Effect of Transition Elements (V, Zr, Ni) on the Kinetic of Hydrogen in Sodium Alanate

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Abstract:- Renewable energy source is wind, solar etc. The use of hydrogen as fuel reduced eliminate the carbon emissions. sodium alante is used to store the hydrogen due to high capicity. The purpose of this work is to investigate the effect of transition metal (Zr, V, Ni) on hydrogen desorption of $NaAlH_4$.The samples prepared doped catalyst Zr, Ni, V and $TiCl_3$with $NaAlH_4$ under argon atmosphere using ball milling and hand milling for 30 minute. The transition metals is improve the kinetics of the hydrogen desorption in $NaAlH_4$ and the rate of desorption increased with increasing the amount of catalyst . Structural properties were characterized by XRD. The maximum hydrogen capacity is 5.2 wt % . Kinetic measurement was taken by PCT.

Keyword:- *Sodium Alanate, Hydrogen, Kinetics, Catalyst, Ball Milling , XRD.*

I. INTRODUCTION

World is facing a problem of energy nowdays. Energy sources are limit and use of energy is increasing due to development of high society and living standard . The solution of this problem is storage of energy with high wt % and low volume and low cost. Renewable energy source are available in sufficient quantity on the Earth which is technically and economically viable. Hydrogen is a secondary energy vector that has many merits, including compatibility with environment, storage capability and convertibility with many fuels and energies.Sodium alanate has attraction in research due to their high volumetric energy density, high storage capacity, low cost and good kinetic and reversible reaction.In recently , researcher has been focused on light weight complex hydrides, which also have high hydrogen capacity by weight ,e.g. $LiBH_4$ [1], $LiBH_4$/ MgH_2 [2,3] and various metal complex hydride [4-8]. These material requires high operating temperatures for the absorption/desorption process.sodium alante has been selected as material to development of storage systems based on light weight metal hydrides and kinetics of desorption.Sodium alante ($NaAlH_4$) is solid state hydrogen storage materials for on board applications because sodium alante has high volumetric hydrogen density and high storage capacity and good kinetics.After the discovery by Bogdanovic and Schwickardi on the reversibility of $NaAlH_4$ by doping with small amounts of transition metal compounds such as $TiCl_3$ [9-11]. $NaAlH_4$ can be release maximum 7.4 wt% hydrogen during thermal decomposition into three steps as shown in Eqs. (1) to (3) .

$$3\ NaAlH_4 \leftrightarrow Na_3AlH_6 + 2\ Al + 3H_2 \quad (3.7\ \%\ wt\ H_2) \quad (1)$$
$$Na_3AlH_6 \leftrightarrow 3\ NaH + Al + 3/2\ H_2 \quad (1.9\ wt\ \%H_2) \quad (2)$$
$$2\ NaH \leftrightarrow 2\ Na + H2 \quad (3)$$

From equation(1) ,The first step reaction releases 3.7 wt% hydrogen at 200^0C and from equation(2) , the second one at 250^0C with 1.8 wt % hydrogen and equation (3) cannot be used for hydrogen storage and commercial purpose, because this reaction is operated in high temperature. Bogdanovic and schwickardi was reported that $NaAlH_4$ mixed with $Ti(OBu^n)_4$ can desorb 3.5-4 wt % hydrogen and reabsorb hydrogen at 170^0 C and 150 bar. After this breakthrough, sodium alanate have been made to modify hydrogen desorption in terms of its kinetics, capacity and reversibility of complex metal hydrides .$NaAlH_4$ has been modified by doping with different catalyst in different forms using different doping techniques under moderate conditions [12]. Ragainy A.at al [13] the dehydradating kinetics of $NaAlH_4$ are improved through both zirconium and titanium doping. The main objective of this work was to investigation on the effects of adding transition metal(Zr, Ni ,V) on hydrogen desorption of $NaAlH_4$ and the effects of the catalyst and reversibility of the hydrides . our focus is on the effect of catalyst as Zr, V, Ni and combined with $TiCl_3$ on the kinetic of hydrogen in Sodium alanate.

II. EXPERIMENTAL

Material sodium alanate ($NaAlH_4$) and Catalyst Ni, V, $TiCl_3$ and Zr were purchased from Sigma Aldrich chemical. Sodium alanate is flammable and active with air and humidity and Sodium alanate is very sensitive to air and water exposure, reacting with O_2 and OH therefore Glove box with argon atmosphere is necessary required for preparations of sample of sodium alanate with different catalyst. Sodium alanate were doped with Zr, Ni, V using a ball mill. Amount of catalyst were varied between 1to 4 % . Samples filled in cylindrical tube in argon atmosphere and samples were weighed 0.20mg. The tube takes place in Furnace.The Furnace temperature was varied 100- 250ºC. First time we vacuum whole PCT system and created hydrogen atmosphere. PCT system is attached computer and all data stored in computer. Data collected in CD and analysis by software. After hydrogen desorption, Structural Characterization of sample analysed at 250ºC by XRD.

