

Improve Kinetics of Hydrogen Storage in Sodium Alante Codoped with TiO₂, TiF₄, TiAl and TiCl₃

Dr. Jameel khan

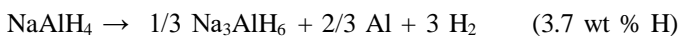
CNCER University of Rajasthan Jaipur Rajasthan, India

Abstract:- Hydrogen energy is an energy carrier, alternative and renewable source of energy in world. However, hydrogen energy is facing many problem such as high capacity, good kinetics, thermodynamics, controllable reversibility. TiO₂, TiF₄, TiAl and TiCl₃ codoped sodium alante (NaAlH₄) were synthesized for Hydrogen storage properties and mechanisms. Samples were prepared using ball milling in glove box under argon atmosphere. All catalyst is used for the dehydrogenation of NaAlH₄ at 250° C and characterization by XRD. Sodium alante appeared in Tetragonal structure with lattice constant a=b=5.02 and c=11.34. NaAlH₄ is completely converted in Na₃AlH₆ at 250°C which is having cubic structure with lattice constant a = b = c = 7.755. Desorption for all P-C-T isotherm of NaAlH₄ doped with catalyst were calculated using dynamic seivert type apparatus in 100° C to 250° C range of temperatures. The amount of hydrogen in sodium alante was desorbed between 3.8 and 5.2 wt % in various catalyst.

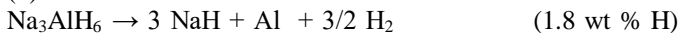
Keyword:- Sodium Alanate, Complex Hydrides, Catalyst, XRD and Seivert Type Apparatus for PCT.

I. INTRODUCTION

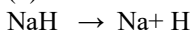
Storage of hydrogen is a challenge in hydrogen economy. Hydrogen is a fascinating energy fuel for automobile and airplane. Our goal is to obtain high volumetric density, storage capacity and favorable thermodynamics mechanics. In 1996, Bogdanovic and Schwickardi [1] showed that NaAlH₄ decomposed in two stages at temperatures of 180°C and 210°C and third stage decomposed at high temperature and pressure.



(1)



(2)



The equilibrium pressure for hydrogen is 1 bar. The reactions are reversible for conversion to sodium alante at 270°C under 175 bar hydrogen pressure in 2-3 hours [3]. The proper catalysts is added into sodium alante to enhancing hydrogen storage capacity. The work of Bogdanovic and Schwickardi [1] was motivated that NaAlH₄ shows good

kinetic and thermodynamics properties when catalyzed is use titanium based materials [4-8]. There are many kinetic and thermodynamics studies on the decomposition of NaAlH₄ either doped with TiCl₃ [9-20] or Ti alkoxides [11]. Ti(OBu)₄ is added directly to Na₃AlH₆ the activation energy for reaction (2). A major disadvantage of sodium alante is low absorption and desorption kinetics which is required high pressure and temperature. Hydrogen storage materials such metal hydride must be favorable thermodynamic properties and good kinetics of hydrogen. Sodium alante has received a fascinating due to its high storage capacity, low cost, good kinetics and good thermodynamics mechanics at suitable temperature and pressure. Therefore sodium alante was the material suitable and important for hydrogen storage in solid form.

II. EXPERIMENTAL

NaAlH₄ and catalyst TiCl₃, TiAl, TiF₄ and TiO₂ has been purchased from Aldrich Chemical. The purity of materials are contend 99% and used without further purification. samples were prepared in an argon filled globe box because samples are sensitive to air and humidity. Planetary ball mill machine was used for milling of TiCl₃, TiAl, TiF₄ and TiO₂. The ball-mill machine is rotated to 350 rpm speed for 2 hour. The ball to powder weight ratio are around 20:1. NaAlH₄, TiCl₃, TiAl, TiF₄ and TiO₂ were weighed under argon atmosphere. The samples were extend over by a kapton foil to avoid to air and humidity during characterization. The apparatus was heated at first to 100° C and then to 250°C. X-ray diffraction pattern of the samples were carry out with Cu-K alpha radiations. The data has been collected in the range between 30° and 80°. The structural characterization of samples with TiCl₃, TiO₂, TiAl, and TiF₄ doped Sodium alante have been performed by X-Ray Diffraction analysis.

III. RESULT AND DISCUSSION

➤ *Structural Characterization:*

X-Ray Diffraction analyzed structural of TiCl₃, TiO₂, TiAl, and TiF₄ doped Sodium alante. The X-ray diffraction pattern is shown in Fig (1) of NaAlH₄ + 4wt % TiCl₃. NaAlH₄ was found in Tetragonal structure with lattice constant a=5.02=5.02 and c=11.34 and 4 wt% TiCl₃ doped sodium alante has been heated at 250° C to remove hydrogen. NaAlH₄ was converted in Na₃AlH₆. Figure (1) shows that

