

Catalyzed alanates for hydrogen storage

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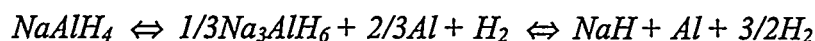
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Abstract

The discovery that hydrogen can be reversibly absorbed and desorbed from complex hydrides (the alanates) by the addition of catalysts has created an entirely new prospect for lightweight hydrogen storage. Unlike the interstitial intermetallic hydrides, these compounds release hydrogen through a series of decomposition / recombination reactions e.g.:



Initial work resulted in improved catalysts, advanced methods of preparation and a better understanding of the hydrogen absorption and desorption processes. Recent studies have clarified some of the fundamental material properties as well as the engineering characteristics of catalyst enhanced sodium alanate. Phase transitions observed real-time through in situ X-ray powder diffraction demonstrate that the decomposition reactions occur through long-range transport of metal species. SEM imaging and EDS analysis verify aluminum segregation to the surface of the material during decomposition. The equilibrium thermodynamics of decomposition have now been measured down to room temperature. They show a plateau pressure for the first reaction of 1 atm at 33 °C, which suggest that, thermodynamically, this material is ideally suited to onboard hydrogen storage for fuel cell vehicles. Room temperature desorption with slow but measurable kinetics has been recorded for the first time. Studies at elevated temperatures (125-165°C), approaching that found in fuel cell operations, were performed on a scaled-up test bed. The bed demonstrated surprisingly good kinetics and other positive material properties. However, these studies also pointed to the need to develop new non-alkoxide based catalysts and doping methods to increase capacity and reduce the level of hydrocarbon impurities found in the desorbed hydrogen. For this reason, new Ti-Cl catalysts and doping processes are being developed which show higher capacities and improved kinetics. An overview of the current state-of-the-art will be presented along with our own studies and the implications for the viability of these materials in on-board hydrogen storage applications.

Keywords: Metal hydride; Complex hydride; Alanate; NaAlH₄; Na₃AlH₆;

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Introduction

The automobile industry appears set to introduce hydrogen-powered fuel-cell vehicles in the near future [1]. To be practical these vehicles will need a safe, lightweight and compact means of on-board hydrogen storage. Liquid, compressed gas and reformer-derived hydrogen all have well-known disadvantages [2]. For this reason, extensive efforts have been made to develop solid-state means of hydrogen storage, including metal hydrides [4,5] and, more recently nano-structured carbons [6,7]. Until recently the development of a high capacity, lightweight metal hydride that could be used to reversibly store hydrogen under ambient conditions seemed all but unattainable. That was until the pioneering work of Bogdanovic' and Schwickardi (1996) which showed that, by the addition of catalysts, the complex hydride NaAlH_4 could be made to reversibly release and absorb approximately 4 wt.% hydrogen for over 30 cycles under moderate conditions [8]. Thus, catalyzed hydride complexes show the greatest promise for meeting the requirements of onboard hydrogen storage.

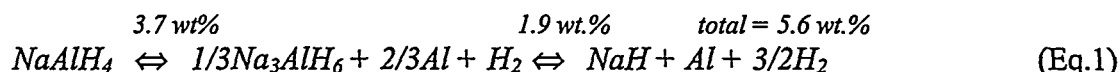
The synthesis of LiAlH_4 in 1947 by Schlesinger [9] was followed by the discovery and study of many other complex hydrides [10-17]. NaAlH_4 was first synthesized by the process of reacting NaH with AlBr_3 (AlCl_3) in a THF solution [18], then by direct synthesis of this compound from the elements under high-pressure hydrogen [19-21] and, eventually through direct melt synthesis without using any solvents [22]. While the potential use of complex hydrides for hydrogen storage had been considered [23], they were principally developed for use as convenient and efficient chemical reducing reagents [24]. However, in the more general class of saline hydrides, compounds such as lithium hydride and particularly calcium hydride, have been used for lightweight hydrogen storage for over half a century. As a typical example, LiH and CaH_2 were widely employed as a portable means of storing hydrogen for inflating meteorological balloons [25]. However, in these examples, hydrogen is generated by reacting the hydride with water. This is a reaction that cannot be reversed in any efficient or practical manner.

Since Bogdanovic' and Schwickardi's discovery, there have been considerable efforts to develop new catalysts, advanced methods of doping and materials processing, as well as a better fundamental and practical understanding of the hydriding mechanisms. Many of the important properties of these materials and development of new catalysts (Ti- and Fe-alcoholates, $(\text{Fe},\text{Ni})\text{Cl}_2$, $(\text{V},\text{RE})\text{Cl}_3$, $\beta\text{-TiCl}_3$, and $(\text{Ti},\text{Zr})\text{Cl}_4$) were the focus recent research by the group of Bogdanovic' [26] and, in particular, the Ph.D. thesis work of Tölle [27]. At the University of Hawaii, Jensen and co-workers have developed an advanced catalyst doping technique in which liquid alkoxide catalyst precursors are mechanically homogenized with purified solid NaAlH_4 . This method was used to produce materials with enhanced kinetics and improved reversible hydrogen capacities [28] compared with samples prepared using the original wet doping technique [8]. This homogenization technique was employed to dope NaAlH_4 with a double catalyst consisting of 2 mol.% each of the alkoxides $\text{Zr}(\text{Opr})_4$ and $\text{Ti}(\text{O}^n)_4$. The two catalysts combined to give better overall dehydriding kinetics and a capacity of about 4.5 wt.% [29]. These improvements can be seen in the thermal programmed desorption (TPD) measurement of Figure 1. At McGill University, Zaluska and co-workers showed that hydrogen absorption and desorption kinetics could also be enhanced directly through mechanically grinding of the sodium alanates as well as by using carbon as an