III. RESULT AND DISCUSSION

Samples were prepared and after preparing of samples, the samples were used for desorption kinetics and desorbed samples were used for structural characterization. The Structural characterization of samples($TiCl_3$, V, Ni and Zr doped Sodium alanate) have been done by X-Ray Diffraction. The Structural Characterization of Zirconium doped Sodium alanate have been performed in Fig (1). $NaAlH_4$ was appear in Tetragonal structure with lattice constant a=5.02, b=5.02 and c=11.34 respectively. $NaAlH_4$ is completely converted in Na_3AlH_6 at 250°C and Na_3AlH_6 is appear Monoclinic structure with lattice constant a= 5.46, b= 5.61, c= 7.80 and NaH in Cubic structure with lattice constant a=b=c=4.890 and Al Cubic structure a=b=c= 4.049 and some content of Zr is appears in Cubic structure a=b=c 3.545. NaH peak represent that Na_3AlH_6 decomposed in NaH and Al. No peaks of $NaAlH_4$ were observed after dehydrogenation. The Structural Characterization of vanadium and Nikal doped Sodium alanate have been seen in Fig (2) and Fig (3). The X–ray diffraction pattern of dehydrogenated $NaAlH_4$ + 1:1 ($TiCl_3$+Zr) and $NaAlH_4$ + 1:1 $TiCl_3$+V samples analyzed by using Powder X and PCPDFWIN program is shown in Fig (4) and Fig (5). 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 respectively. The X–ray diffraction pattern of dehydrogenated $NaAlH_4$ + 1:1 $TiCl_3$+Ni sample analyzed by using Powder X and PCPDFWIN program is shown in Fig (6). Ni is appears in Cubic structure having lattice constant a=b=c =3.027. The product is NaH and Al after complete decomposition. Storage capacity and kinetics of sodium alante were presented by fig.(7) to (15). Now the prepared samples were transferred into the stainless steel hydrogenation set up designed to work under argon atmosphere. 0.20 gm (dry mass) of doped samples with catalysts was placed in to Cr-Al thermocouple. Seivert type system started at temperature 100°C to 250°C for 2.30 hrs and data store in PC which attached by Seivert type apparatus and then data analysized for desorption kinetics. The amount of desorbed hydrogen is calculated in wt%. The calibration of the volume of the whole system was performed with He which comes out to be 50.11 cc and 51.72 cc for absorption and desorption cycles respectively .The samples in the sample holder is placed on the bottom thermocouple with a Cr-Al. Kinetic curves of $NaAlH_4$ + x wt % Zr (x=1,2) are shown in Figure (7) to Figure (8). Fig (7) is a curve for hydrogen desorbed by $NaAlH_4$ +1 wt %Zr vs time at different temperature 100^0 C – 250° C. The sample released about 4.5 wt % hydrogen at 250° C. The capacity is lower than the theoretical capacity 5.6% wt % because $NaAlH_4$ partially decomposes.in the study, the catalytic effects of Zr on desorption of $NaAlH_4$ were investigated and resulted faster desorption kinetics and lower desorption temperature than as reported temperature. Kinetic curves of $NaAlH_4$ + x wt % V (x=1, 2) are shown in Fig. (9) and Fig. (10). Curves in Fig (9) provide the information concerning the amount of desorbed hydrogen capacity as well as time at different temperature 100^0 C– 250° C. 1wt % V doped $NaAlH_4$ release about 5.2 wt% hydrogen at 250°C.The desorbed hydrogen capacity of $NaAlH_4$ is almost equal to the theoretical capacity 5.6% wt % because $NaAlH_4$ completely decomposes. 2 wt % V doped $NaAlH_4$ released about 4.8 wt % hydrogen at 250° C temperature. The hydrogen desorption capacity is poor with increasing content of vanadium catylist and kinetics is slower than other catalyst. Kinetic curve of NaAlH4+1 wt % Ni is shown in Fig(11).1 wt % Ni doped $NaAlH_4$ released about 5.0 wt % hydrogen at 250° C.

