Hydrogen Desorption Mechanism of Sodium Alanate Doped with different Catalyst

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Abstract: A comparative study of sodium alanate doped TiCl₄, TiO₂, TiF₄, TiAl, Zr, Ni, V PbCl₂, CeCl₃, and Nb₂O₅ is to study in this paper. The object of this work was to investigate the effect of different catalyst on hydrogen desorption of NaAlH₆. Experimental work was performed under argon atmosphere in glove box. NaAlH₆ 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 was investigated systematically. Structural properties of all samples are observed by X-ray diffraction (XRD). XRD resulted showed the formation of Na₃AlH₆ 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° – 250° 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, Sevient 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.% H₂) 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 /dehydriding kinetics under moderate temperature and pressure[20,21]. Sodium alanate is having 7.5wt% hydrogen which can be released in following three steps:

\[
\text{NaAlH}_6 \rightarrow 1/3 \text{Na}_{3}\text{AlH}_6 + 2/3 \text{Al} + 3 \text{H}_2 (3.7 \text{ wt } \% \text{H}) \quad (1)
\]

\[
\text{Na}_{3}\text{AlH}_6 \rightarrow 3 \text{NaH} + \text{Al} + 3/2 \text{H}_2 (1.9 \text{ wt } \% \text{H}) \quad (2)
\]

\[
\text{NaH} \rightarrow \text{Na} + \text{H} \quad (3)
\]

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 NaAlH₆ improved by ballmaling doping with a suitable catalyst such as TiO₂, TiCl₄, TiAl, TiF₄, Zr, Ni and V etc. Generally, Ti - based NaAlH₆ 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 NaAlH₆ was found. Bogdanovic et al[5] reported decomposition temperature of the first reaction was lowered co-doping NaAlH₆ 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 TiO₂ powder on hydrogen desorption kinetics of NaAlH₆. Sodium alanate catalyzed with TiO₂ desorbs about 5.0wt % hydrogen during the first cycle with the enhanced kinetics. Pakazhelvan et al [25] are reported that NaAlH₆ catalyzed with oxides such viz. TiO₂, CeO₂, La₂O₃, Pr₂O₃, Nd₂O₃, Sm₂O₃, Eu₂O₃ and Gd₂O₃ as catalysts improve the hydrogen desorption kinetics. They concluded that the TiO₂ nano particles exhibits better catalytic performance in both the desorption and reversibility. Rafi-ud-din et al [26] has shown that nanosized Nb₂O₅ and TiO₂ doped sodium alanate improved hydrogen performance as compared to undoped as well as Cr₂O₃ doped sodium alanate. CeCl₃ - doped NaAlH₆ 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 alanate with TiCl₄, TiO₂, TiF₄, TiAl, Zr, Ni, PbCl₂, CeCl₃ and Nb₂O₅. Evolution of alanate phase of the samples is investigated using XRD analysis.

2. Experimental

Sodium alanate and TiCl₄, TiO₂, TiF₄, TiAl, Zr, Ni, V, PbCl₂, CeCl₃ and Nb₂O₅ 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 catalysts. 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 powder weight ratio was around 20:1. NaAlH₄ and different catalysts 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) NaAlH₄ + x TiCl₄ (x=1, 2 and 4% wt %)
2) NaAlH₄ + x TiF₄ (x=1, 2 and 4% wt %)
3) NaAlH₄ + x TiAl (x=1, 2 and 4% wt %)
4) NaAlH₄ + x TiO₂ (x=1, 2 and 4% wt %)
5) NaAlH₄ + x Zr (x=1, 2%)
6) NaAlH₄ + x V (x=1, 2%)
7) NaAlH₄ + x Ni (x=1, 2%)
8) NaAlH₄ + 1:1 (Ni + TiCl₄)
9) NaAlH₄ + 1:1 (V + TiCl₄)
10) NaAlH₄ + 1:1 (Zr + TiCl₄)
11) NaAlH₄ + x PbCl₂ (x=1, 2%)
12) NaAlH₄ + x CeCl₃ (x=1, 2%)
13) NaAlH₄ + x Nb₂O₅ (x=1, 2%)
14) NaAlH₄ + 1:1 (PbCl₂ + TiCl₄)
15) NaAlH₄ + 1:1 (CeCl₃ + TiCl₄)
16) NaAlH₄ + 1:1 (Nb₂O₅ + TiCl₄)

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° and 80° with a step width of 0.02 at a rate of 2.5°/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°C to 250°C.

