Hydrogen Desorption Mechanism of Sodium Alanate Doped with different Catalyst

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Abstract: ***A comparative study of sodium alante doped $TiCl_3$, TiO_2 TiF_4 TiAl, Zr, Ni,V $PbCl_2$,$CeCl_3$ and Nb_2O_5 is to study in this paper. The object of this work was to investigate the effect of different catalyst on hydrogen desorption of $NaAlH_4$. Experimental work was performed under argon atmosphere in glove box.$NaAlH_4$ and different catalysts were mixture with x (1, 2,4) wt % and were weighed in glove box. The samples were covered with a Kapton tape due to the air sensitivity. Hydrogen storage properties and mechanisms of sodium alanate with different catalyst were investigated systematically. Structural properties of all samples are observed by X- ray diffraction (XRD).XRD resulted showed the formation of Na_3AlH_6 and NaH and no evidence of any Na containing phase. The study of kinetics of catalyst doped sodium alanate is done by PCT in temperature range between 100^o – 250^o C. The Weight of desorption hydrogen storage is varies 3.5 % to 5.4 % at temperature range. Hydrogen storage capacity is increased as increasing amount of catalyst.***

Keyword: Sodium alanate, Complex hydrides, XRD, Seviert type apparatus

1. Introduction

Hydrogen is a renewable energy source. Hydrogen energy is useful due to low price, developing safe and high storage capacity, environmental friendly energy carrier, and convertibility with many fuels and energies and the produces zero pollution. Hydrogen energy is capable of reversibly storing hydrogen at moderate temperature and pressures. Hydrogen storage material has one of the important problems for the development of hydrogen energy utilization due to lack of high density [1]. Hydrogen has been stored in various forms e.g. liquid, compressed gas, in carbon nano tubes, lightweight complex hydrides, metal oxide etc. Various types of hydrogen storage materials [2-7] are useful for various applications. Solid state hydrogen storage is a suitable option [8]. It is necessary to reversibly store hydrogen under operating conditions [9, 10] for onboard automobile applications. Light weight metal hydride has emerged as potential materials for future hydrogen energy applications [11].Sodium alanate is suitable complex hydrides for hydrogen storage [12] which recently has received considerable attention due to high hydrogen capacity (7.5 wt.% H_2) obtained by adding a dopant . Different classes of metal hydrides such as intermetallic hydrides [11-13], light weight binary hydrides [14,16] and Complex hydride [17,18] have been investigated. Complex metal hydride system has been proposed by many researchers as a high energy density hydrogen storage system [19]. Complex metal hydrogen promise to improved their hydrogen /dehydrating kinetics under moderate temperature and pressure[20,21].Sodium alanate is having 7.5wt% hydrogen which can be released in following three steps:

$$NaAlH_4 \rightarrow 1/3\ Na_3AlH_6 + 2/3\ Al + 3\ H_2\ (3.7\ wt\ \%H) \quad (1)$$
$$Na_3AlH_6 \rightarrow 3\ NaH + Al + 3/2\ H_2\ (1.9\ wt\ \%\ H) \quad (2)$$
$$NaH \rightarrow Na + H \quad (3)$$

Theoretically, the first reaction releases 3.7 wt% amount hydrogen at 185°C temperature and the second reaction gives out 1.8 wt % hydrogen at 260°C.The third reaction releases hydrogen above 300°C temperature .Third step is not useful for commercial due to high temperature. The kinetics of $NaAlH_4$ improved by ballmaling doping with a suitable catalyst such as TiO_2 $TiCl_3$, TiAl, TiF_4, Zr, Ni and V etc. Generally, Ti - based $NaAlH_4$ provides only about 3.0 wt % hydrogen capacity at about 120°C. Zidan et al [3] show that a unique behavior between Ti and Zr with co-doping $NaAlH_4$ was found. Bogdanovic et al[5] reported decomposition temperature of the first reaction was lowered co-doping $NaAlH_4$ with Ti and Fe compared to using either Ti or Fe alone as the dopant. Oxide catalysts improved desorption of hydrogen from alanates. Polanski et al [24] investigated the catalytic effect of micron sized TiO_2 powder on hydrogen desorption kinetics of $NaAlH_4$. sodium alanate catalyzed with TiO_2 desorbs about 5.0wt % hydrogen during the first cycle with the enhanced kinetics. Pukazhselvan et al [25] are reported that $NaAlH_4$ catalyzed with oxides such viz. TiO_2, CeO_2, La_2O_3, Pr_2O_3, Nd_2O_3, Sm_2O_3, Eu_2O_3 and Gd_2O_3 as catalysts improve the hydrogen desorption kinetics. They concluded that the TiO_2 nano particles exhibits better catalytic performance in both the desorption and reversibility. Rafi-ud-din et al [26] has shown that nanosized Nb_2O_5 and TiO_2 doped sodium alanate improved hydrogen performance as compared to undoped as well as Cr_2O_3 doped sodium alanate.CeCl3 - doped $NaAlH_4$ with, the mechanism of the enhancement of the kinetics is not revealed, neither is the nature of active cerium species[27-31].Metal catalysts in the Group (Ti, Zr, and Hf) appear to be the effective dopant in the reaction. In this paper,we compare the kinetic and amount of dehydrogenation of sodium alante with $TiCl_3$, TiO_2, TiF_4 ,TiAl, Zr, Ni, $PbCl_2$,$CeCl_3$ and Nb_2O_5. Evolution of alanate phase of the samples is investigated using XRD analysis.

2. Experimental

Sodium alanate and $TiCl_3$, TiO_2, TiF_4, TiAl, Zr, Ni, V, $PbCl_2$, $CeCl_3$ and Nb_2O_5 were purchased from Aldrich with purity of 99.95%. All samples were prepared by planetary Ball milling technique and hand milling. A planetary ball

milling apparatus was used for milling different catalyst. The ball-milling was performed with rotation speed of 350 rpm for 2 hour. The ball is made of stainless steel with a diameter of 1 cm .The ball to power weight ratio was around 20: 1. $NaAlH_4$ and different catalylist were weighed and put into the mortar under argon atmosphere. Sample handling was done in argon atmosphere inside a glove box to avoid with oxygen and water content.
The Following samples were prepared.