Fig. (11) shows that desorption kinetics of Ni doped Sodium alnate is slow but storage capacity is richer than others transition metals and desorption temperature has been reduced than reported temperature in [1].Kinetic curves of $NaAlH_4$+ 1:1 wt%$TiCl_3$+Zr are shown in Fig (12). 1:1mol% $TiCl_3$+Zr doped $NaAlH_4$ release about 4.6 wt % hydrogen at 250° C. Zr is the same group in the periodic table as Ti thus a similar catalytic effect can be anticipated. The combination of Zr and Ti Catalyst precursors helps to improve the desorption kinetics [13]. X-ray diffraction studies were carried out the lattice constant of $NaAlH_4$ [14]. Codoping Zr and $TiCl_3$ improves the kinetics for hydrogen desorption compared to sole doping with Zr. Ti catylist is a better than Zr. Zr is not good for promoter for Ti. Kinetic curve of $NaAlH_4$ +1:1 wt % $TiCl_3$+V is shown in Fig (13). 1:1 wt % $TiCl_3$+Vdoped $NaAlH_4$ released about 4.0 wt % hydrogen at 250° C. The desorbed hydrogen capacity of this system is lower. It is suggested that Ti lacks the long order to form Ti – Al crystal structure and V shows the strong formation of V- Al crystalline. The formation of Al_3V is a stable compound that would decrease the activity of the catalyst and reduce the amount of desorption hydrogen. Therefore, catalytic effect of 1:1 $TiCl_3$+ V co-doping with sodium alanate is not good for desorption and storage applications. Kinetic curves of $NaAlH_4$ + $TiCl_3$+Ni (1:1wt %) are shown in Fig (14). Form as Ti –Al amorphous be dispersed particle on $NaAlH_4$ which evidence by XRD while Ni shows the weak formation of Ni-Al crystalline. The formation of intermetallic is not stable compound that would increase the activity of the catalyst. Therefore, catalytic effect of 1:1 $TiCl_3$+ Ni co-doping with sodium alanate is almost good for desorption. $NaAlH_4$ sample decomposes into two steps while the samples doped with metals behave differently. It is observed through kinetics figure that kinetics is very fast about 10-15 minute and after this time, kinetics observed approximately constant. Finally, in the present study storage capacity of hydrogen in sodium alante is increased with increasing amount of catalyst.

IV. CONCLUSION

In the first part of this study, there are explained the process of sample preparation under argon atmosphere and structural characterization by X- ray diffraction (XRD). XRD diffraction pattern of all samples were investigated after desorption.

In the second part, the catalyst effect in hydrogen storage is reported with different amount of catalyst. The hydrogen desorption of the samples were release about 4.0-

5.2 wt %. The Kinetics of sodium alante doped catalyst Zr and V is slower but Ni catalyst is good for desorption. The effect of three different catalyst species (Ni, Zr, and V) were studied individually and with all possible combinations of their binary and ternary mixtures . Codoping $NaAlH_4$ with Zr and $TiCl_3$ improves the kinetics for hydrogen desorption compared to sole doping with Zr. Ti metal is a better than Zr. Zr is not as good promoter for Ti .crystal structure would form as Ti –Al amorphous and V shows the strong formation of V- Al crystalline. The formation of Al_3V is a stable compound that would decrease the activity of the catalyst. In other words, the high stability of Al_3V would affect the deformation to $NaAlH_4$. In addition, the formation of crystal Al_3V would reduce the amount of desorption hydrogen. Therefore, catlytic effect of 1:1 $TiCl_3$+ V co-doping with sodium alanate is not good for desorption and storage applications. Ni shows the weak formation of Ni-Al crystalline. The formation of intermetallic is not stable compound that would increase the activity of the catalyst. Therefore, catalytic effect of 1:1 $TiCl_3$+ Ni co-doping with sodium alanate is almost rich for desorption .It is concluded that enhanced storage capacity can be achieved and temperature is reduced 285°C to 250 °C for desorption due to doping of various catalysts.