NaH is observed in cubic structure with lattice constant $a=b=c=4.890$ and Na_3AlH_6 is Monoclinic structure with lattice constant $a=5.46$, $b=5.61$, $c=7.80$ and catalyst TiCl_3 appears in structure having $a=b=6.143$, $c=11.71$. Fig. (2) shows XRD patterns in dehydrogenation of catalyst TiO_2 doped NaAlH_4 which samples was analyzed by Powder X and PCPDFWIN program. NaAlH_4 was found in Tetragonal structure with lattice constant $a=5.02=5.02$ and $c=11.34$. It was observed that NaAlH_4 is converted to Na_3AlH_6 at 250°C and Na_3AlH_6 is converted Na_3AlH_6 in Monoclinic 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 is observed in cubic structure $a=b=c=4.049$ and TiO_2 appears Orthorhombic structure $a=4.531$, $b=5.501$, $c=4.906$ etc. NaAlH_4 decomposed in NaH and Al. $\text{NaAlH}_4 + 4 \text{ wt } \% \text{ TiAl}$ samples analyzed by XRD Diffraction method is shown in figure (3). It was notice that NaAlH_4 was observed in Tetragonal structure and NaAlH_4 is converted in Na_3AlH_6 and NaH at 250°C . NaH is not completely decomposed so peaks of Na are not observed. The higher formation of crystallites is due to increase in the catalytic activity and cycling stability which is presented to the increase in the peak intensity and the narrow peak of Al and NaH. Samples were characterized by the X-ray diffractometer to confirm the different particle size. NaAlH_4 was found in Tetragonal structure with lattice constant $a=5.02=5.02$ and $c=11.34$ and Na_3AlH_6 is appear cubic structure with lattice constant $a=b=c=7.755$ and TiF_4 is appears orthorhombic structure.

➤ Hydrogenation and Kinetics:

Hydrogen desorption curves of $\text{NaAlH}_4 + x \text{ wt } \% \text{ TiCl}_3$ ($x=1,2,4 \text{ wt } \%$) are shown in Fig (5) to Fig (7). All Kinetic measurement for desorption were determined using Dynamic Seiverts type apparatus at 100°C to 250°C temperatures. Fig (5) is a curve for desorbed hydrogen by $\text{NaAlH}_4 + 1 \text{ wt } \% \text{ TiCl}_3$ vs time at different temperature. It was seen that the sample releases hydrogen about $4.5 \text{ wt } \%$ in the temperature range between 100° and 250°C which is low than the theoretical capacity of $5.6\% \text{ wt } \%$ of NaAlH_4 . TiCl_3 doped NaAlH_4 desorbed hydrogen fastly at 175° and 250°C . After some time desorption rate is constant. Fig (6) is a curve for desorbed hydrogen by $\text{NaAlH}_4 + 2 \text{ wt } \% \text{ TiCl}_3$ vs time at different temperature. The sample releases about $4.8 \text{ wt } \%$ hydrogen at 250°C . The sample releases hydrogen fastly at 175° and 250°C . Amount of desorbed hydrogen is increased with increase amount of catalysts TiCl_3 . Desorption for all Kinetic measurement of $4 \text{ mol } \% \text{ TiCl}_3$ doped NaAlH_4 were determined using by Dynamic seivert's apparatus at 100°C to 250°C temperatures. Fig (7) is a curve for desorbed hydrogen by $\text{NaAlH}_4 + 4 \text{ wt } \% \text{ TiCl}_3$ vs time at different temperature. It is found that sample releases about $5.2 \text{ wt } \%$ hydrogen temperature range between 100° and 250°C . TiCl_3 doped NaAlH_4 shows fast desorption rate up to about 5 min at 175° and 250°C . After 5 min desorption rate is constant. Amount of released hydrogen is increased with increase amount of catalyst TiCl_3 . The desorption hydrogen capacity was found to be $4.5 \text{ wt } \%$, $4.8 \text{ wt } \%$ and $5.2 \text{ wt } \%$ with TiCl_3 (1% , 2%