1) $NaAlH_4$ + x $TiCl_3$ (x= 1% , 2 % and 4 % wt %)
2) $NaAlH_4$ + x TiF_4 (x= 1% , 2 % and 4 % wt %)
3) $NaAlH_4$ + x TiAl (x= 1% , 2 % and 4 % wt %)
4) $NaAlH_4$ + x TiO_2 (x= 1% , 2 % and 4 % wt %)
5) $NaAlH_4$ + x Zr (x= 1%, 2 %)
6) $NaAlH_4$ + x V (x= 1%, 2 %)
7) $NaAlH_4$ + x Ni (x= 1% , 2 %)
8) $NaAlH_4$ + 1:1 (Ni +$TiCl_3$)
9) $NaAlH_4$ + 1:1 (V +$TiCl_3$)
10) $NaAlH_4$ + 1:1 (Zr +$TiCl_3$)
11) $NaAlH_4$ + x $PbCl_2$ (x= 1% , 2 %)
12) $NaAlH_4$ + x $CeCl_3$ (x= 1% , 2 %)
13) $NaAlH_4$ + x Nb_2O_5 (x= 1% , 2 %)
14) $NaAlH_4$ + 1:1 ($PbCl_2$ +$TiCl_3$)
15) $NaAlH_4$ + 1:1 ($CeCl_3$ +$TiCl_3$)
16) $NaAlH_4$ + 1:1 (Nb_2O_5+$TiCl_3$

The structural characterization has been done by using X-ray Diffraction (XRD) with Cu Kα radiation at 40 kV and 40 mA. The data were collected in the range between 30^o and 80^o with a step width of 0.02 at a rate of 2.5^o /min. PCT system is attached computer and all data stored in computer. Data collected in CD and analysis by software. The volume of sample holder had a thermocouple located in the center of the sample to monitor temperature in the reaction zone. For dehydrogenation, the measurement processed at a constant pressure 1 atm. The apparatus was heated at 100^o C to 250^o C.

3. Result and Discussion

3.1 Structural Characterizations

The structural characterization of $TiCl_3$, TiO_2, TiAl, Zr ,Ni, V $CeCl_3$ $PbCl_3$ Nb_2O_5 and TiF_4 doped Sodium alanate have been performed by X-Ray Diffraction . The structural characterization of samples have been shown in fig (1) to fig (15) . $NaAlH_4$ was found in Tetragonal phase with lattice constant a=5.02, b=5.02 and c=11.34 , Na_3AlH_6 in Monoclinic structure with lattice constant a= 5.46, b= 5.61, c= 7.80, $TiCl_3$ appears in structure having a=b=6.143 , c= 11.71and NaH in Cubic structure with lattice constant a=b=c=4.890 and Al Cubic structure having a=b=c= 4.049 and TiO_2 appears Orthorhombic structure with lattice constant a= 4.531,b=5.501,c= 4.906 and TiAl are appears Tetragonal structure with lattice constant a= b=3.853, c= 8.583 and Zr is appears in Cubic structure a=b=c 3.545and V is appears Cubic a=b=c =3.027and V is appears Cubic structure a=b=c =3.027 and $TiCl_3$ observed in monoclinic structure having a= 6.051, b= 10.56, c =7.80 and Ni is appears in Cubic structure having lattice constant a=b=c =3.027 and $PbCl_2$is appears Hexagonal structure with lattice constant a= b= 14.04, c= 8.601 and $CeCl_3$ is appears Hexagonal form with lattice constant a= b= 14.04, c= 8.601 and $PbCl_2$ is appears Hexagonal structure with lattice constant a= b= 13.04, c= 3.545 and Nb_2O_5 is appears Hexagonal structure with lattice constant a= b= 13.04, c= 3.545.

3.2 Hydrogenation and Kinetics

The prepared samples were transferred into dynamic seveirt type apparatus under one bar vacuum.0.20 gm samples was closed with a filtered stainless steel cap and inserted in the stainless steel high pressure rector. The temperature was monitored with a Cr-Al thermocouple .Kinetic curves of $NaAlH_4$ + x wt % $TiCl_3$ (x=1,2,4 wt %) are shown in Fig 16 to Fig 18. All Kinetic for desorption were determined using Dynamic Seiverts type apparatus at 100^o C to 250^o C temperatures. Fig 16 is a curve for desorption hydrogen by $NaAlH_4$ +1 wt % $TiCl_3$ vs time at different temperature.$NaAlH_4$ +1 wt % $TiCl_3$ sample releases about 4.5 wt % hydrogen in the temperature range between 100^o and 250^o C. The desorbed hydrogen capacity is much lower than the theoretical capacity of 5.6% wt % of $NaAlH_4$. $TiCl_3$ doped $NaAlH_4$ shows very fast desorption kinetics up to about 20 min at 175^o and 250^oC. After 20 min desorption kinetics is approximately constant. Fig 17 is a curve for $NaAlH_4$ +2 wt % $TiCl_3$ vs time at different temperature. It shows that sample releases about 4.8 wt % hydrogen. Fig 18 is a curve for hydrogen desorbed by $NaAlH_4$ +4 wt % $TiCl_3$ vs time at different temperature. Sample releases about 5.4 wt % hydrogen at 250^o C. The desorbed hydrogen capacity is almost equal to the theoretical capacity 5.6% wt % of $NaAlH_4$. Amount of desorbed hydrogen is increased with increase amount of catalysts $TiCl_3$. The desorption hydrogen capacity was found to be 4.5 wt %, 4.8 wt % and 5.4 wt % with $TiCl_3$ (1%, 2 % and 4%) which is approximate to theoretical value as reported. Kinetic curves of NaAlH4 + x wt % TiO_2 (x=1, 2, 4 wt %) are shown in Fig 19 to Fig 21. The desorption hydrogen capacity was found to be 3.6 wt %,4.8 wt % and 5.1 wt % with TiO_2 (1,2 and 4 wt %).It shows that amount of desorption hydrogen is increased with TiO_2 due catalytic effect of TiO_2 with temperature.Kinetic curves of $NaAlH_4$ + x wt % TiAl (x=1, 2, 4) are shown in Fig 22 to Fig 24. The desorption hydrogen capacity was found to be 4.0 wt % , 4.2 wt % and 4.6 wt % with TiAl (1 %, 2 % and 4%) respectively .Kinetic curves of $NaAlH_4$ + x wt % TiF_4 (x=1, 2, 4 wt %) are shown in Fig 25 to Fig 27.TiF_4 is good catalylist for $NaAlH_4$. The desorption hydrogen capacity was found to be 4.0 wt %, 4.8 wt % and 5.4 wt % with TiF_4 (1%, 2 % and 4%) respectively. Amount of desorption hydrogen wt % is increased with content of TiF_4. TiF_4 is very good catalysts for desorption hydrogen and kinetics. Kinetic curves of $NaAlH_4$ + x wt % $PdCl_2$ (x=1, 2 wt %) are shown in Fig 28 to Fig 29. Fig 28 is a curve for hydrogen desorption by $NaAlH_4$ + 1 wt % $PdCl_2$ vs time at different temperature 100^0 C – 250^o C. It show that sample released about 3.3 wt % hydrogen in temperature between 100^o and 250^o C. The Catalyst $PdCl_2$ is recently not reported. However $PdCl_2$ is a good catalyst and can improve the wt % of hydrogen. In Fig.29 Desorption for Kinetics is shown . 2 wt % $PdCl_2$ doped $NaAlH_4$ released about 3.5wt % hydrogen in range between 100^o and 250^o C. Kinetic curves of $NaAlH_4$ + x wt % $CeCl_3$ (x=1,2) are shown in Fig 30 to Fig 31. Fig 30 is a curve for hydrogen desorption by $NaAlH_4$ +1 wt % $CeCl_3$ vs time at different temperature 100^0 C – 250^o C. $CeCl_3$ doped sample released about 4.9 wt % hydrogen in temperature range between 100^{o} and 250^{o} C. $CeCl_3$ doped $NaAlH_4$ shows very fast desorption kinetics up to about 30 min during and after 30 min desorption rate is approximately constant. The Catalyst $CeCl_3$ is recently reported. However CeCl3 is a good catalyst. In Fig.31 .2 wt % $CeCl_3$ doped $NaAlH_4$ released about 5.4 wt % hydrogen in a desorption temperature at 250^{o} C. The desorbed hydrogen capacity is almost equal to the theoretical capacity 5.6% wt % of $NaAlH_4$. Kinetic curves of $NaAlH_4$ + x wt % $TiCl_3$+$PdCl_2$ (1:1wt %) are shown in Fig.32. $NaAlH_4$ with 1 :1 wt % $TiCl_3$+$PdCl_2$ release about 5.0 wt %hydrogen in a desorption temperature at 250^{o} C. Kinetic curves of $NaAlH_4$ + x wt % $TiCl_3$+Nb_2O_5 (1:1wt %) are shown in Fig.33 . sample released about 4.8 wt % hydrogen in temperature range between 100^{o} and 250^{o} C. Nb_2O_5 doped sodium alanate is release low amount of hydrogen. Mixture of catalyst $TiCl_3$+Nb_2O_5 doped $NaAlH_4$ increased amount of wt % desorbed hydrogen. The catalysts effective of TiCl3 is more than Nb_2O_5. Kinetic curves of $NaAlH_4$ + x wt % $TiCl_3$+$CeCl_3$ (1:1 wt %) are shown in Fig 34. Fig 34 is a curve for hydrogen desorption by $NaAlH_4$ + 1:1 wt % ($TiCl_3$+ $CeCl_3$) vs time at different temperature 100^{0} C–250^{o} C. sample released about 4.5 wt % hydrogen in temperature range between 100^{o} and 250^{o} C. Mixture of catalyst $TiCl_3$+$CeCl_3$ doped $NaAlH_4$ increased amount of dehydrogen. The catalysts effective of $TiCl_3$ is more than $CeCl_{3.}$ The dehydrogenation with catalytic amounts of Ti and Ce doped complex aluminum hydrides represent an interesting new type of a catalytic reaction. Ce has recently been reported .Kinetic curves of $NaAlH_4$ + x wt % Nb_2O_5 (x=1, 2 wt %) are shown in Fig 35 and Fig 36.Fig 35 is a curve for hydrogen desorption by $NaAlH_4$ + 1 wt % Nb_2O_5 vs time at different temperature 100^{0} C – 250^{o} C. sample released about 4.8 wt % hydrogen in temperature range between 100^{o} and 250^{o} C. Nb_2O_5 doped $NaAlH_4$ shows very fast desorption kinetics up to about 20 min at 250^{o} C. Fig 36 shows that $NaAlH_4$ catalyzed using 2 wt % Nb_2O_5 released 5.0 wt % hydrogen during desorption in temperature range between 100^{o} and 250^{o} C. The reaction is very fast and released approximately 5.0 wt% in 15 minute.

