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Long term cycling behavior of titanium doped NaAlH₄ prepared through solvent mediated milling of NaH and Al with titanium dopant precursors

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Abstract

A simple and an efficient synthesis route, solvent mediated milling of NaH and Al with 2 mol% of the dopant precursor, Ti(OBu)₄ followed by hydrogenation, has been developed and employed to synthesize Ti-doped NaAlH₄. The long-term hydrogenation and dehydrogenation, up to 100 cycles were carried out systematically. Reversibility of about 3.4 wt.% hydrogen release was obtained during the first dehydrogenation (160 °C) run after the initial hydrogenation of Ti-doped (NaH + Al) at 150 °C; ~11.4 MPa H₂ for 12 h. In the subsequent cycles, the storage capacity increased, reaching an optimum of 4.0 wt.%. This capacity was retained for 40 cycles with the dehydrogenation kinetic curves showing remarkable reproducibility. Comparison of the X-ray diffraction profiles of Ti-doped (NaH + Al) from initial and final stages of the cycling study reveals a growing resistance to the hydrogenation of Na₃AlH₆ to NaAlH₄. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Alkali and alkaline earth metal based complex aluminum hydrides, MAlH₄ [M = Na, Li, K] and Mg(AlH₄)₂, have been found to have great potential as viable modes of storing hydrogen at moderate temperatures and pressures. These hydrides have been demonstrated to have higher hydrogen storage capacities at moderate temperatures and lower cost than conventional intermetallic metal hydride systems such as AB₅H₆, ABH₂, AB₂H₃, and A₂BH₄₋₆ [1,2]. Among the various alkali based complex hydrides investigated in the recent years [3–38], titanium doped sodium aluminum hydride; NaAlH₄, has shown the greatest promise as a reversible hydrogen storage material.

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The decomposition reactions of Ti-doped NaAlH₄ to $NaH + Al + 3/2H_2$ with intermediate stage $1/3Na_3AlH_6 +$ $2/3Al + H_2$ have been investigated extensively on the basis of structural phase determination [10,16,34-37] and the release of hydrogen [3-8,11,17-21,28,38]. However, fewer studies have focused on the hydrogenation of mixtures of Na/Al or NaH/Al to NaAlH₄. Ashby and co-workers [39-41], accomplished the synthesis of NaAlH₄ by reacting sodium under high hydrogen pressure (10-35 MPa) and temperature (140-160 °C) with an aluminum alkyl catalyst in the solvent, tetrahydrofuran (THF), for several hours. Dymova et al. [42] found that, in absence of solvent medium, a temperature of at least 280 °C and a hydrogen pressure of 17-18 MPa were necessary to accomplish this transformation. The high temperature was required to attain a liquid state of sodium. Bogdanovic and Schwickardi [43] successfully demonstrated the preparation of Ti-doped NaAlH₄ by hydrogenating (\sim 33 cycles) NaH powder and Al grindings with Ti(OBu)₄ as the dopant precursor. However, their synthesis process involves a complicated purification procedure

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of NaH and Al grindings and a catalyst doping mechanism prior to the hydrogenation. Recently, Majzoub and Gross demonstrated an *indirect Ti-doping method*, where TiCl₂/TiCl₃ dopant was pre-reacted with LiH by mechanical milling [44,45]. The resulting powder was then milled with 6 mol% of (NaH + Al) mixture. This method of producing NaAlH₄ adds extra weight to the sample due to the addition of LiH. Also, they did not report the long-term cycling behavior of the dopant precursors. For an ideal hydrogen storage material, the cycling stability and the overall weight of the sample must be evaluated, but work on these aspects is sparsely reported. Moreover, the role of titanium dopant on the cycling characteristics of NaAlH₄ is not easily intelligible.

We therefore have explored means of improving Bogdanovic's preparation of Ti-doped NaAlH₄ through simple milling of NaH and Al with Ti(OBu)₄. Our approach resembles Ashby's simple and efficient, solvent mediated hydrogenation of mixtures of NaH and Al, that is basis of the commercial manufacture of NaAlH₄ by Albemarle Corp. However, our process is mediated by the presence of only a minimal amount of solvent during milling with the dopant precursor and does not require an alkyl aluminum catalyst. The dehydrogenation performance in the first few cycles of the Ti-doped NaAlH₄ prepared through this process is markedly improved compared to the materials obtained through dry milling route. We have also carried out the hydrogenation and dehydrogenation up to 100 cycles and the kinetic features were correlated with the observed structural characteristics of Ti-doped (NaH + Al) in the initial and final stages of cycling.