and 4%) respectively which is approximate to theoretical value as Reported. It observed that increased TiCl_3 content increased the overall storage capacity of the complex hydride due to catalytic effect of TiCl_3 with temperature and effect of catalyst and kinetic rate is increased with temperature and surface area. Structure of sodium alanate is change at 250°C temperature. Hydrogen desorption curves of $\text{NaAlH}_4 + x \text{ wt } \% \text{ TiO}_2$ ($x=1,2,4 \text{ wt } \%$) are shown in Fig (8) to Fig (10). All Kinetic measurement of NaAlH_4 with $1 \text{ mol } \% \text{ TiO}_2$ for desorption were determined using Dynamic seiverts type apparatus at 100°C to 250°C temperatures. Fig (8) is a curve for desorbed hydrogen by $\text{NaAlH}_4 + 1 \text{ wt } \% \text{ TiO}_2$ vs time at different temperature range. Sodium alanate releases about $3.8 \text{ wt } \%$ hydrogen in presence of catalyst between 100° and 250°C . TiO_2 doped NaAlH_4 shows fast desorption kinetics at 250°C and after some time desorption rate is constant. Some wt % hydrogen released at 100° and 150°C . Desorption hydrogen wt % with TiO_2 is low but kinetics rate is very good compare to TiCl_3 . Fig (9) is a curve for desorbed hydrogen by $\text{NaAlH}_4 + 2 \text{ wt } \% \text{ TiO}_2$ vs time at different temperature. the sample releases about $4.8 \text{ wt } \%$ hydrogen in the temperature range between 100° and 250°C . TiO_2 doped NaAlH_4 shows fast desorption kinetics up to 10 min at 175° and 250°C . After 10 min desorption kinetics is constant. Fig (10) is a curve for hydrogen desorbed by $\text{NaAlH}_4 + 4 \text{ wt } \% \text{ TiO}_2$ vs time at different temperature $100^\circ\text{C} - 250^\circ\text{C}$. $4 \text{ wt } \% \text{ TiO}_2$ doped NaAlH_4 with release about $5.1 \text{ wt } \%$ hydrogen at temperature range between 200° and 250°C . Catalyst TiO_2 reacts with NaAlH_4 due to its extremely large interfacial area. Fig 10 shows that TiO_2 doped NaAlH_4 is fast desorption kinetics up to about 10 min in temperature range 175° and 250° . After 10 min desorption rate is constant. The desorption hydrogen capacity was found to be $3.6 \text{ wt } \%$, $4.8 \text{ wt } \%$ and $5.1 \text{ wt } \%$ with TiO_2 ($1, 2$ and $4 \text{ wt } \%$) respectively which is approximate to theoretical value. amount of hydrogen is increased due to catalytic effect of TiO_2 and temperature. In this study TiO_2 shows a better catalytic for the cycle. Hydrogen desorption curves of $\text{NaAlH}_4 + x \text{ wt } \% \text{ TiAl}$ ($x=1, 2, 4$) are shown in Fig (11) to Fig (13). Fig (11) is a curve for hydrogen desorbed by $\text{NaAlH}_4 + 1 \text{ wt } \% \text{ TiAl}$ vs time at different temperature $100^\circ\text{C} - 250^\circ\text{C}$. It is interesting to see that $1 \text{ wt } \% \text{ TiAl}$ doped NaAlH_4 with release about $3.8 \text{ wt } \%$ hydrogen at temperature range between 200° and 250°C . Fig (11) shows that TiAl doped NaAlH_4 have been very fast desorption kinetics. After 10 min desorption rate is constant. TiAl is good catalyst for NaAlH_4 . Fig (12) is a curve for desorbed hydrogen by $\text{NaAlH}_4 + 2 \text{ TiAl wt } \% \text{ vs time at different temperature range } 100^\circ\text{C} - 250^\circ\text{C}$. It observed $2 \text{ wt } \% \text{ TiAl}$ doped NaAlH_4 with release about $4.2 \text{ wt } \%$ hydrogen at temperature range between 200° and 250°C . Amount of hydrogen storage capacity is increased with increase of amount of TiAl . $4 \text{ wt } \% \text{ TiAl}$ doped NaAlH_4 release $4.6 \text{ wt } \%$ hydrogen in a desorption temperature range between 200° and 250°C . The desorption hydrogen capacity was found to be $4.0 \text{ wt } \%$, $4.2 \text{ wt } \%$ and $4.6 \text{ wt } \%$ with TiAl (1% , 2% and 4%) respectively. It seen that increased TiAl content increased storage capacity of the sodium alanate due catalytic effect of TiAl with temperature.

Hydrogen desorption curves of $\text{NaAlH}_4 + x \text{ wt } \% \text{ TiF}_4$ ($x=1, 2, 4 \text{ wt } \%$) are shown in Fig (14) to Fig (16). Desorption for all Kinetic measurement of 1 mol % TiAl doped NaAlH_4 were determined using Dynamic seiverts type apparatus at 100°C to 250°C temperatures. Fig (14) is a curve for desorbed hydrogen at $\text{NaAlH}_4 + 1 \text{ wt } \% \text{ TiF}_4$ different temperature $100^\circ \text{C} - 250^\circ \text{C}$. 1 wt % TiF_4 doped NaAlH_4 released about 4.3 wt % hydrogen at 250°C . The desorbed hydrogen capacity of TiF_4 doped NaAlH_4 is lower. Fig (14) shows that reaction of TiF_4 doped NaAlH_4 is very fast desorption kinetics up to about 12 min. After 12 min desorption rate is constant. TiF_4 is good catalyist for NaAlH_4 . Desorption for all Kinetic measurement of 2 mol % TiAl doped NaAlH_4 were determined using Dynamic Seiverts type apparatus at 100°C to 250°C temperatures. Fig (15) is a curve for hydrogen capacity at $\text{NaAlH}_4 + 2 \text{ wt } \% \text{ TiF}_4$ different temperature $100^\circ \text{C} - 250^\circ \text{C}$. 2 wt % TiF_4 doped NaAlH_4 released 4.8 wt % hydrogen at 250°C . Fig (16) shows that reaction of TiF_4 doped NaAlH_4 is fast desorption kinetics up to 8 min. 4 wt % TiF_4 doped NaAlH_4 released about 5.2 wt % at 250°C . The desorption hydrogen capacity was found to be 4.0 wt % , 4.8 wt % and 5.2 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 catalyists for desorption hydrogen and kinetics.

IV. CONCLUSIONS

Sodium alanate NaAlH_4 was appeared in Tetragonal with lattice parameter $a=5.02=5.02$ and $c=11.34$. NaAlH_4 is completely converted in Na_3AlH_6 at 250°C . Na_3AlH_6 is in cubic structure with lattice constant $a=b=c= 7.75$. Different type of catalyst such as TiCl_3 , TiO_2 , TiAl and TiF_4 is doped with sodium alanate. All Kinetic measurement of NaAlH_4 with different type of catalyst for desorption were determined using by Dynamic Seiverts type apparatus at 100°C to 250°C temperatures. Amount of hydrogen is desorbed 3.8 wt % to 5.2 wt % at 250°C with various type of catalyst. Kinetics of catalyst is fast but TiCl_3 and TiO_2 , TiF_4 catalyst is very good for desorption.

ACKNOWLEDGEMENT

Jameel Khan is thankful to Council of Scientific and Industrial Research Delhi Indai for funding for research work. Jameel khan is thankful to RSIC, Panjab University, and Chandigarh, India for providing XRD and SEM charactering techniques for samples.