4. Conclusion

Sodium alanate $NaAlH_4$ was found in Tetragonal structure with lattice constant a=5.02, b=5.02 and c=11.34. $NaAlH_4$ is completely converted in Na_3AlH_6 at 250^{o}C. Na_3AlH_6 is appears in cubic structure with lattice constant a= b=c= 7.755. Catalyst such as $TiCl_3$, TiO_2, TiAl, Zr, Ni, V $CeCl_3$ $PbCl_3$ Nb_2O_5 and TiF_4 is doped with sodium alanate. Kinetic measurement of $NaAlH_4$ with different type of catalyst for desorption were determined using by Dynamic Seiverts type apparatus at 100^{o} C to 250^{o} C temperatures. Amount of hydrogen is desorbed 3.6 wt % to 5.4 wt % at 250^{o}C with different type of catalyst. Kinetics of all catalyst is slower but Ni catalyst is very good for desorption and automobile applications. The effect of three different catalyst transition metal (Ti, Zr, and V) were studied individually and with combinations .Ti is a better single metal than Zr. Zr is not as good for a promoter for Ti as Fe is for both Ti and Zr . Zirconium is inferior to titanium as a catalyst for the dehydriding of $NaAlH_4$ to Na_3AlH_6 .V shows the strong formation of V- Al crystalline. The formation of Al_3V intermetallic is a stable compound that would decrease the activity of the catalyst. For the Ti – doped hydride , it seems that the formation of the unstable Ti –Al amorphous promotes the reduction of Al metallic to hydride , compared with those of the undoped and V doped hydrides. Transition metal reduce dehydrogen storage capacity of sodium alanate. But mixture of titanium chloride and transition metal the increase dehydrogen storage capacity. In brief concluded that mixture of titanium $TiCl_3$ and Transition metal is good for storage capacity and automobile application. Sodium alanate is not active for hydrogen desorption and therefore needs catalysis for making it active for hydrogen. Hence in the present study different catalyst such as Ti series, halides, oxides and transition metals have been used to activate $NaAlH_4$. Sodium alanate doped with 1, 2 and 4wt % of different catalyst have been dehydrogenated at 250^{o} C. XRD results reveal that catalyst causes complete conversion of tetragonal $NaAlH_4$ into Na_3AlH_6 having cubic or monoclinic structure. kinetics desorption was found to be good for $TiCl_{3,}$ TiO_2 and TiF_4 catalyst. Catalyst $CeCl_3$ $_{is}$ very good catalyst for desorption. $CeCl_3$ catalyst has fast kinetics and high weight for onboard applications. The hydrogen Kinetics of all catalyst (Zr, Ni and V) is slower but Ni catalyst is very good for desorption and automobile applications. Titanium series and Halide catalyst is good for desorption compare to Oxide and transition metal type catalyst.

5. Acknowledgement

Jameel Khan is thankful to Council of Scientific and Industrial Research for providing fellowship of the work. I am thankful to RSIC, Panjab University, Chandigarh, India for providing XRD charactering techniques.