V. ACKNOWLEDGEMENTS

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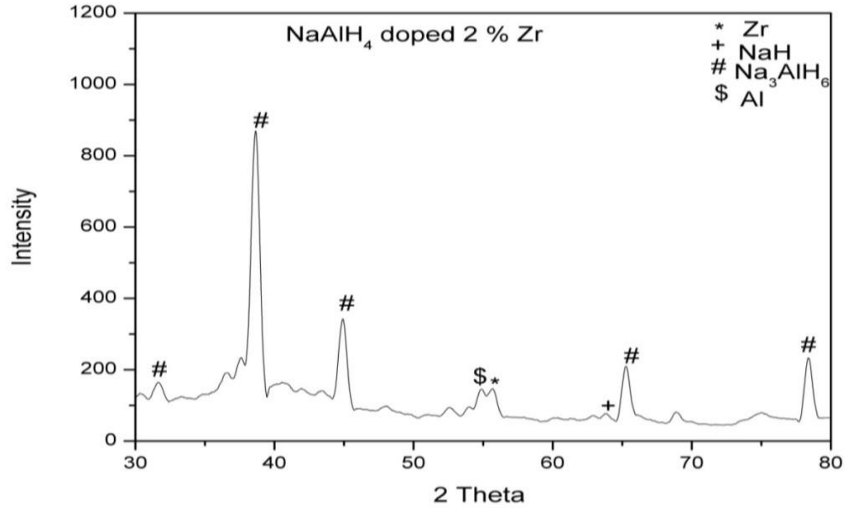