REFERENCES

- [1]. Bogdanovic B, Schwickardi M. Ti doped alkali metal aluminium hydrides as otential novel reversible hydrogen storage materials. *J Alloy Compd* 1997 ; 253-254: 1-9
- [2]. Bogdanovic B, Brand RA, Majanovic A, Schwickardi M, Tolle J. Metal -doped sodium aluminium hydrides as otential new hydrogen storage materials . *J. Alloy Compd* 2000; 302: 36-58 .
- [3]. Jensen CM, Gross KJ. Development of catalytically enhanced sodium aluminum hydride as a hydrogen storage material. *Appl phys A* 2001;72:213-9
- [4]. Sandrock G, Gross K, Thomas G. Effect of Ti catalyst content on the reversible hydrogen properties of the sodium alanates. *J Alloys comps* 2002 ; 339: 299-308
- [5]. Wang P, Kang XD, Cheng M, improved hydrogen-storage performance on preparation conditions in TiF_3 doped NaAlH_4 *J Alloys comps* 2006;421:217-22.
- [6]. Termtanum M, Rangsunvigitt P, Kitiyanan B, Kulprathipanja S, Tanthapanichakoon W. Effect of metal type and loading on hydrogen storage on NaAlH_4 . *Sci techno Adv Mater* 2005; 6: 348 -51.
- [7]. Genma r, Uchida HH , Okada N, Nishi Y. Hydrogen reactivity of Li- containing hydrogen storage materials *J. AlloysCompd* 2003 ; 356-357 : 358-62
- [8]. [8] Okada N, Genma R, NishiY, Uchida H-H . RE -oxide doped alkaline hydrogen storage materials prepared by mechanical activation. *J Mater Sci* 2004; 39: 358-62.
- [9]. Ma XZ, Martinez- Franco E, Dornheim M, Klassen T, Bormann R. Catalyzed $\text{Na}_2\text{LiAlH}_6$ for hydrogen storage . *J Alloys Compd* 2005; 404- 406: 5503-6.
- [10]. Genma R, Okada N, Sobue T, Uchida H-H. Mechanically milled alanates as hydrogen storage materials. *Int J hydrogen energy* 2006; 31: 309-11.
- [11]. Suttisawat Y, Jannatisin V, Rangsunvigitt P, Kitiyanan B, Muangsin N, Kulprathipanja S. Understanding the effect of TiO_2 , VCl_3 , and HfCl_4 on hydrogen desorption / absorption of NaAlH_4 . *J power Sources* 2007;163: 997-1002.
- [12]. Jung KS, Kim DH , Lee KS . Hydrogen sorption of magnesium hydride doped with nano -sized TiO_2 . *Catal Today* 2007; 120: 270-5.
- [13]. Gil -jae Lee Jae-Hyeok shim, Young whan Cho , Kyung Sub Lee. Improvement in desorption kinetics of NaAlH_4 catalyzed with TiO_2 nanopowder *Int. J. hydrogen energy* 33(2008) 3748-3753.
- [14]. P. Wang, C.M. Jensen , Method for preparing Ti-doped NaAlH_4 using Ti powder. *J. Alloys Compd* . 379 (2004) 99-102.
- [15]. P.Wang, X. D. Kang, H.M. Cheng. Exploration of the nature of active Ti species in metallic Ti doped NaAlH_4 . *J.Phys. Chem. B* 109 (2005) 20131- 20136.
- [16]. A.G. Haiduc, H.A. Stil, M. A. Schwarz, P.Paulus, J.J.C. Geerlings. Hydrogen technology : Mobile and portable applications., *J. Alloys Compd*. 393 (2005) 252-263.

- [17]. C.Weidenthaler, A.Pommerin, M.Felderhoff, B.Bogdanovic, F. On the state of the titanium and zirconium in Ti or Zr doped NaAlH₄ hydrogen storage material Phys.chem. chem. phys 5 (2003) 5149-5153.
- [18]. K.Yvon , B. Bertheville, Magnesium based ternary metal hydrides containing alkali and alkaline-earth elements.J.Alloys compd. 425(2006) 101-108
- [19]. Schlapbachl, Zuttel A. Hydrogen Storage materials for mobile applications. Nature 2001; 414: 353-8
- [20]. Bogdanovic B, Felderhoff m, Hartel M, pommering A, Schuth F, et al . Investigation of hydrogen discharging and recharging processes of Ti doped NaAlH₄ by X –ray diffraction analysis (XRD) and Solid state NMR Spectroscopy. J Alloys Compds 2003; 350 : 246-55.