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Fig

Fig 1. XRD pattern of desorbed 4mol% $TiCl_3$ doped $NaAlH_4$ at 250^0C

Fig 2. XRD pattern of desorbed 4mol% TiO_2 doped $NaAlH_4$ at 250^0C

Fig 3. XRD pattern of desorbed 4mol% TiAl doped $NaAlH_4$ at 250^0C

Fig 4 XRD pattern of desorbed 4mol% TiF_4 doped $NaAlH_4$ at 250^0C

Fig 5: XRD pattern of desorbed 2 mol% Zr doped $NaAlH_4$ at 250^0C

Fig 6: XRD pattern of desorbed 2 mol% V doped $NaAlH_4$ at 250^0C

Fig 7: XRD pattern of desorbed 2 mol% Ni doped $NaAlH_4$ at 250^0C

Fig 8: XRD pattern of desorbed 1:1 mol% (TiCl3+Zr) doped $NaAlH_4$ at 250^0C

Fig 9 XRD pattern of desorbed 1:1 mol% ($TiCl_3$+V) doped $NaAlH_4$ at 250^0C

Fig 10: XRD pattern of desorbed 1:1 mol% ($TiCl_3$+Ni) doped $NaAlH_4$ at 250^0C

Fig 11: XRD pattern of desorbed 2wt% $PbCl_2$ doped $NaAlH_4$ at 250^0C.t

Fig12: XRD pattern of desorbed 2 wt % $CeCl_3$ doped $NaAlH_4$ at 250^0C

Fig13: XRD pattern of desorbed (1:1) wt %$TiCl_3$ and $PbCl_2$ doped $NaAlH_4$ at 250^0C

Fig14: XRD pattern of desorbed (1:1) wt %$TiCl_3$ andNb_2O_5 doped $NaAlH_4$ at 250^0C

Fig 15 XRD pattern of desorbed Nb_2O_5 doped $NaAlH_4$ at 250^0C

Fig 16 Hydrogen desorption curves of NaAlH4 with 1 wt % $TiCl_3$
Fig 17 Hydrogen desorption curves of NaAlH4 with 2 wt % $TiCl_3$
Fig 18 Hydrogen desorption curves of NaAlH4 with 4 wt % $TiCl_3$
Fig 19 Hydrogen desorption curves of NaAlH4 with 1 wt % TiO_2
Fig 20 Hydrogen desorption curves of NaAlH4 with 2 wt % TiO_2
Fig 21 Hydrogen desorption curves of NaAlH4 with 4 wt % TiO_2
Fig 22 Hydrogen desorption curves of NaAlH4 with 1 wt % TiAl
Fig 23 Hydrogen desorption curves of NaAlH4 with 2 wt % TiAl
Fig 24 Hydrogen desorption curves of NaAlH4 with 4 wt % TiAl
Fig 25 Hydrogen desorption curves of NaAlH4 with 1 wt % TiF_4
Fig 26 Hydrogen desorption curves of NaAlH4 with 2 wt % TiF_4
Fig 27 Hydrogen desorption curves of NaAlH4 with 4 wt % TiF_4
Fig 28 Hydrogen desorption curves of NaAlH4 with 1 wt % $PdCl_2$
Fig 29 Hydrogen desorption curves of NaAlH4 with 2 wt % $PdCl_2$
Fig 30 Hydrogen desorption curves of NaAlH4 with 1 wt % $CeCl_3$
Fig 31 Hydrogen desorption curves of NaAlH4 with 2 wt % $CeCl_3$
Fig 32 Hydrogen desorption curves of NaAlH4 with (1:1) wt % $TiCl_3$ and $PdCl_2$
Fig 33 Hydrogen desorption curves of NaAlH4 with (1:1) wt % $TiCl_3$ and Nb_2O_5
Fig 34 ydrogen desorption curves of NaAlH4 with (1:1) wt % $TiCl_3$ and $CeCl_3$
Fig 35 Hydrogen desorption curves of NaAlH4 with 1 wt % Nb_2O_5
Fig 36 Hydrogen desorption curves of NaAlH4 with 2 wt % Nb_2O_5

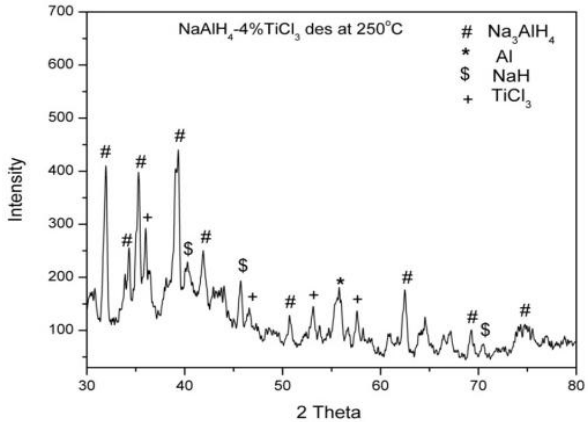
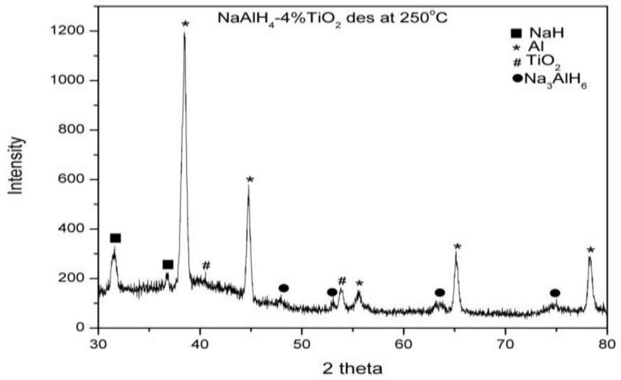


Figure 1



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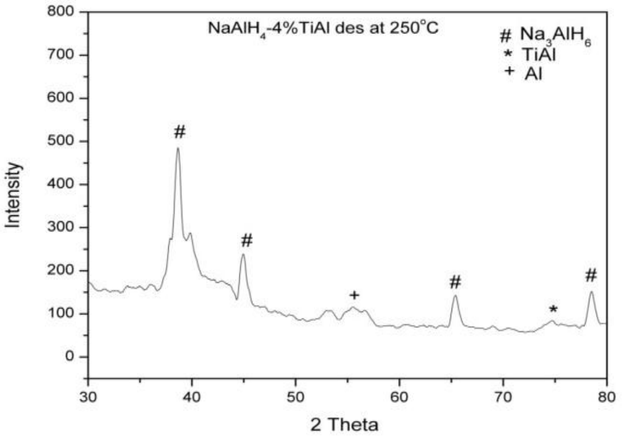

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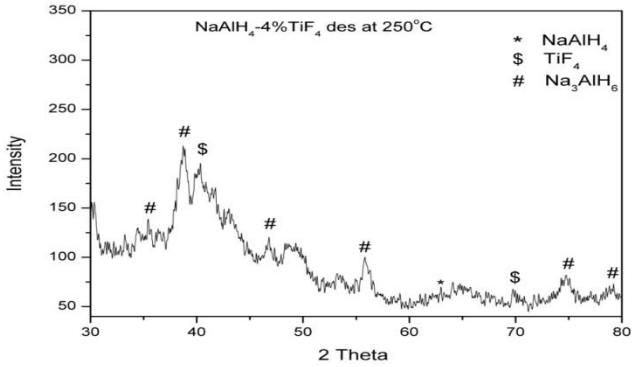