Fig 1:- XRD pattern of desorbed 2 mol% Zr doped $NaAlH_4$ at 250^0C

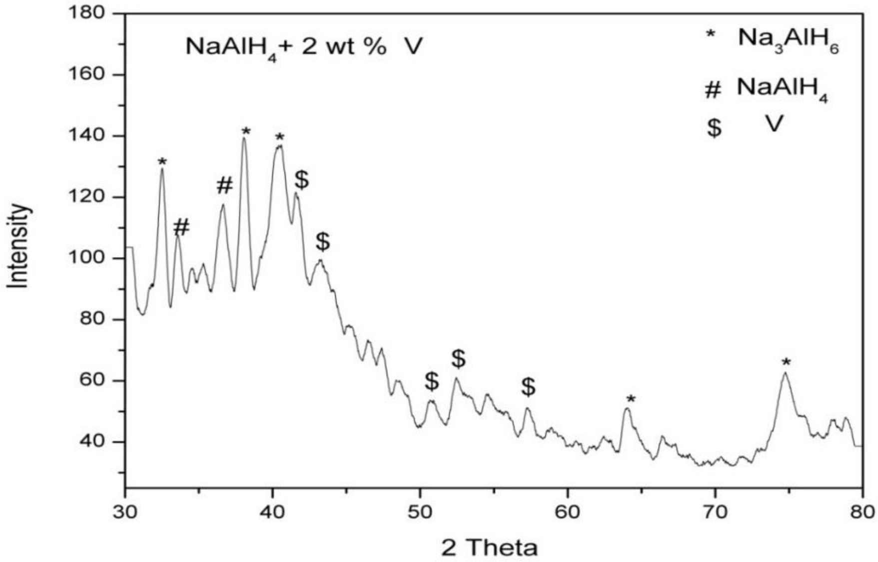

Fig 2:- XRD pattern of desorbed 2 mol% V doped $NaAlH_4$ at 250^0C

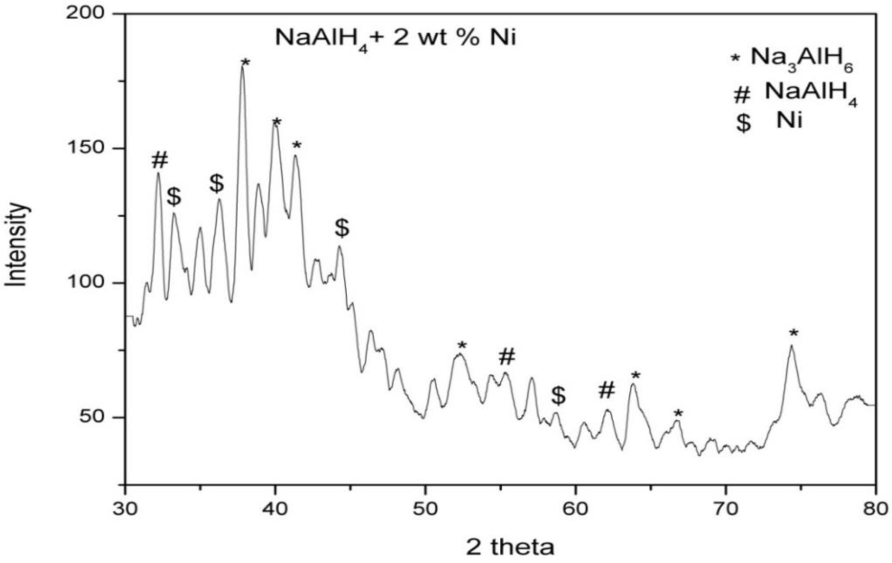

Fig 3:- XRD pattern of desorbed 2 mol% Ni doped $NaAlH_4$ at 250^0C

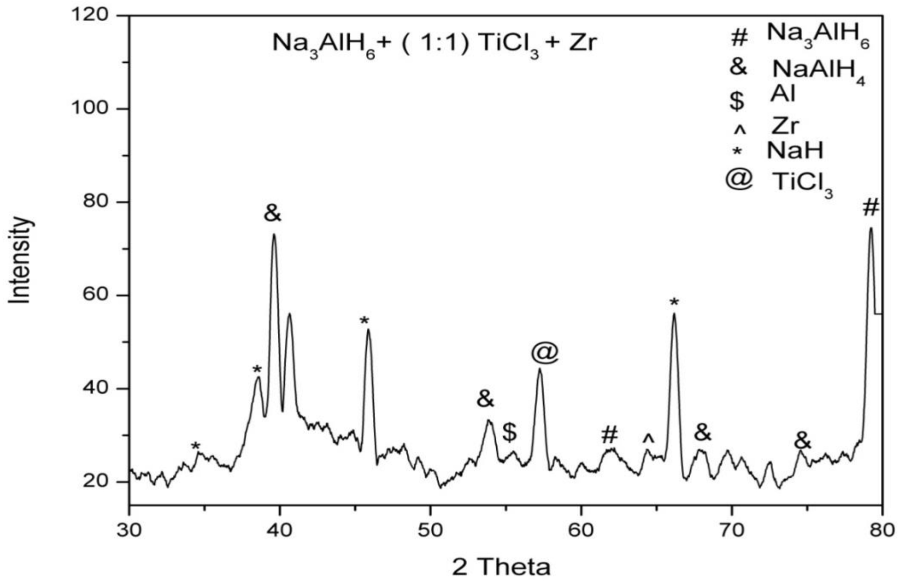

Fig 4:- XRD pattern of desorbed 1:1 mol% (TiCl3+Zr) doped $NaAlH_4$ at 250^0C