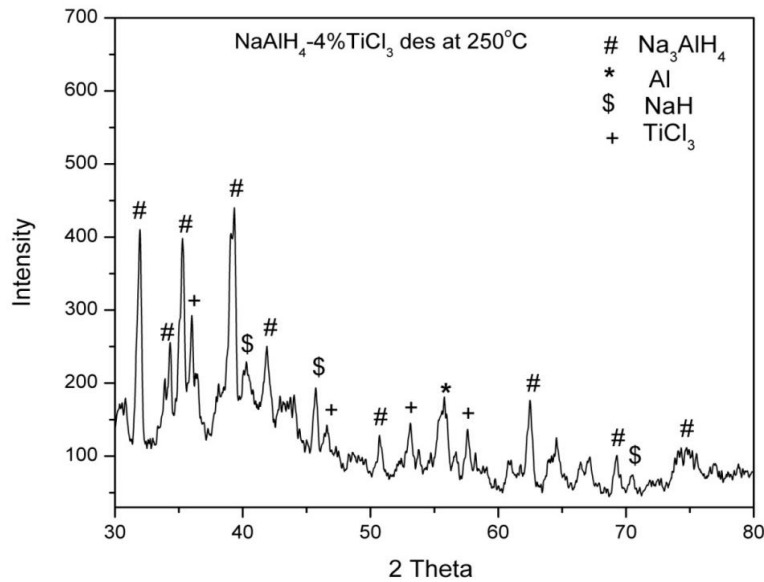


Fig. 1:- XRD curve of desorbed 4mol% TiCl₃ doped NaAlH₄ at 250°C

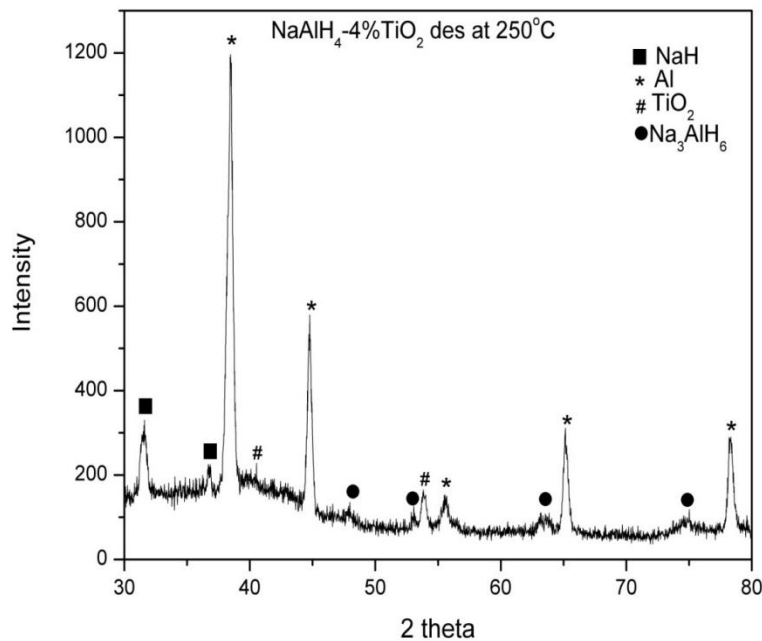


Fig. 2:- XRD curve of desorbed 4mol% TiO₂ doped NaAlH₄ at 250°C

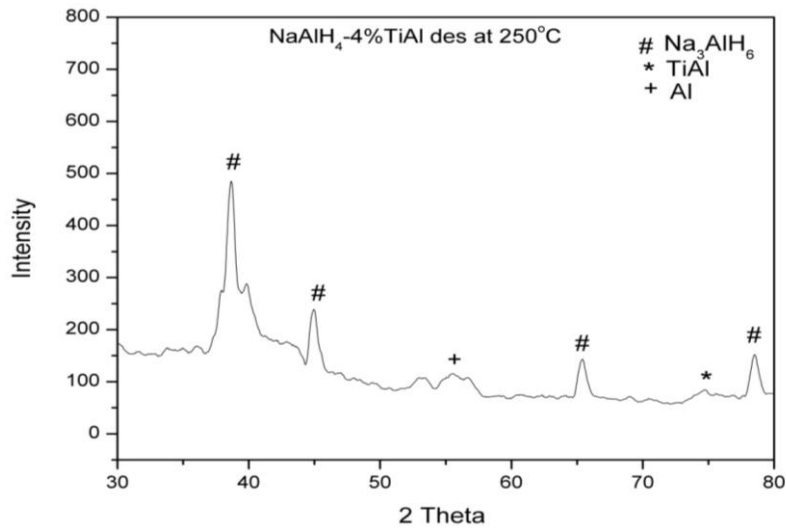


Fig. 3:- XRD curve of desorbed 4mol% TiAl doped NaAlH₄ at 250°C

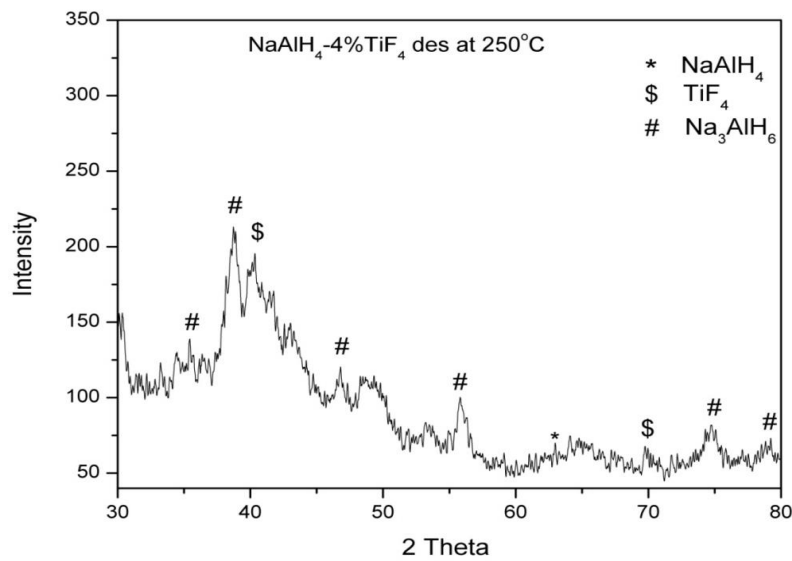


Fig. 4:- XRD curve of desorbed 4mol% TiF₄ doped NaAlH₄ at 250°C