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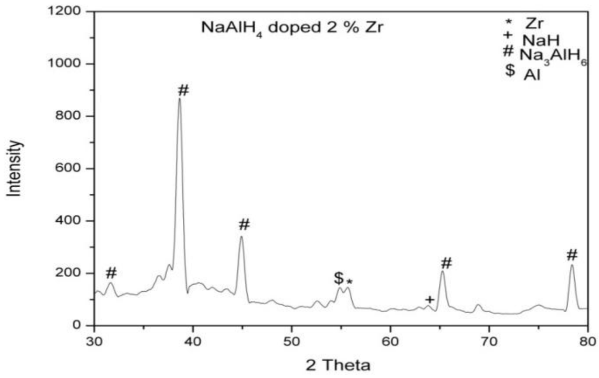

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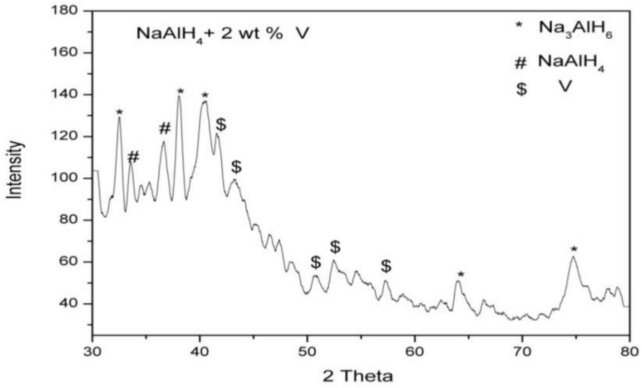

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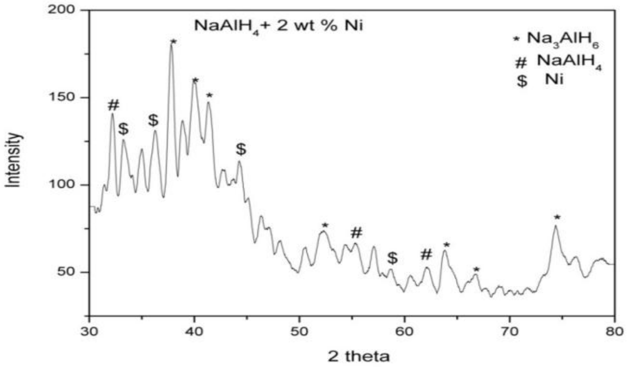

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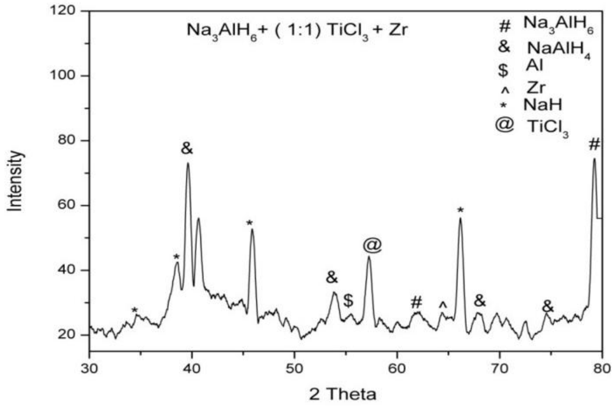

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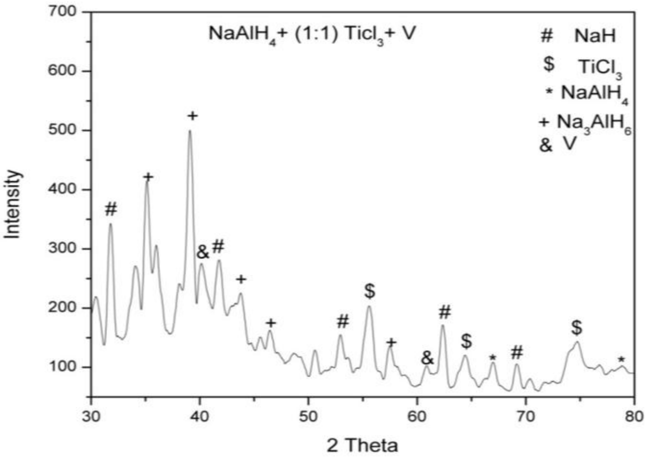

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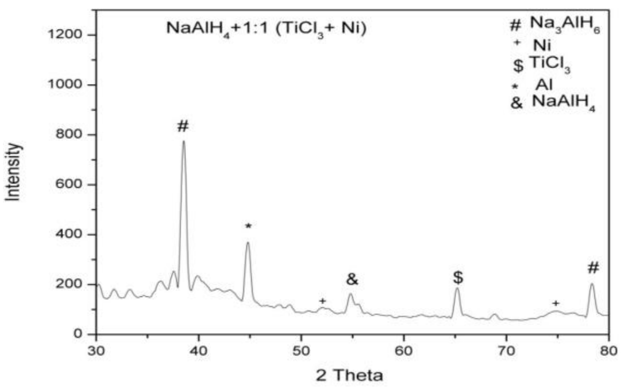

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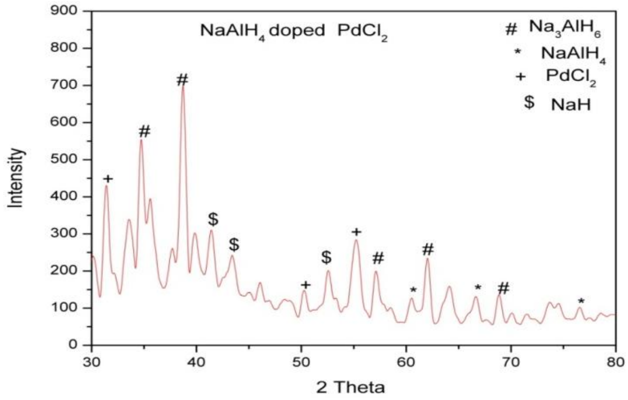

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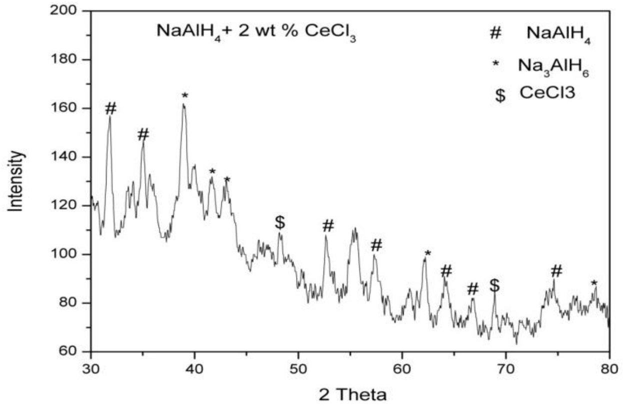

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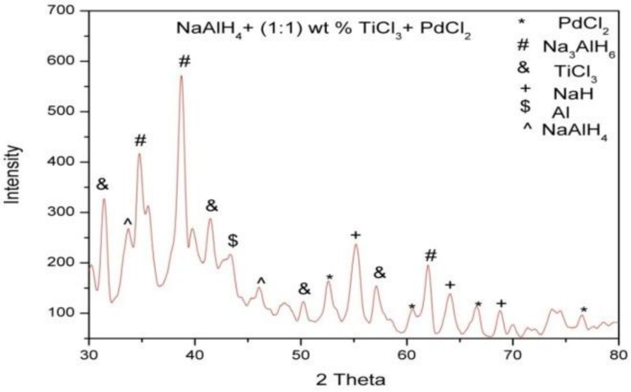