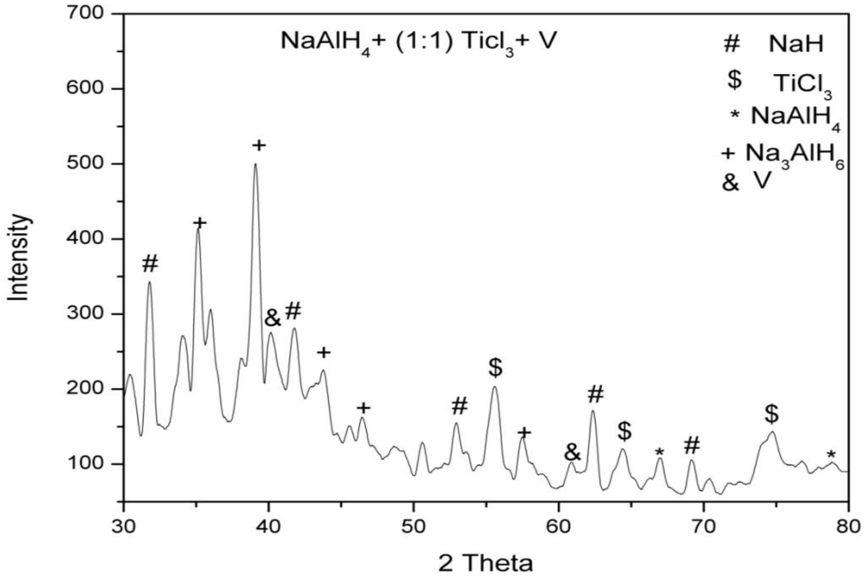

Fig 5:- XRD pattern of desorbed 1:1 mol% ($TiCl_3$+V) doped $NaAlH_4$ at 250^0C

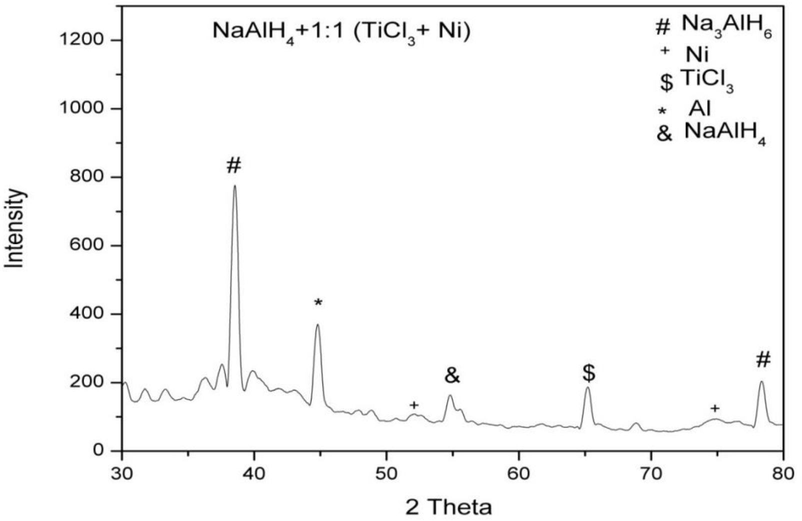

Fig 6:- XRD pattern of desorbed 1:1 mol% ($TiCl_3$+Ni) doped $NaAlH_4$ at 250^0C

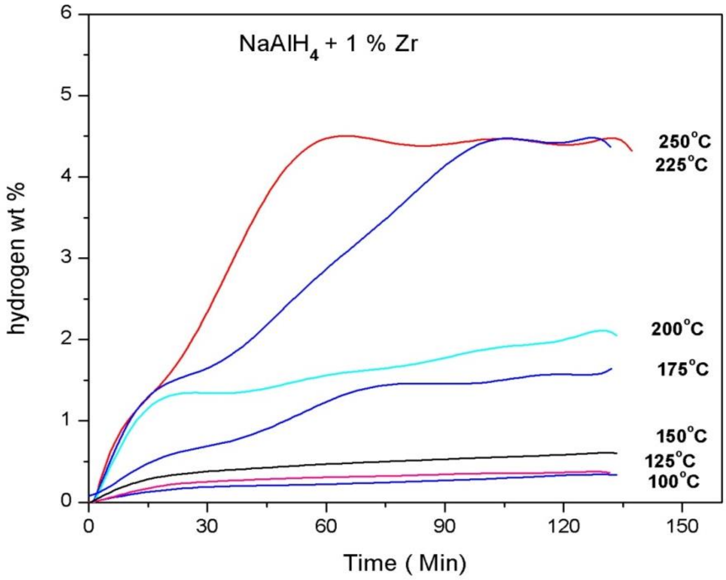

Fig 7:- Hydrogen desorption curves of $NaAlH_4$ with 1 mol % Zr