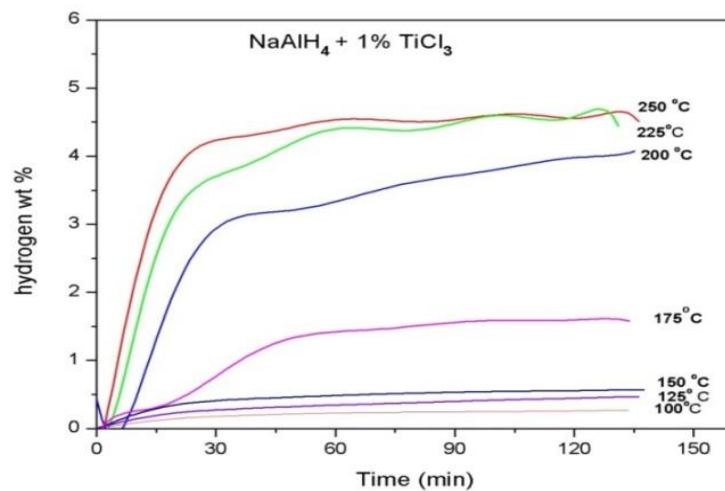


Fig. 5:- Hydrogen desorption curve of desorbed 1mol% TiCl₃ doped NaAlH₄

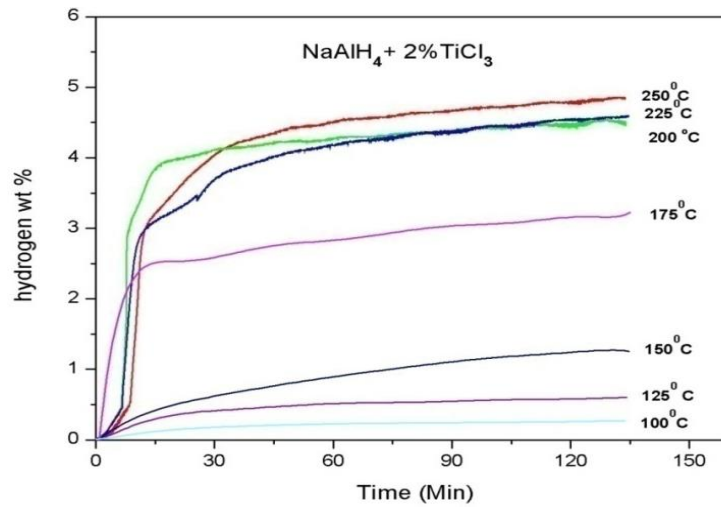


Fig. 6:- Hydrogen desorption curve of desorbed 2% mol TiCl₃ doped NaAlH₄

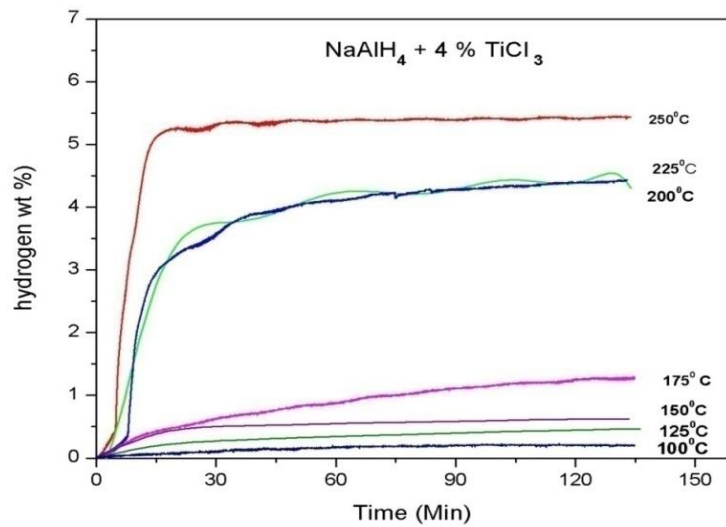


Fig. 7:- Hydrogen desorption curve of desorbed 4 mol% TiCl₃ doped NaAlH₄

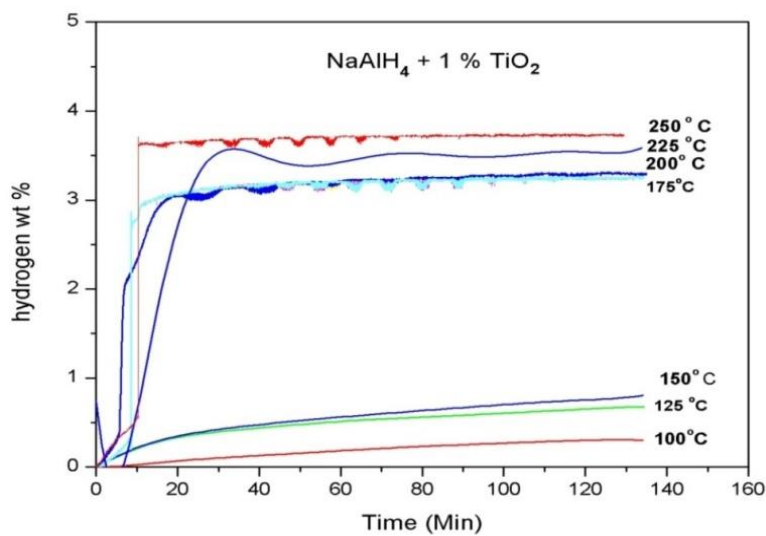


Fig. 8:- Hydrogen desorption curve of desorbed 1mol TiO₂ doped NaAlH₄