3. Result and Discussion

3.1 Structural Characterizations

The structural characterization of TiCl₄, TiO₂, TiAl, Zr, Ni, V, CeCl₃, PbCl₂, Nb₂O₅, and TiF₄ doped Sodium alanate have been performed by X-Ray Diffraction. The structural characterization of samples have been shown in fig (1) to fig (15). NaAlH₄ was found in Tetragonal phase with lattice constant a=5.02, b=5.02 and c=11.34. Na₃AlH₆ in Monoclinic structure with lattice constant a=5.46, b=5.61, c=7.80, TiCl₄ appears in structure having a=b=6.143, c=11.71 and NaAlH₄ in Cubic structure with lattice constant a=b=c=4.890 and Al cubic structure having a=b=c=4.049 and TiO₂ 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=3.027 and V is appears Cubic structure a=b=c=3.027 and TiCl₄ 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 PbCl₂ is appears Hexagonal structure with lattice constant a=b=14.04, c=8.601 and CeCl₃ is appears Hexagonal form with lattice constant a=b=14.04, c=8.601 and PbCl₂ is appears Hexagonal structure with lattice constant a=b=13.04, c=3.545 and Nb₂O₅ 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 seive 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 reactor. The temperature was monitored with a Cr-Al thermocouple. Kinetic curves of NaAlH₄ + x wt % TiCl₄ (x=1,2,4 wt %) are shown in Fig 16 to Fig 18. All Kinetic for desorption were determined using Dynamic Seive type apparatus at 100°C to 250°C temperatures. Fig 16 is a curve for desorption hydrogen by NaAlH₄ +1 wt % TiCl₄ vs time at different temperature.NaAlH₄ +1 wt % TiCl₄ sample releases about 4.5 wt % hydrogen in the temperature range between 100° and 250°C. The desorbed hydrogen capacity is much lower than the theoretical capacity of 5.6% wt % of NaAlH₄. Amount of desorbed hydrogen is increased with increase amount of catalysts TiCl₄. The desorption hydrogen capacity was found to be 4.5 wt %, 4.8 wt % and 5.4 wt % with TiCl₄ (1%, 2% and 4%) which is approximate to theoretical value as reported. Kinetic curves of NaAlH₄ + x wt % TiO₂ (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 TiO₂ (1.2 and 4 wt %). It shows that amount of desorption hydrogen is increased with TiO₂ due catalytic effect of TiO₂ with temperature. Kinetic curves of NaAlH₄ + 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 NaAlH₄ + x wt % TiF₄ (x=1, 2, 4 wt %) are shown in Fig 25 to Fig 27.TiF₄ is good catalyst for NaAlH₄. The desorption hydrogen capacity was found to be 4.0 wt %, 4.8 wt % and 5.4 wt % with TiF₄ (1%, 2% and 4%) respectively. Amount of desorption hydrogen wt % is increased with content of TiF₄. TiF₄ is very good catalysts for desorption hydrogen and kinetics. Kinetic curves of NaAlH₄ + x wt % PdCl₂ (x=1, 2 wt %) are shown in Fig 28 to Fig 29. Fig 28 is a curve for hydrogen desorption by NaAlH₄+1 wt % PdCl₂ vs time at different temperature 100°C – 250°C. It shows that sample released about 3.3 wt % hydrogen in temperature between 100° and 250°C. The Catalyst PdCl₂ is recently not reported. However PdCl₂ is a good catalyst and can improve the wt % of hydrogen. In Fig 29 Desorption for Kinetics is shown. 2 wt % PdCl₂ doped NaAlH₄ released about 3.5wt % hydrogen in range between 100° and 250°C. Kinetic curves of NaAlH₄ + x wt % CeCl₃ (x=1,2) are shown in Fig 30 to Fig 31. Fig 30 is a curve for hydrogen desorption by NaAlH₄+1 wt % CeCl₃ vs time at different temperature 100°C – 250°C. CeCl₃ doped sample released about 4.9 wt % hydrogen in temperature range.
between 100° and 250° C. CeCl₃ doped NaAlH₄ shows very fast desorption kinetics up to about 30 min during and after 30 min desorption rate is approximately constant. The Catalyst CeCl₃ is recently reported. However CeCl₃ is a good catalyst. In Fig. 31 2 wt % CeCl₃ doped NaAlH₄ released about 5.4 wt % hydrogen in a desorption temperature at 250° C. The desorbed hydrogen capacity is almost equal to the theoretical capacity 5.6 wt % of NaAlH₄. Kinetic curves of NaAlH₄ + x wt % TiCl₃+PdCl₂ (1:1 wt %) are shown in Fig. 32. NaAlH₄ with 1:1 wt % TiCl₃+PdCl₂ release about 5.0 wt % hydrogen in a desorption temperature at 250° C. Kinetic curves of NaAlH₄ + x wt % TiCl₃+Nb₂O₅ (1:1wt %) are shown in Fig. 33. Sample released about 4.8 wt % hydrogen in temperature range between 100° and 250° C. Nb₂O₅ doped sodium aludate is released low amount of hydrogen. Mixture of catalyst TiCl₃+Nb₂O₅ doped NaAlH₄ increased amount of wt % desorbed hydrogen. The catalysts effective of TiCl₃ is more than Nb₂O₅. Kinetic curves of NaAlH₄ + x wt % TiCl₃+CeCl₃ (1:1 wt %) are shown in Fig. 34. Fig 34 is a curve for hydrogen desorption by NaAlH₄ + 1:1 wt % (TiCl₃+CeCl₃) vs time at different temperature 100° C–250° C. Sample released about 4.5 wt % hydrogen in temperature range between 100° and 250° C. Mixture of catalyst TiCl₃+CeCl₃ doped NaAlH₄ increased amount of hydrogen. The catalysts effective of TiCl₃ is more than CeCl₃. The dehydrogenation with catalytic amounts of Ti and Ce doped complex aluminium hydrides represent an interesting new type of a catalytic reaction. Ce has recently been reported. Kinetic curves of NaAlH₄ + x wt % Nb₂O₅ (x=1, 2 wt %) are shown in Fig. 35 and Fig. 36. Fig 35 is a curve for hydrogen desorption by NaAlH₄ + 1 wt % Nb₂O₅ vs time at different temperature 100° C–250° C. Sample released about 4.8 wt % hydrogen in temperature range between 100° and 250° C. Nb₂O₅ doped NaAlH₄ shows very fast desorption kinetics up to about 20 min at 250° C. Fig. 36 shows that NaAlH₄ catalyzed using 2 wt % Nb₂O₅ released 5.0 wt % hydrogen during desorption in temperature range between 100° and 250° C. The reaction is very fast and released approximately 5.0 wt% in 15 minute.

