (CuCrO_4) (a hydrogenation catalyst) and nickel metal (an active catalyst for hydrogen dissociation) were expected to decrease the desorption temperature and improve the amount of released hydrogen of $\text{HfCl}_4\text{-NaAlH}_4$.

The 4mol% $\text{CuCrO}_4\text{-NaAlH}_4$ sample (S9) begins to decompose at 145 °C and continues to release hydrogen until 220 °C. The amount of the released hydrogen in the first cycle is 4.6 wt%. It can be observed that the decomposition temperature of the milled 4mol% $\text{CuCrO}_4\text{-NaAlH}_4$ is lower (145 °C) than that of the theoretical one (185 °C; Bogdanovic *et al.*, 2000), but higher than that of the 4% $\text{HfCl}_4\text{-NaAlH}_4$ (90 °C).

The sample of 0.1 mol% $\text{CuCrO}_4\text{-HfCl}_4\text{-NaAlH}_4$ (S10) begins to decompose at 162 °C and continues to release hydrogen until 260 °C. It shows 4.1 wt% of the released (see Table 4.3). When adding more catalysts, the desorption temperature and the amount of released hydrogen of $\text{HfCl}_4\text{-NaAlH}_4$ still could not be further improved (Figure 4.13) and the subsequent desorption is not occurred. This phenomena is the same as adding the H_2TPP and HfCl_2TPP as a co-catalyst. Then, mixed 4 mol% $\text{HfCl}_4\text{-NaAlH}_4$ before added 0.1 mol% CuCrO_4 (S11), the 1st decomposition begins at 62 °C to 270 °C. The subsequent decomposition occurs at 117 °C which is lower than the subsequent desorption temperature of $\text{HfCl}_4\text{-NaAlH}_4$ (150 °C). The amount of released hydrogen of S11 1st desorption shows 5.9wt% (more than the theoretical, 5.6 wt%). The subsequent desorption is 1.7 wt% (Figure 4.14).

The sample with 4mol%Ni-4mol% $\text{HfCl}_4\text{-NaAlH}_4$ shows 5.6 wt% of released hydrogen in the 1st desorption and 1.0 to 1.2 wt% in the subsequent desorption. The 1st desorption start at 88 °C and complete at 280 °C. The subsequent desorption occurs at a bit higher temperature (90 °C) than the 1st desorption temperature (88 °C) (see Table 4.3). Although the desorption temperature and the amount of released hydrogen of the sample with CuCrO_4 (S11) or Ni (S12) doped are better than the other one without CuCrO_4 or Ni, the amount of released hydrogen in subsequent desorption is not reach an expected level.

Table 4.4 Effects of HfCl_4 , CuCrO_4 and Ni doping on NaAlH_4

| Samples | Catalyst doped on NaAlH_4 (%mol) | | | Hydrogen capacity (wt%) | | Temperature of desorption in range ($^{\circ}\text{C}$) | |
|--------------------|--|------------------|----|-------------------------------|--------------------------|--|--------------------------|
| | HfCl_4 | CuCrO_4 | Ni | 1 st desorption | Subsequent desorption | 1 st desorption | Subsequent desorption |
| S1 | - | - | - | 5.5 | - | 185-260 | - |
| S2 | 4 | - | - | 5.6 | 2.2-2.6 | 90-260 | 150-220 |
| S9 | - | 4 | - | 4.6 | - | 145-220 | - |
| S10 | 4 | 0.1 | - | 4.1 | - | 162-260 | - |
| S11 ^(b) | 4 | 0.1 | - | 5.9 | 1.5-1.7 | 62-250 | 117-250 |
| S12 | 4 | - | 4 | 5.6 | 1.0-1.2 | 88-280 | 90-280 |