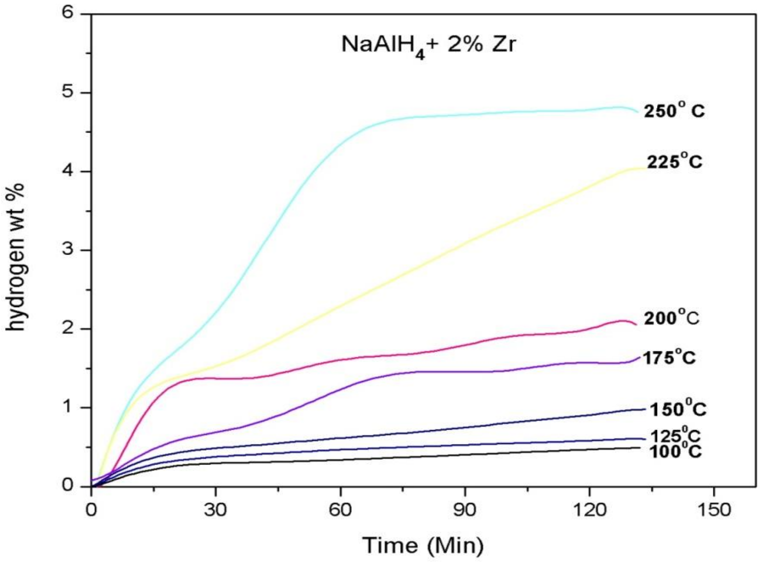

Fig 8:- Hydrogen desorption curves of $NaAlH_4$ with 2 mol % Zr

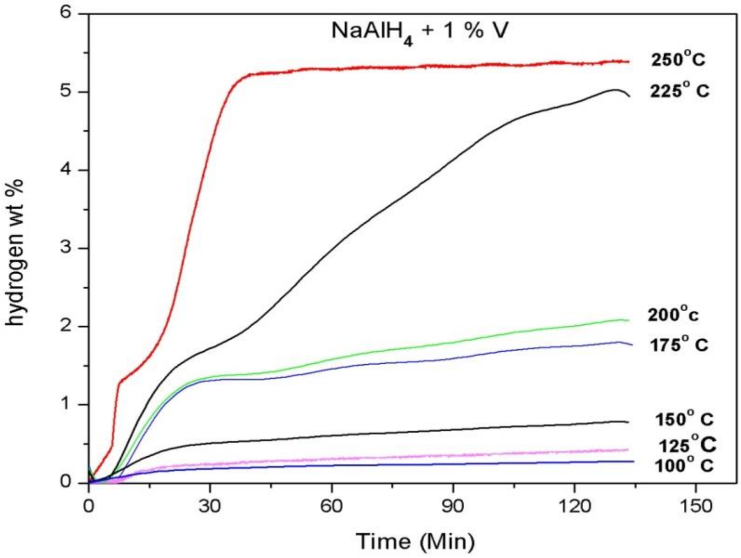

Fig 9:- Hydrogen desorption curves of $NaAlH_4$ with 1 mol % V

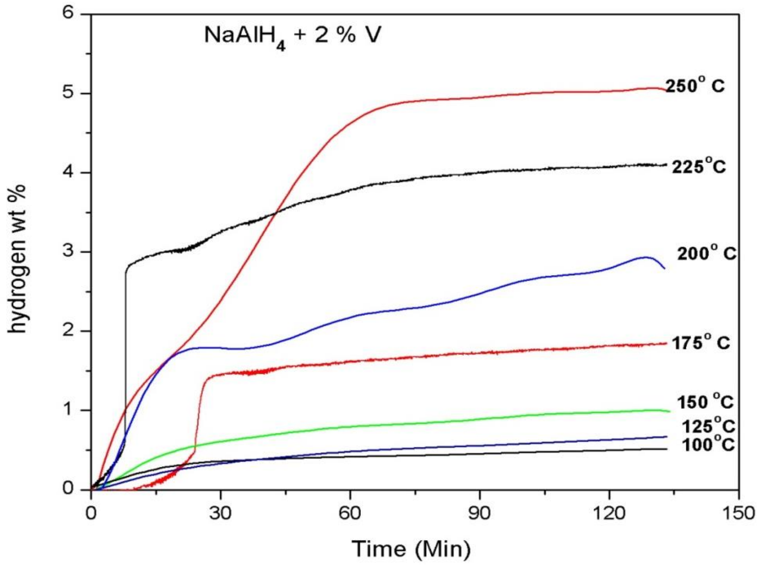

Fig 10:- Hydrogen desorption curves of NaAlH$_4$ with 2 mol % V

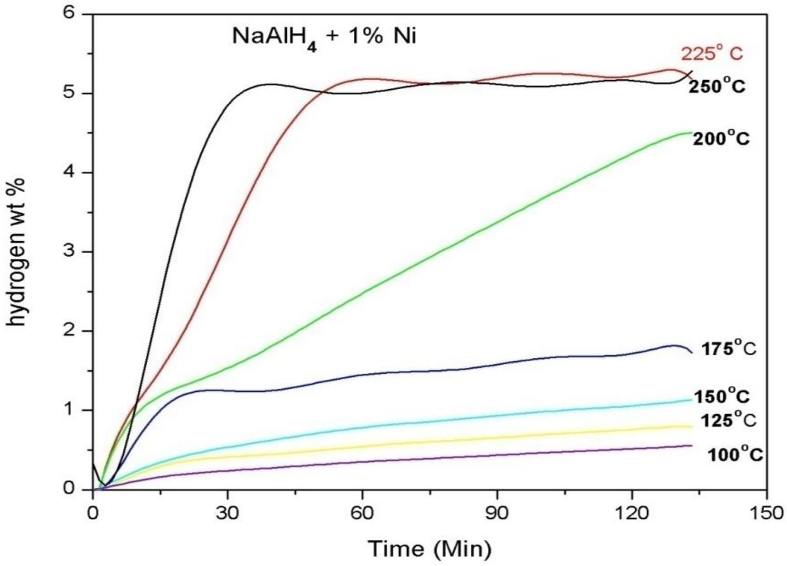

Fig 11:- Hydrogen desorption curves of NaAlH$_4$ with 1 mol % Ni