2. Experimental details

2.1. Materials and method

Titanium butoxide Ti(OBu)₄, NaH (95% dry) and Al (99.95%, -200 mesh) were obtained from Aldrich Chemical Co. and used as received. Sodium hydride and aluminum (1:1 mole ratio) were loaded into a chrome-nickel stainless steel bowl (250 ml) with balls (10 mm) under nitrogen filled glove box. The weight ratio between the balls and the powder was 20:1. Approximately 100 ml of distilled pentane was injected into the bowl and the lid was covered tightly with foil. The assembly was then transferred to Fritsch Pulverisette 6 planetary mill. The milling was carried out at a speed of 300 rev/min with two rotations of forward and reverse directions for 30 min each, totaling 60 min. Immediately after the completion of milling, the bowl containing the milled sample was transferred to the glove box and filtered to separate the (NaH + AI) mixture from the solvent under nitrogen ambient. The yield of the milled sample obtained was \sim 95% in the form of slurry. The successive step of adding and blending 2 mol% of Ti(OBu)₄ [called as Ti-doped hereafter] to the slurry, using a syringe, was carried out and this blended mixture was milled in a same manner described above for only 5 min. The Ti-doped (NaH + Al) mixture thus obtained was dried in the glove box and then loaded (0.5 g) in a stainless steel reactor for hydrogenation and dehydrogenation studies. For the dry milling process, (NaH + Al) mixture was blended with Ti(OBu)₄ and milled under a nitrogen atmosphere for 2 h with the same milling parameters mentioned above.

2.2. Hydrogenation and dehydrogenation cycling measurements

The hydrogenation and dehydrogenation cycling was performed using a Sieverts type volumetric apparatus [LESCA Co., Japan], which allowed for the accurate volumetric determination of the amount of hydrogen evolved. Rapid heating of the sample to the desired temperature was accomplished by immersing the sample reactor into a pre-heated silicon oil bath (accuracy of ± 1 °C). The cycling studies were performed by repeated hydrogenation (150–120 °C, ~11.5 MPa, 12 h) and dehydrogenation (160 °C, against 0.1 MPa for 3 h). The hydrogen capacity is presented in terms of wt.% and normalized to the weight of NaAlH₄ without including the weight of the catalyst.

2.3. Structural (PXD) characterization

The powder X-ray diffraction of Ti-doped (NaH + Al) before and after 100 cycles were performed using Swiss-Norwegian beam line (station BM1B) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The sample was loaded in a 0.5 mm boron–silica–glass capillary. The wavelength of the X-ray used was 0.50024 Å at 22 °C from channel-cut Si(111) monochromator. The measurement of intensity was done with the step scan rate of $\Delta(2\theta) = 0.003$ –0.005°. Rietveld refinement of the X-ray diffraction profiles of the Ti-doped (NaH + Al) was carried out using Fullprof software [46].

3. Results

3.1. Dehydrogenation kinetics and cycling stability

The experimental parameters, such as the pressure and temperature of hydrogenation and dehydrogenation temperature with the hydrogen capacity obtained, are listed in Table 1.

Fig. 1 represents the dehydrogenation kinetic curves of Ti-doped NaAlH₄, prepared from the solvent mediated milling and hydrogenation of Ti-doped (NaH + Al). These curves were plotted by calculating the total release of hydrogen in terms of weight percentage with respect to the dehydrogenation time. The release of hydrogen at $160 \,^{\circ}\text{C}$ under 0.1 MPa corresponds to $3.4 \,\text{wt.\%}$ during the initial dehydrogenation run. In the subsequent cycles, the hydro-

Table 1

Cycle(s) number	Hydrogenation pressure (MPa)	Hydrogenation temperature (°C)	Dehydrogenation temperature (°C)	Hydrogen capacity (wt.%)	
1-4	~11.50	150	160	3.74 ^a	
5-40	~ 11.40	120	160	4.0 ^a	
41-100	~11.35	120	160	3.5 ^a	

Total released hydrogen capacity with ongoing hydrogenation and dehydrogenation cycling of Ti-doped NaAlH₄, prepared through solvent mediated milling and subsequent hydrogenation of Ti-doped (NaH + Al)

^a Average value.