^(b) mix 4mol% HfCl_4 - NaAlH_4 before added 0.1mol% CuCrO_4

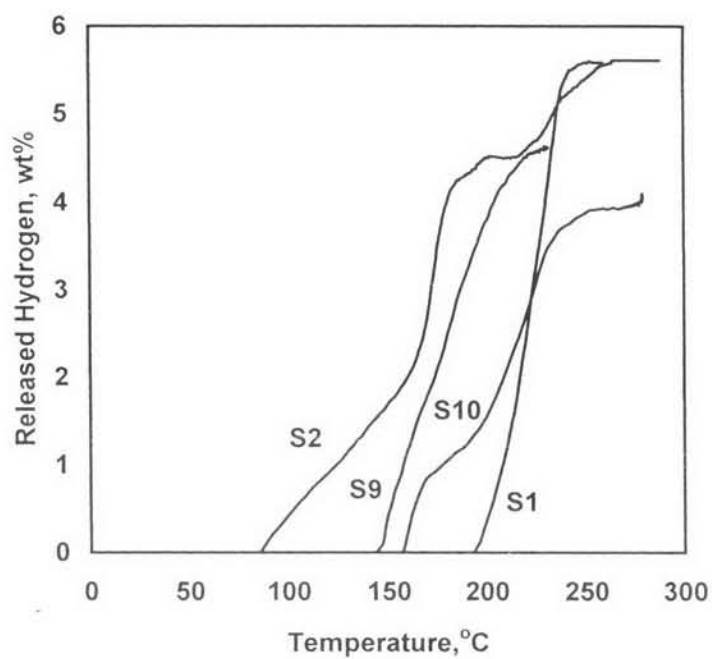


Figure 4.13 Temperature program desorption from room temperature to 280 $^{\circ}\text{C}$ of S9 and S10 compared to S1 and S2.

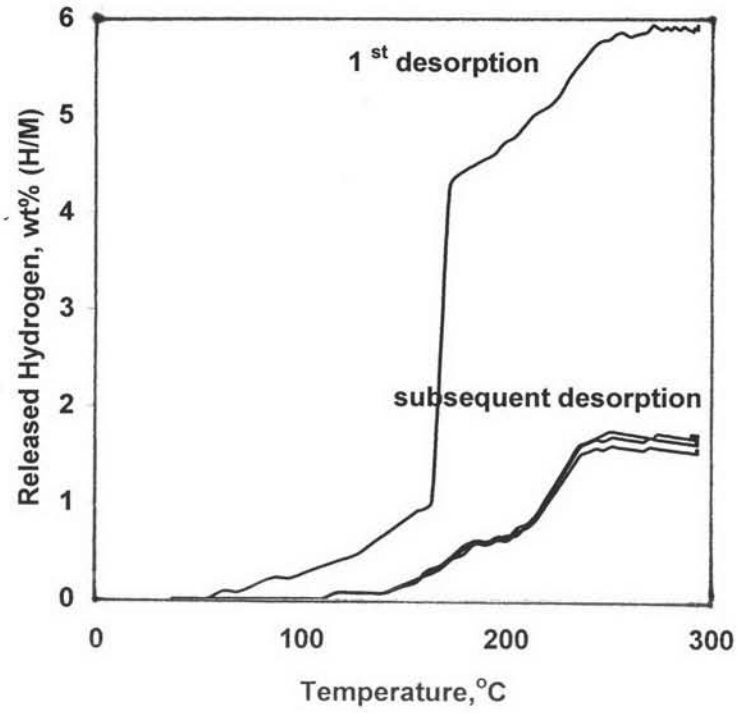


Figure 4.14 Temperature program desorption from room temperature to 280 °C of S11.