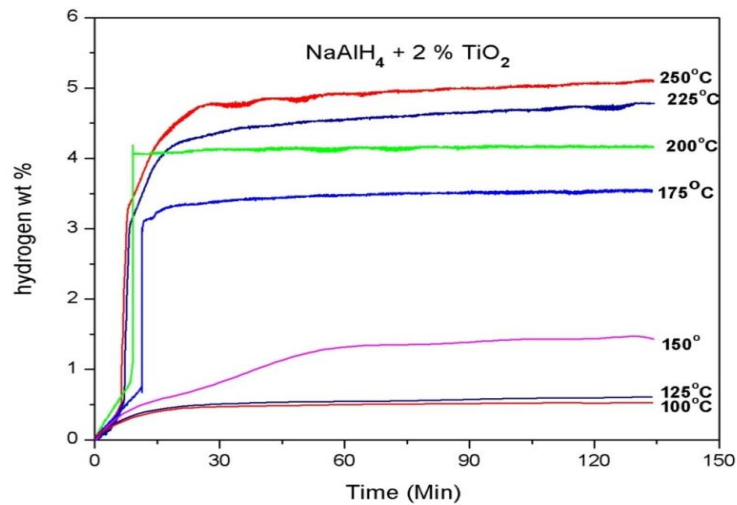


Fig 9:- Hydrogen desorption curve of desorbed 2 mol TiO₂ doped NaAlH₄

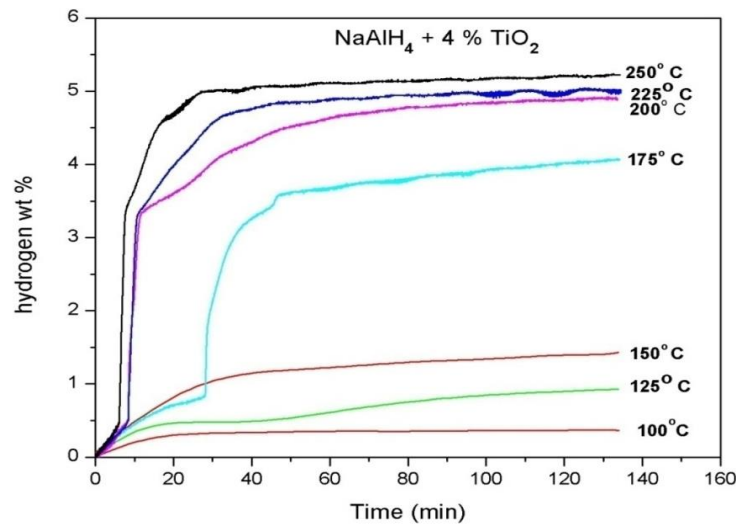


Fig. 10:- Hydrogen desorption curve of desorbed 4 mol% TiO₂ doped NaAlH₄

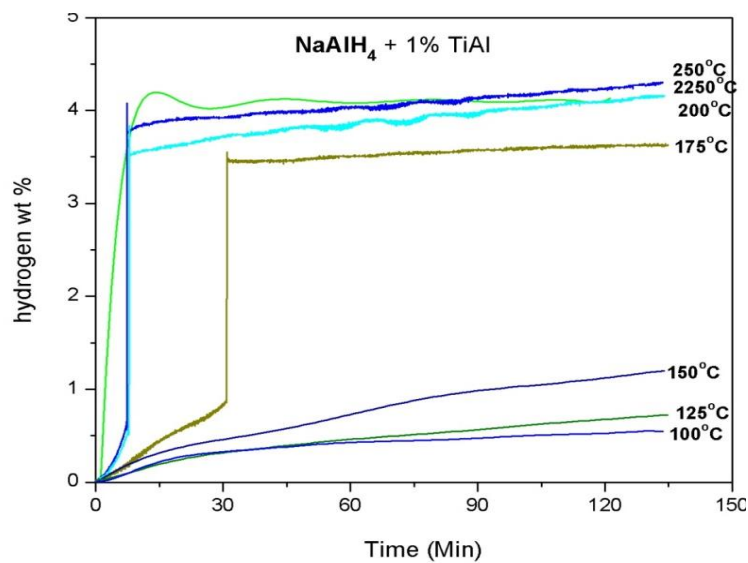


Fig. 11:- Hydrogen desorption curves of NaAlH₄ with 1 mol % TiAl

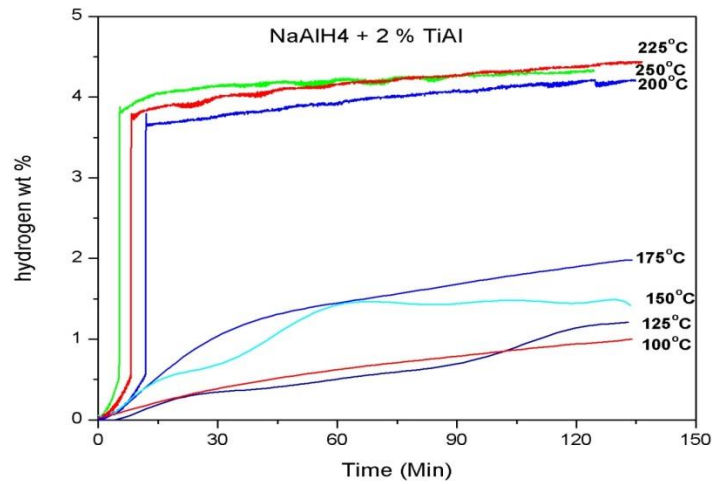


Fig. 12:- Hydrogen desorption curves of NaAlH₄ with 2 mol % TiAl