gen capacity increased attaining an optimum capacity of 4.0 wt.% in the fourth dehydrogenation run. This value corresponds to 70% of the hydrogen capacity calculated according to Eq. (1):

$$NaH + Al + 3/2H_2 \leftrightarrow NaAlH_4 \tag{1}$$

Also, the release of hydrogen occurs in two stages, which is represented by a bifurcated broken line as shown in Fig. 1. This clearly indicates that the dehydrogenation of (Ti-doped) NaAlH₄ follows the known two-step reactions given by Eq. (2):

$$NaAlH_4 \leftrightarrow 1/3Na_3AlH_6 + 2/3Al + H_2$$
$$\leftrightarrow NaH + Al + 3/2H_2$$
(2)

The release of hydrogen in the first four-dehydrogenation runs of the Ti-doped NaAlH₄, obtained from the dry milling of Ti-doped (NaH + Al) is shown in Fig. 2. The dehydrogenation kinetics and the total release of hydrogen from the Ti-doped NaAlH₄ obtained from the solvent mediated milling process (see Fig. 1) was markedly improved compared to the material prepared through dry milling route (see Fig. 2).

The dehydrogenation kinetic curves of Ti-doped NaAlH₄ at $160 \,^{\circ}$ C between the 5th and 40th cycles are shown in Fig. 3. It is interesting to note that the storage capacity of about 4.0 wt.% was maintained on an average in these cycles.



Fig. 1. The dehydrogenation kinetic curves of Ti-doped NaAlH₄ as prepared from the solvent mediated milling of Ti-doped (NaH+Al) at 160 °C, 0.1 MPa.

This capacity was retained with dehydrogenation kinetic curves showing remarkable reproducibility. The two-step decomposition is indicated in Fig. 3 by a broken bifurcated line.

The amount of hydrogen discharged during the 100 cycles of these kinetic studies of Ti-doped NaAlH₄ is shown in Fig. 4. It is to be mentioned that the storage capacity of 3.4 wt.% was obtained in the very first dehydrogenation run and increased with increasing number of cycles. An optimum hydrogen capacity of about 4.0 wt.% was obtained



Fig. 2. The dehydrogenation kinetic curves of Ti-doped NaAlH₄ as prepared from the dry milling of Ti-doped (NaH + Al) at $160 \degree C$, 0.1 MPa.



Fig. 3. The group of dehydrogenation kinetic curves of Ti-doped NaAlH4 from 5 to 40 cycles at 160 $^\circ C,~0.1\,MPa.$



Fig. 4. The release of hydrogen (wt.%) vs. number of cycles.

in the fourth dehydrogenation run. A capacity of 4.3 wt.% was achieved in 29th cycle and an average total capacity of 4.0 wt.% was maintained up to 40 cycles. At the end of the 100th cycle, the hydrogen capacity was slightly reduced from 4.0 to 3.5 wt.%. Comparative dehydrogenation kinetic curves of 4th and 100th cycles are depicted in Fig. 5. The junction between the two-step dehydrogenation reactions for these extreme cycles was marked by an arrow and also shown with smaller scale in the inset of Fig. 5.

3.2. Structural (PXD) characterization

Powder X-ray diffraction characterizations using synchrotron radiation were carried out on the samples of



Fig. 5. Comparative kinetic curves of 4th and 100th dehydrogenation runs of Ti-doped NaAlH₄. The small scale drawing of the graph is represented in the inset.

Ti-doped (NaH + Al) before and after 100 cycles. Fig. 6 represents the PXD pattern of the Ti-doped (NaH + Al) before undergoing hydrogenation and dehydrogenation cycling experiments. The Rietveld profile fitting (refinement) was employed and the peaks were identified as NaH and Al. No other impurities or Ti/Ti–Al inflection peaks were traced out. The concentration, in mol%, of each phase and their corresponding lattice parameters obtained from the refinement are given in Table 2.

The PXD fitting profile of Ti-doped (NaH + Al) at the 100th dehydrogenation cycle is shown in Fig. 7. An addi-



Fig. 6. PXD profile fitting of the Ti-doped (NaH + Al) mixture before hydrogenation-dehydrogenation cycling. The solid circle and the line are the observed and calculated intensities, respectively. The difference pattern is shown at the bottom.

Table 2

The phase composition in mol% and corresponding lattice constant values determined using synchrotron powder X-ray diffraction and Rietveld profile refinement

Sample	Concentration (mol%)			Lattice constants (Å)				
	NaH	Al	Na ₃ AlH ₆	NaCl	NaH	Al	Na ₃ AlH ₆ ^a	NaCl
Ti-doped NaH + Al before cycling	57.1	42.9			4.88136	4.04991		
Ti-doped NaH + Al after 100 cycling	35.3	54.6	8.7	1.3	4.88003	4.04904	5.41014 5.53615 7.75615	5.64154



^a Unit cell volume of Na_3AlH_6 : 232.306 Å³.