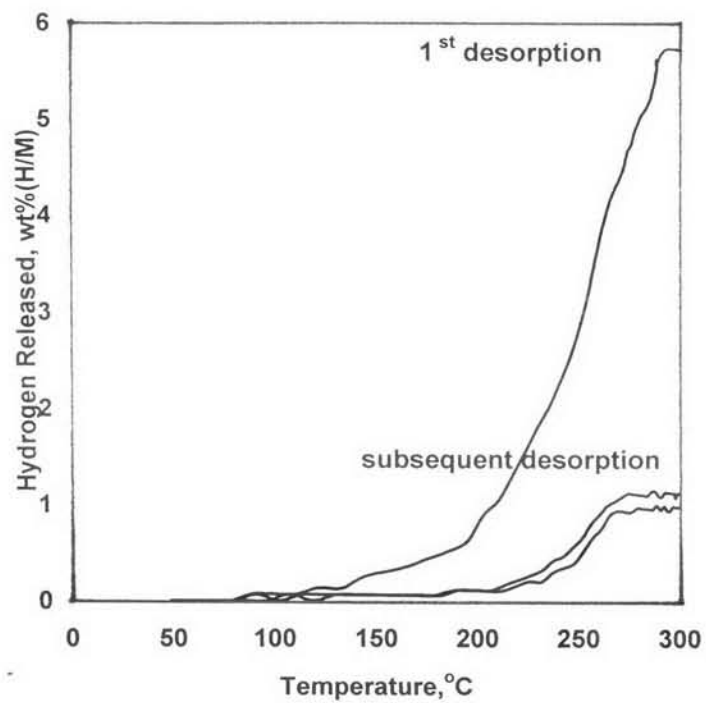
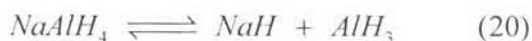


Figure 4.15 Temperature program desorption from room temperature to 280 °C of S12.

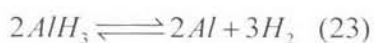
4.2.2 X-ray diffraction patterns of CuCrO₄ as a co-catalyst on the hydrogen desorption of HfCl₄-NaAlH₄

The XRD patterns of the sample 4 mol% CuCrO₄-NaAlH₄ (S9) and 0.1 mol% CuCrO₄- HfCl₄-NaAlH₄ (S10) before desorption show in Figure 4.16(a) and (c), respectively . It was observed the peaks of NaAlH₄ and CuCrO₄ in sample S9 fresh (Figure 4.16(a)). That is NaAlH₄ not react with CuCrO₄.

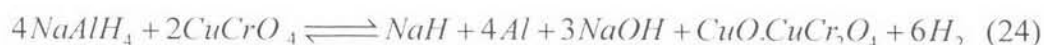
After desorption, the XRD pattern of the sample 4mol% CuCrO₄-NaAlH₄ (S9) show the peak of NaH, Al and NaOH (Figure 4.16(b)). NaH and Al are the products which was obtained from the dehydrogenation of NaAlH₄. NaAlH₄ decompose to NaH and AlH₃ (eq.20). Because the desorption system take place at high temperature (up to 300°C) then CuCrO₄ would decomposed to give CuO.CuCr₂O₄ and [O] (eq.21). NaH can react with [O] to produce NaOH. The reaction which produce NaOH, shows in eq. 22.



AlH₃ would decompose to Al and H₂ (eq.23).



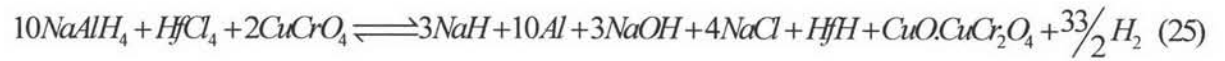
The hydrogen desorption reaction of NaAlH₄ doped with 4 mol% CuCrO₄ (S9) is shown in eq.24.



The XRD pattern of 0.1 mol% CuCrO₄- HfCl₄-NaAlH₄ (S10) fresh shows the peaks of NaAlH₄ and the small peaks of NaCl (Figure 4.16(c)). NaCl may form from NaAlH₄ decomposition when HfCl₄ was added. The reaction is shown above in equation 2 (the mechanism of NaAlH₄ doped with HfCl₄)

The sample **S10** after desorption shows the peaks of NaH, Al, NaOH and NaCl (Figure 4.16(d)). The reaction of NaOH is already shown in eq.22.