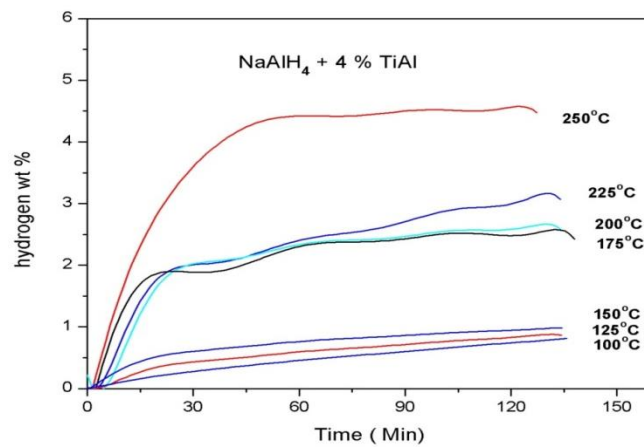


Fig. 13:- Hydrogen desorption curves of NaAlH₄ with 4 mol % TiAl

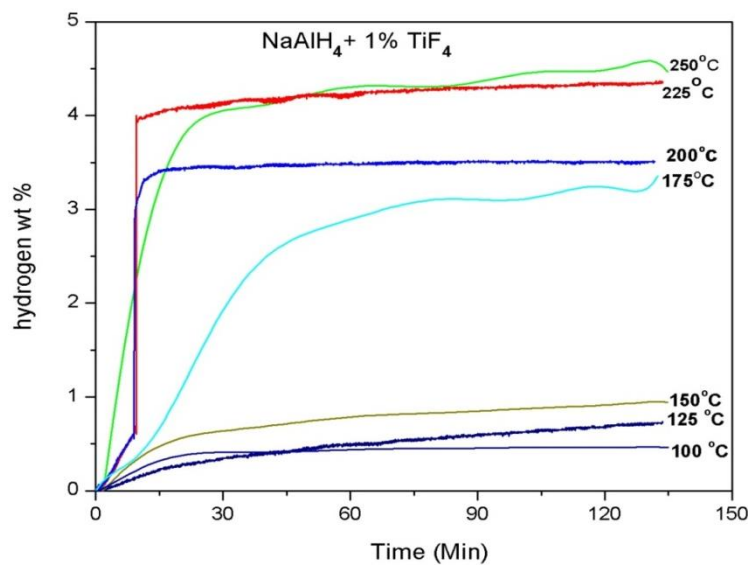


Fig. 14:- Hydrogen desorption curves of NaAlH₄ with 1 mol % TiF₄

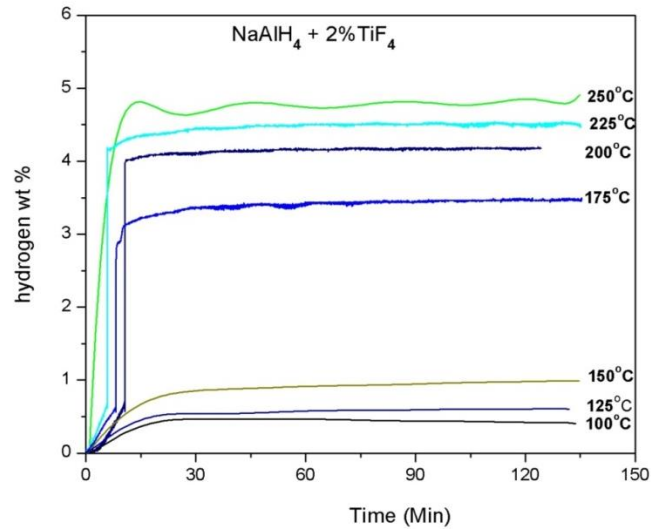


Fig .15:- Hydrogen desorption curves of NaAlH₄ with 2 mol % TiF₄

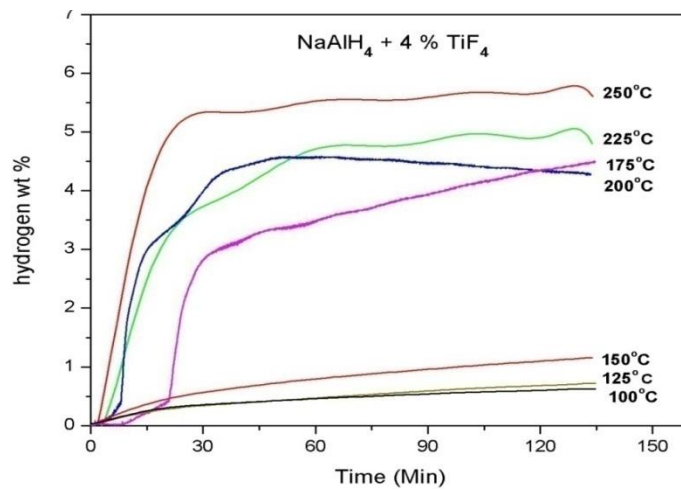


Fig. 16:- Hydrogen desorption curves of NaAlH₄ with 4 mol % TiF₄