Fig. 7. PXD pattern of Ti-doped (NaH + Al) after the completion of 100 cycles.

tional reflection corresponds to Na_3AlH_6 and NaCl was observed in addition to NaH and Al. The amount of NaCl or NaCl-related structure was very small (less than 2 mol%), and hence it is negligible from the present discussion.

4. Discussion

The long term cycling studies of Ti-doped NaAlH₄ and its structural correlation were discussed in this section. The PXD pattern of the elemental mixture Ti-doped (NaH + Al) shows no extra reflections of impurities and ensures the correct stoichiometric ratio of NaH:Al (see Table 2). This mixture was hydrogenated under high-pressure and the cycling experiments were further carried out. The initial dehydrogenation of Ti-doped NaAlH₄ at 160 °C exhibits the fast kinetics of the first and second steps and the total hydrogen

release estimated was 3.4 wt.% (Fig. 1). In the consecutive hydrogenation and dehydrogenation cycles, the capacity was increased and attained an optimum of 4.0 wt.% in the 40th cycle. The contribution of the second reaction as per Eq. (2), i.e. Na₃AlH₆ to NaH, to the total effective hydrogen capacity was found in these cycles (Fig. 3). The storage capacity decreased from 4.0 to 3.5 wt.%, between the 40th and 100th cycle (Fig. 4). This results from the partial reversibility of the two-step reaction, which is in accordance with the hypothesis proposed by Kiyobayashi et al. [38]. According to their theory, the delocalization of titanium catalyst may be the cause for the poor dehydrogenation rate of Na₃AlH₆, which in turn affects the overall hydrogen capacity. The comparative dehydrogenation curves of Fig. 5 reveal the following features: (i) the kinetics of the first step of dehydrogenation reaction has been reduced; (ii) the second dehydrogenation reaction proceeds to a significantly reduced extent. The PXD

studies of the Ti-doped (NaH + Al) after 100 cycles show the presence of an additional phase related to the Na₃AlH₆ structure besides the starting mixture (NaH + Al). The presence of Na₃AlH₆ indicates that the reaction of Eq. (2) is not complete and also supports the argument of Majzoub and Gross [44]. However, formation of crystalline Ti or TiAl₃ intermetallic phase was not observed in this 100-cycle measurement. This is in agreement with the recent finding that after 7 cycles, $\sim 1/3$ of the Ti is present as Al_{0.93}Ti_{0.07} and that the remainder of the Ti is apparently present in a highly dispersed fashion in the host lattice [47].

5. Conclusion

A simple and efficient synthesis method, solvent mediated milling and hydrogenation, was developed and employed in order to prepare Ti-doped NaAlH₄ from the basic materials, NaH and Al in the presence of Ti(OBu)₄. Unlike Bogdanovic's approach [43], this method does not involve complicated purification of NaH/Al and doping procedures prior to hydrogenation. Also our synthesis requires no precursor formation, which was earlier adopted by Gross et al. [45]. The dehydrogenation kinetic measurements of Ti-doped NaAlH₄, obtained from solvent mediated milling and subsequent hydrogenation of Ti-doped (NaH + Al)were carried out at a constant temperature of 160 °C under 0.1 MPa for up to 100 cycles. A release of 3.4 wt.% of hydrogen capacity was obtained in the very first dehydrogenation run. In the subsequent cycles, the capacity increased and optimum hydrogen storage of about 4.0 wt.% was achieved by the fourth dehydrogenation run. This capacity remained through 40 cycles. Significant decrease in the capacity from 4.0 to 3.5 wt.% was observed at the end of the 100th cycle. Synchrotron powder X-ray diffraction and Rietveld profile fitting analysis of Ti-doped (NaH+Al) after 100 cycles showed the presence of additional phases which are apparently linked to the observed diminishing dehydrogenation characteristics. Decreases in dehydrogenation kinetics and the total amount of released hydrogen over a number of cycles will be interpreted as follows: the appearance of the phase, Na₃AlH₆ in the prolonged cycling samples, indicates a reduced effectiveness of the Ti-dopant for the hydrogenation of Na₃AlH₆ to NaAlH₄. This may be due to delocalization of titanium dopant, which hinders the release of hydrogen from the hexahydride (Na_3AlH_6) phase. Further work is under progress to achieve the high hydrogen capacity with ongoing cycling by optimizing the experimental conditions and adopting new processing such as re-grinding and manipulating the dopant concentration.

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