The mechanism for hydrogen desorption/absorption for HfCl₄-NaAlH₄ doped with CuCrO₄ as a co-catalyst was proposed in the following equation (eq.25).



The results of the hydrogen released of 5.9 wt% which is higher than the theoretical value of 5.6 wt% can be explained by the equation 25. The equivalent mole of hydrogen per one equivalent mole NaAlH₄ is 33/2 or 1.65, which is higher than 3/2 or 1.5 that obtained from NaAlH₄ doped with only HfCl₄ (eq.13) This is consistent with the result of hydrogen released from the system further doped with CuCrO₄ (5.9 wt%) and the system without CuCrO₄ (5.6 wt%).

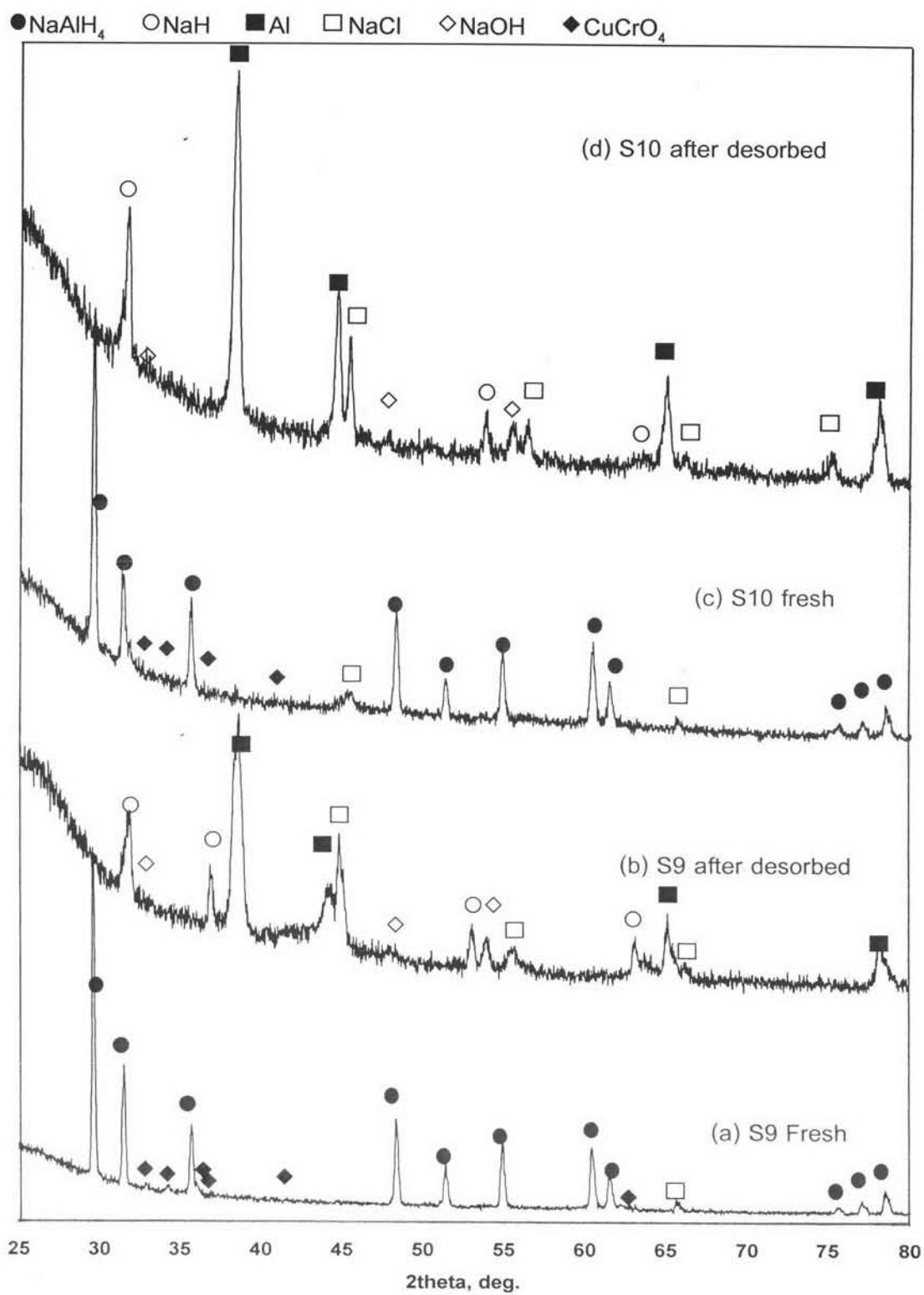


Figure 4.16 XRD patterns of samples S9 (4 mol% $\text{CuCrO}_4\text{-NaAlH}_4$) and S10 (0.1 mol% $\text{CuCrO}_4/4$ mol% $\text{HfCl}_4\text{-NaAlH}_4$); (a) S9 fresh, (b) S9 after desorbed, (c) S10 Fresh and (d) S10 after desorbed.

4.3 Hydrogen Absorption kinetics