4. Conclusion

Sodium alanate NaAlH₄ was found in Tetragonal structure with lattice constant a=5.02, b=5.02 and c=11.34. NaAlH₄ is completely converted in Na₃AlH₇ at 250°C. Na₃AlH₇ is appears in cubic structure with lattice constant a=b=c=7.755. Catalyst such as TiCl₃, TiO₂, TiAl, Zr, Ni, V, CeCl₃, PbCl₂, Nb₂O₅, and TiF₃ is doped with sodium aludate. Kinetic measurement of NaAlH₄ with different type of catalyst for desorption were determined using by Dynamic Sieverts type apparatus at 100° C to 250° C temperatures. Amount of hydrogen is desorbed 3.6 wt % to 5.4 wt % at 250°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 dehydrogening of NaAlH₄ to Na₃AlH₇ .V shows the strong formation of V−Al crystalline. The formation of Al₃V 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 TiCl₃ and Transition metal is good for storage capacity and automobile application. Sodium alanate is not active for hydrogen desorption and therefore needs catalyst 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 NaAlH₄. Sodium alanate doped with 1, 2 and 4wt % of different catalyst have been dehydrogenated at 250°C XRD results reveal that catalyst causes complete conversion of tetragonal NaAlH₄ into Na₃AlH₇ having cubic or monoclinic structure. Kinetics desorption was found to be good for TiCl₃, TiO₂ and TiF₂ catalyst. Catalyst CeCl₃ was very good catalyst for desorption. CeCl₃ 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.

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References


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Fig 16 Hydrogen desorption curves of NaAlH4 with 1 wt % TiCl3
Fig 17 Hydrogen desorption curves of NaAlH4 with 2 wt % TiCl3
Fig 18 Hydrogen desorption curves of NaAlH4 with 4 wt % TiCl3
Fig 19 Hydrogen desorption curves of NaAlH4 with 1 wt % TiO2
Fig 20 Hydrogen desorption curves of NaAlH4 with 2 wt % TiO2
Fig 21 Hydrogen desorption curves of NaAlH4 with 4 wt % TiO2
Fig 22 Hydrogen desorption curves of NaAlH4 with 1 wt % TiAl
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Fig 33 Hydrogen desorption curves of NaAlH4 with (1:1) wt % TiCl3 and Nb2O5
Fig 34 Hydrogen desorption curves of NaAlH4 with (1:1) wt % TiCl3 and CeCl3
Fig 35 Hydrogen desorption curves of NaAlH4 with 1 wt % Nb2O5
Fig 36 Hydrogen desorption curves of NaAlH4 with 2 wt % Nb2O5

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Figure 30

Figure 31

Figure 32

Figure 33

Figure 34

Figure 35

Figure 36