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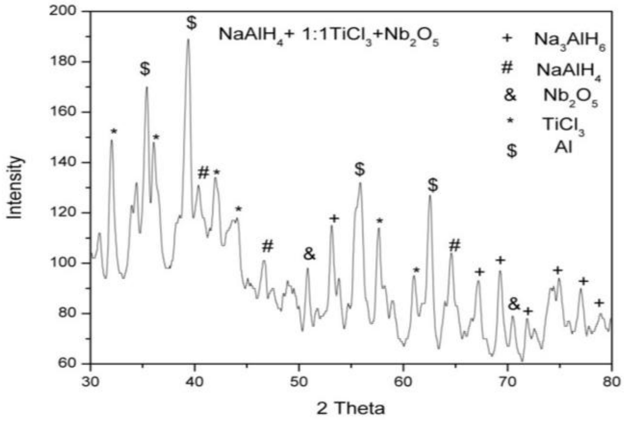

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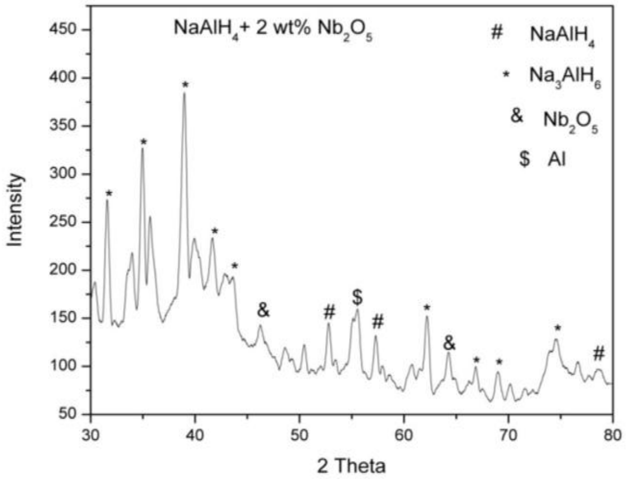

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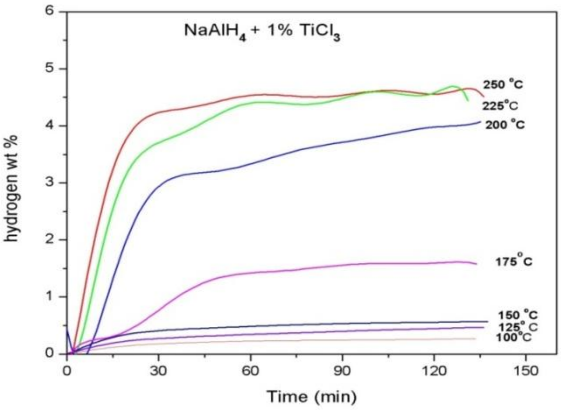

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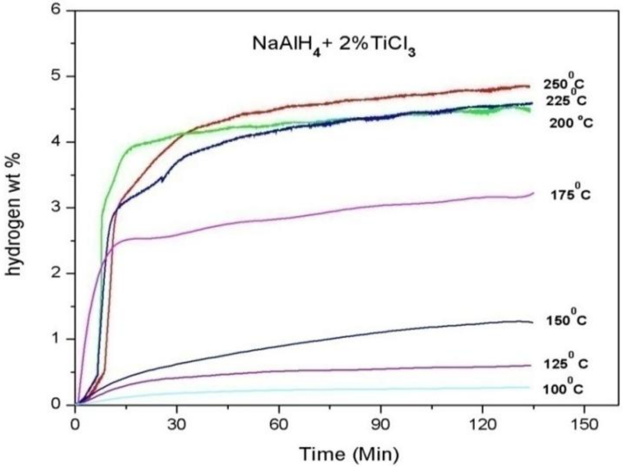

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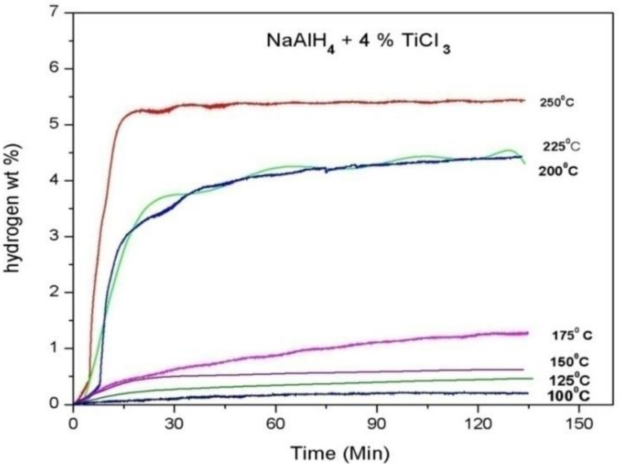

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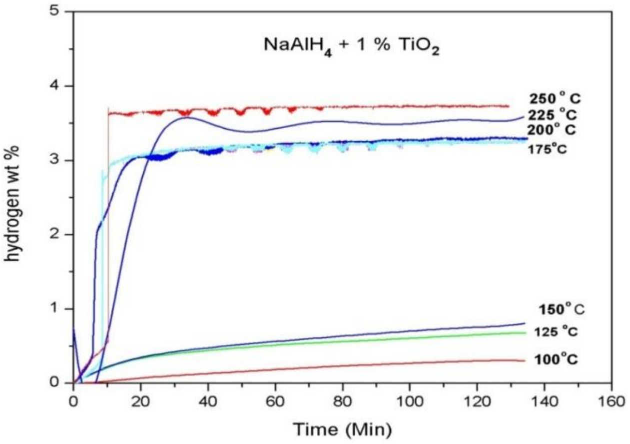

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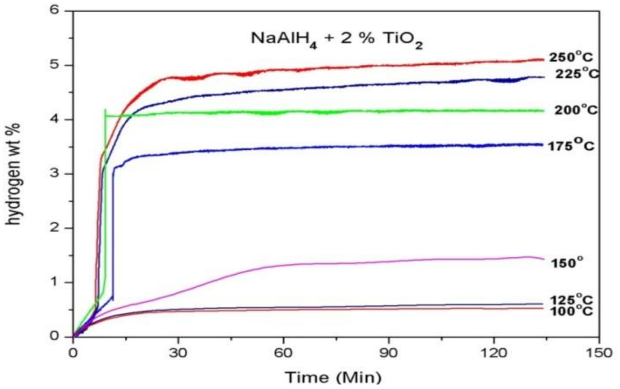