Real-time absorption kinetics at room temperature to 280 °C shown in Figure 4.17 represents hydrogen capacity as a function of time. The sample doped with 0.1 mol% H_2TPP as co-catalyst exhibits the fastest absorption kinetics in the first 40 min (Figure 4.17(c)) and the lowest absorption kinetics is belong to the sample of 4 mol% $HfCl_4$ - $NaAlH_4$ doped with 0.1 mol% $CuCrO_4$ (Figure 4.17(d)). The sequence of the sample which present the absorption kinetics from the lowest to the fastest absorption kinetics : $NaAlH_4$ doped with 0.1mol% $CuCrO_4$ -4 mol% $HfCl_4$ (d), 4 mol% $HfCl_4$ (a), 4 mol% Ni-4 mol% $HfCl_4$ (b) and 0.1 mol% H_2TPP -4 mol% $HfCl_4$ (c) (see Figure 4.17) .

After 6 hr, the hydrogen capacity of the doped $NaAlH_4$ with 4 mol% $HfCl_4$ shows the highest hydrogen capacity. The hydrogen capacity of the doped $NaAlH_4$ with 4 mol% $HfCl_4$ is 1.4 wt% (see Figure 4.18(a) and Table 4.5). The hydrogen capacity of the sample which 4 mol% $HfCl_4$ - $NaAlH_4$ was doped with 4 mol% Ni, 0.1 mol% H_2TPP and 0.1mol% $CuCrO_4$ as a co-catalyst are 0.9 wt%, 0.8 wt% and 0.8 wt%, respectively (see Figure 4.18(b)-(d) and Table 4.5).