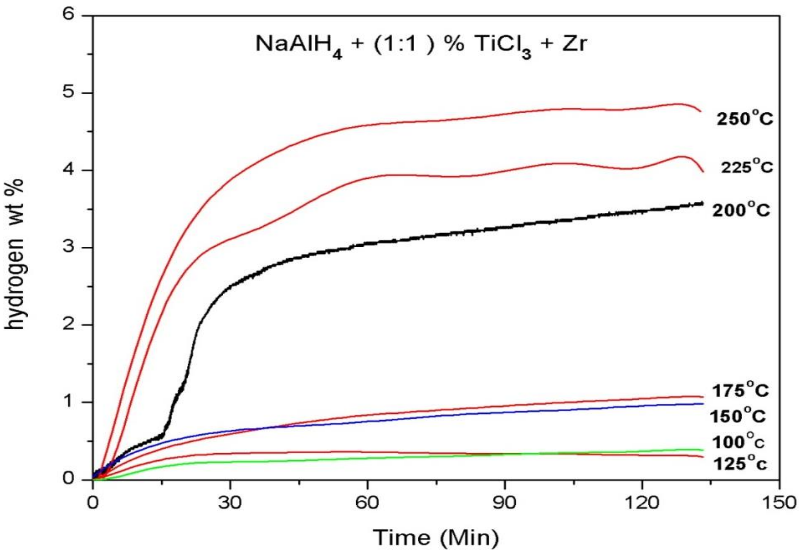

Fig 12:- Hydrogen desorption curves of NaAlH$_4$ + 1:1 wt % TiCl3+ Zr at 250^{0}C

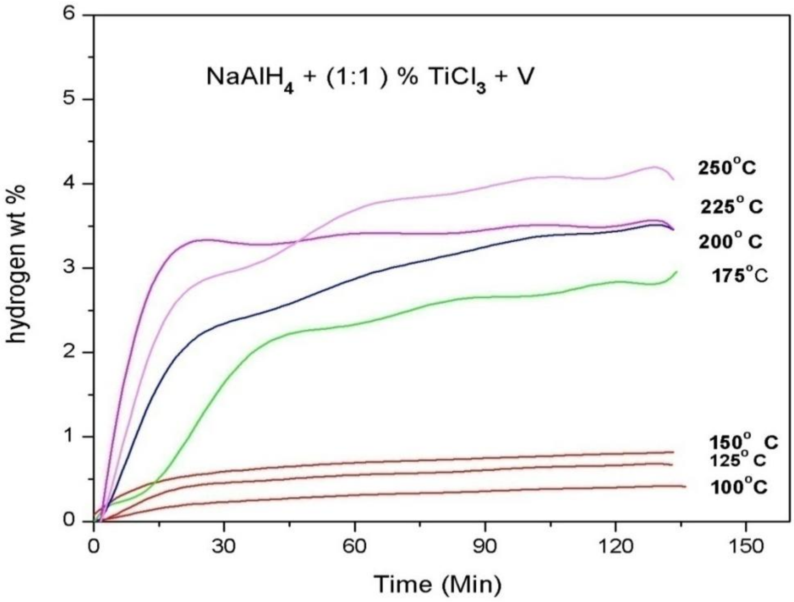

Fig 13:- Hydrogen desorption curves of $NaAlH_4$ + 1:1 wt % $TiCl_3$+ V at 250^0C

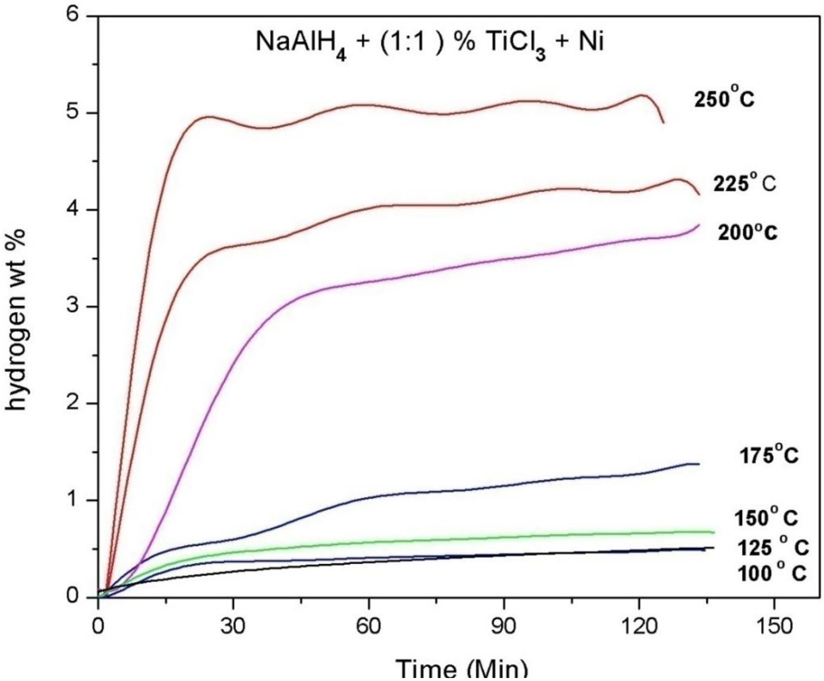

Fig 14:- Hydrogen desorption curves of $NaAlH_4$ + 1:1 wt % $TiCl_3$+ Ni at 250^0C