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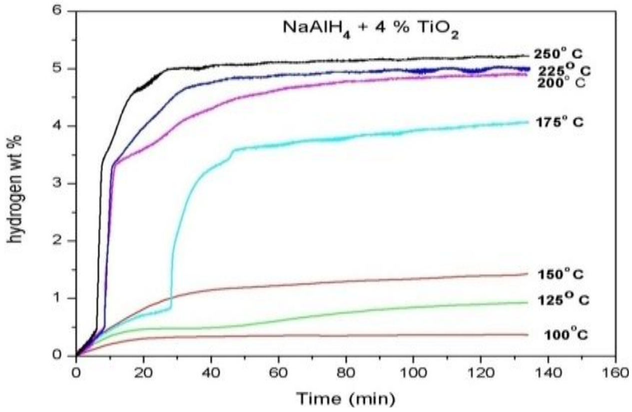

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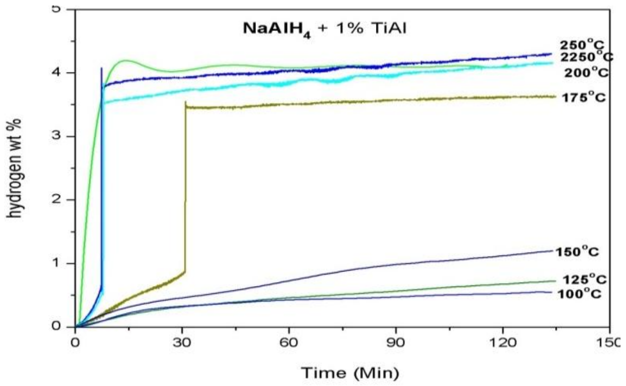

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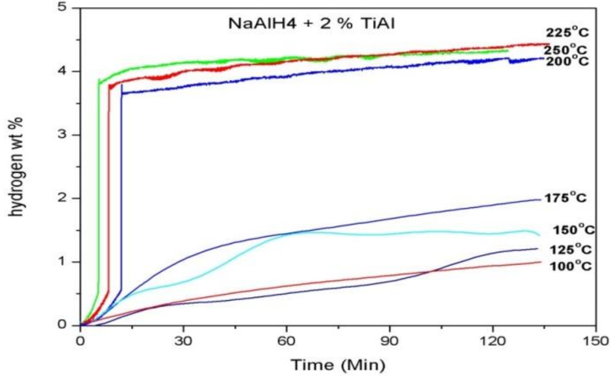

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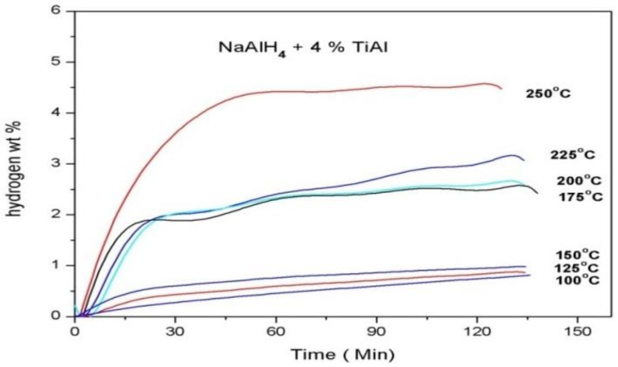

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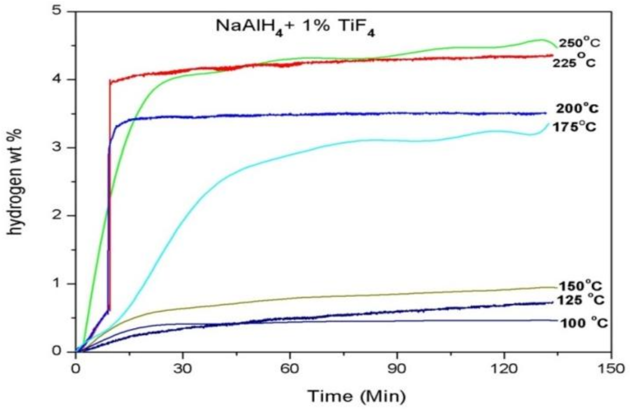

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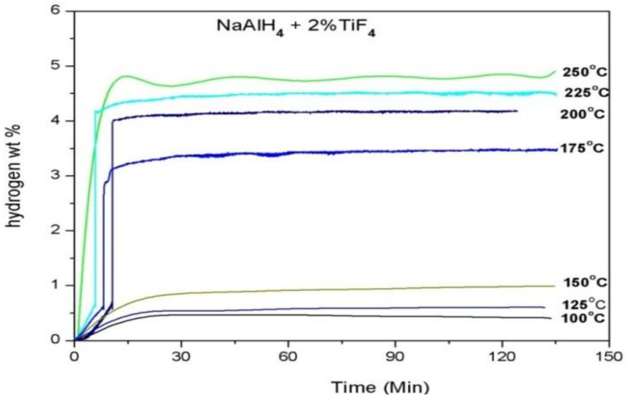

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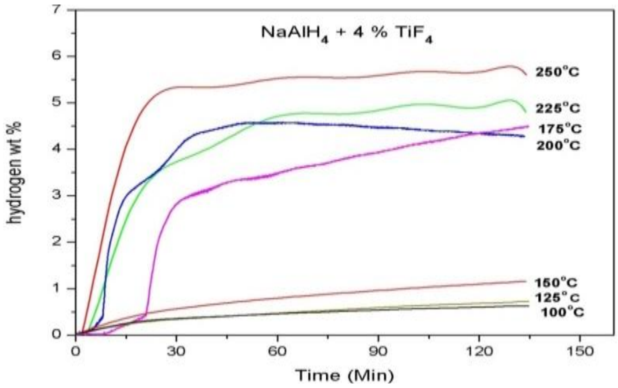

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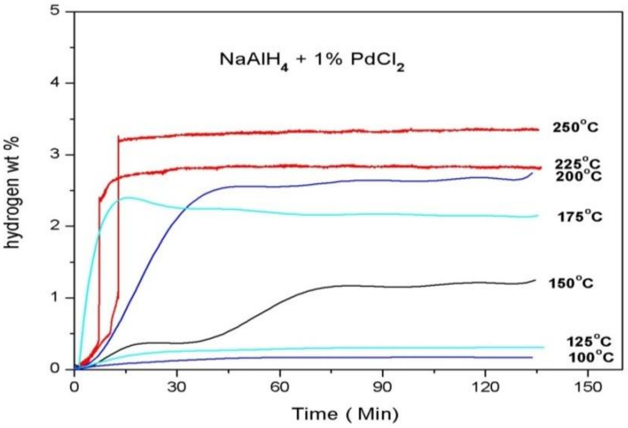