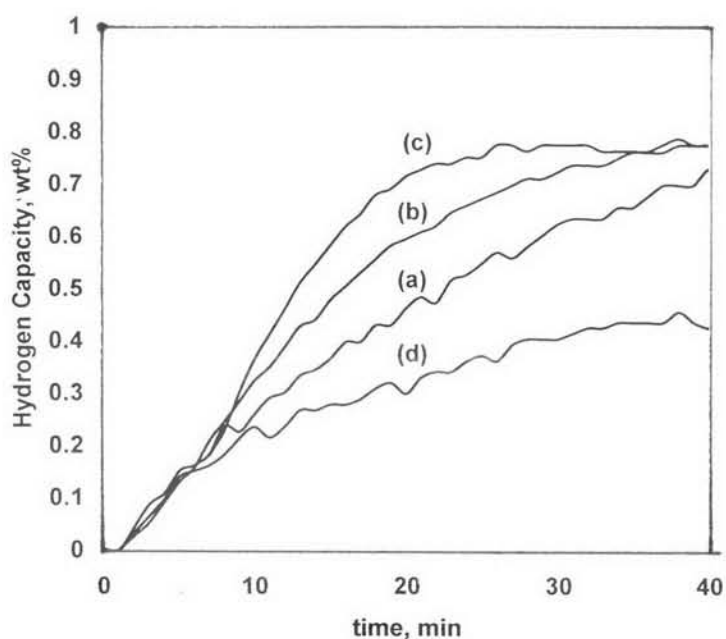


Figure 4.17 Hydrogen absorption kinetics of $NaAlH_4$ doped with (a) 4 mol% $HfCl_4$, (b) 4 mol% Ni-4 mol% $HfCl_4$ (c) 0.1 mol% H_2TPP -4 mol% $HfCl_4$ and (d) 0.1 mol% $CuCrO_4$ -4 mol% $HfCl_4$ at first 40 min.

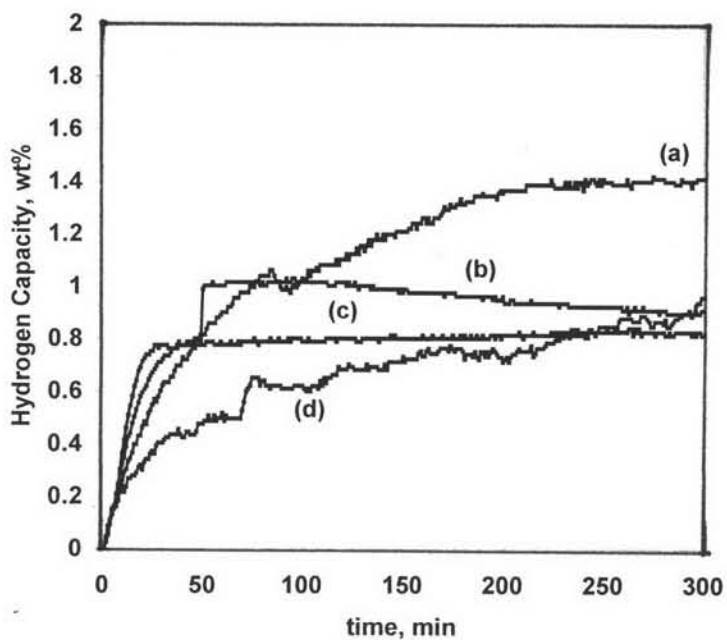


Figure 4.18 Hydrogen absorption kinetics of NaAlH_4 doped with (a) 4 mol% HfCl_4 , (b) 4 mol% Ni-4 mol% HfCl_4 (c) 0.1 mol% H_2TPP -4 mol% HfCl_4 and (d) 0.1 mol% CuCrO_4 -4 mol% HfCl_4 in 6 hr.

Table 4.5 shows the total hydrogen capacities measured by absorption and desorption procedure, including the estimated degree of rehydrogenation at different types of doped catalysts. The recycle ability, a portion of absorption of absorption and desorption capacity, is called the degree of rehydrogenation (Bogdanovic, 2000 [9]). All of the doped samples are not entirely reversible, which general shows lower absorption capacity than the desorption capacity.

Table 4.5 Total hydrogen capacities measured by absorption and desorption procedure, including the estimated degree of rehydrogenation at different types of doped catalysts.

| Hydrogen capacities (wt%) | | | Degree of rehydrogenation (%) |
|---|------------|------------|-------------------------------|
| Type of catalysts loading on NaAlH_4 | Desorption | Absorption | |
| 4 mol% HfCl_4 | 5.6 | 1.4 | 25.0 |
| 4 mol% Ni-4 mol% HfCl_4 | 5.6 | 0.9 | 16.2 |
| 0.1 mol% H_2TPP -4 mol% HfCl_4 | 5.2 | 0.8 | 15.4 |
| 0.1 mol% CuCrO_4 -4 mol% HfCl_4 | 5.9 | 0.8 | 13.0 |