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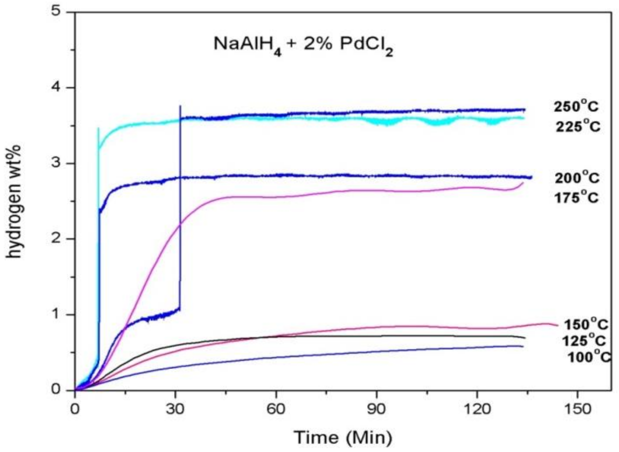

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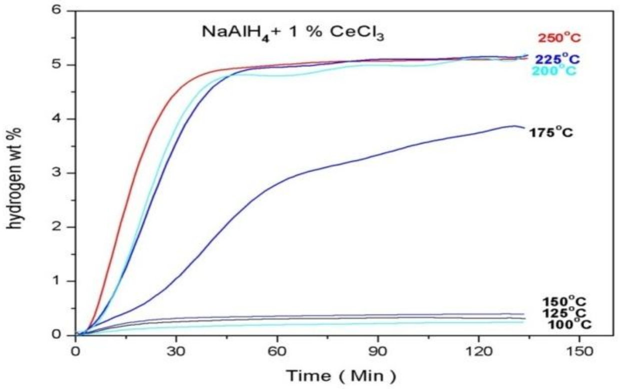

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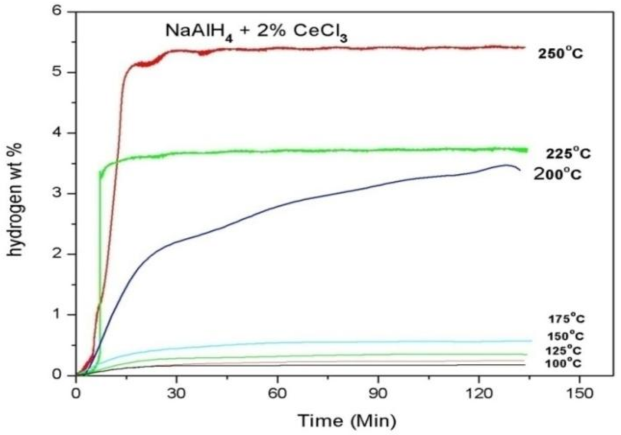

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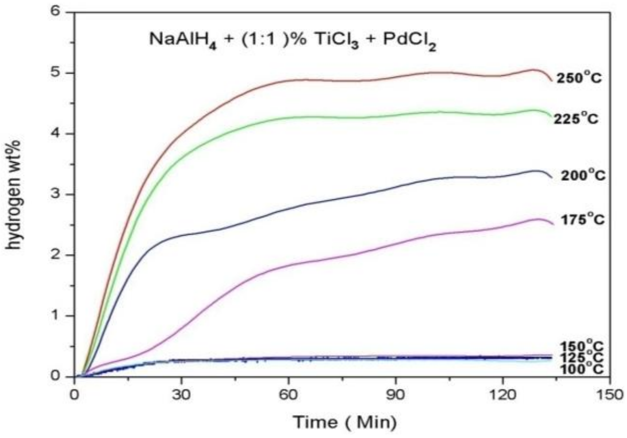

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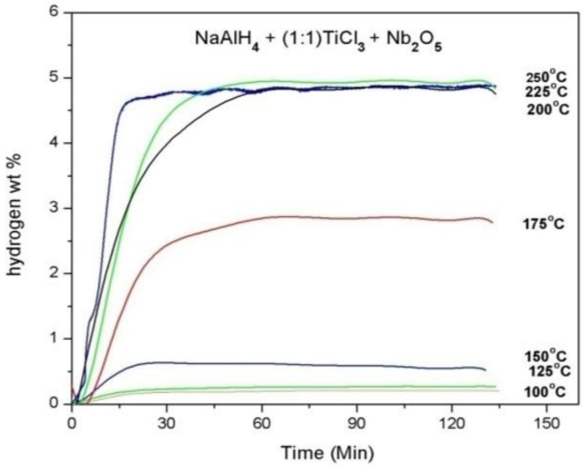

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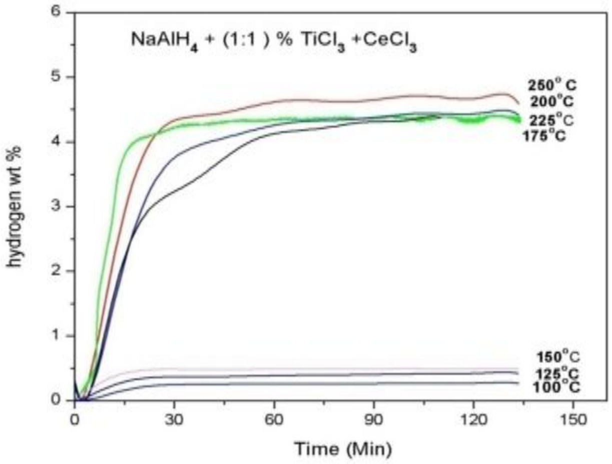

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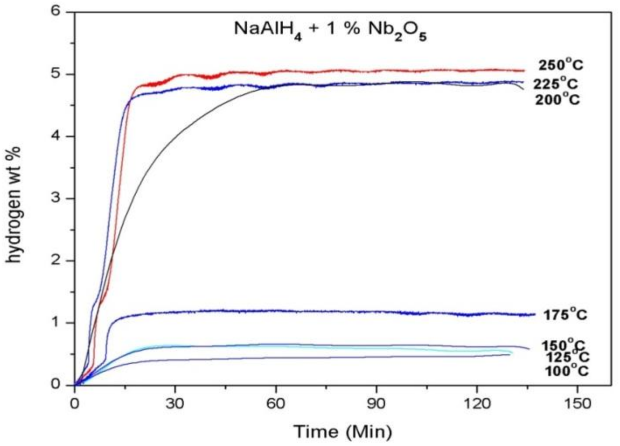

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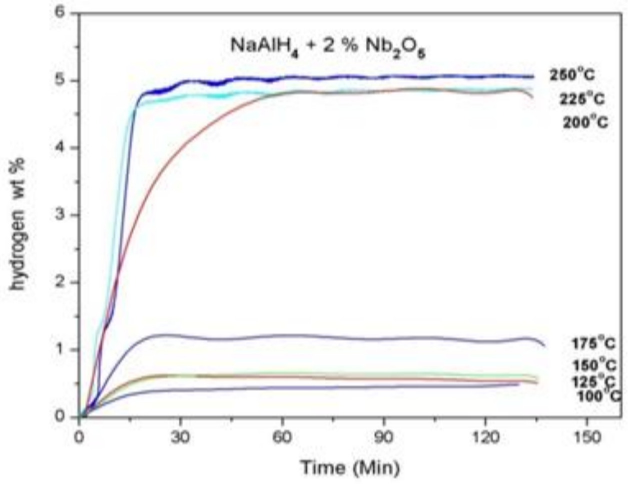

Figure 36