additive in the milling process [30]. That work that supported the notion that reduced particle size also plays an important role in improving kinetics. This idea was confirmed through the observation of kinetic enhancement when the catalyzed NaAlH₄ particle size was decreased by precipitation using different solvents [26]. The mechanical milling technique was also employed to directly synthesis the alanates. This included the mechanical-alloying synthesis of Na₃AlH₆, Na₂LiAlH₆ [31], Li₃AlH₆, and (Li-Na-B)₃AlH₆ [32].

Collaborative research at Sandia National Laboratories (SNL) and the University of Hawaii (UH) has focused on the development and characterization of new hydrogen storage materials. In this paper we will present an overview of some of our most recent advances, including the development of new catalysts [33,34].

It is critical for the ultimate use of complex hydrides as practical hydrogen storage materials to gain a complete understanding of the mechanisms by which hydrogen is absorbed and desorbed in these materials. Unlike, the classic interstitial metallic hydrides, NaAlH₄ is believed to release hydrogen through a series of decomposition reactions [35-37]:



Dymova and co-workers were the first to make pressure vs. composition isotherm measurements (PCT) for the decomposition of undoped NaAlH₄ [38]. Two separate plateaus appeared in their measurements corresponding to the two decomposition reactions of the Equation 1. We recently verified this two-step process in the solid-state decomposition of catalyzed NaAlH₄ using dynamic in-situ x-ray diffraction [39]. Moreover, that study demonstrated the liquid-state decomposition of uncatalyzed NaAlH₄ (melting temperature 180°C) and showed that an additional polymorphic phase transition of Na₃AlH₆ may also occur as an intermediate decomposition step [40,41]. The PCT measurements of Dymova [38] and later Bogdanovic' [8] provided equilibrium pressures from which the heats of decomposition of NaAlH₄ (liquid) and Na₃AlH₆ (solid) could be calculated. Equilibrium pressure measurements of the decomposition of NaAlH₄ in the solid-state were made at Sandia National Laboratories [41] and also by Tölle and Bogdanovic' [26,27]. Advances in the catalytic activity of these materials now allow desorption measurements to be made down to room temperature [42]. These low temperature desorption measurements and, in particular, accurate van't Hoff analysis will be presented in this paper.

The other fundamental aspects of the decomposition/reformation processes that must be understood are the catalytic interactions and transport processes involved in these solid state reactions. The observations of the formation of sub-micron aluminum crystallites by dynamic in-situ x-ray diffraction experiments [39], as well as by a microscopic elemental analysis [43,26,27] demonstrated the existence of long-range transport of metal atoms. Transport phenomenon, the effects of particle size, and catalytic activity are some of the subjects of ongoing investigations [40,43].

The net reaction of the equation 1 represents a theoretical reversible hydrogen capacity of 5.6 wt.%. The equilibrium thermodynamics of these reactions indicate the potential to liberate all of this hydrogen at above 1 atmosphere of pressure and temperatures of 110°C. Such an

achievement would be extremely valuable for the on-board storage of hydrogen in low-temperature fuel-cell vehicles. However, significant progress remains to be made in achieving the rapid hydrogen absorption and desorption kinetics required for vehicular applications. The work presented here summarizes recent cooperative activities between Sandia National Laboratories and the University of Hawaii to develop advanced catalyzed complex-hydride hydrogen-storage materials. In particular, our recent work focused on determining 1) the positive as well as the detrimental aspects of our current catalysts-doping procedures, 2) the development of new and improved catalysts, 3) engineering aspects and the fundamental properties of these materials. More details of our joint work on the catalyzed alanates can be found elsewhere in this volume [33,34,40,43].

1. Sample Preparation and Experimental Details

Some results are reproduced here from published data of the work at the Max-Planck-Institut für Kohlenforschung and McGill University. Sample preparation for those results is described briefly in the figure captions and details can be found in the accompanying references. Much of the collaborative efforts of Sandia National Laboratories and the University of Hawaii were done using double catalysts of Ti- and Zr-alkoxides. The homogenization technique developed at the University of Hawaii [28] was generally employed for sample preparation. This consisted of adding 2 mol.% each of liquid $\text{Ti}(\text{O}^n\text{Bu})_4$ and $\text{Zr}(\text{OPr})_4$ to solid NaAlH_4 which had been purified from (THF) solution and vacuum dried. The mixture was ground together with a mortar and pestle and finally milled in a SPEX® mixer/mill for 30 seconds. Sandia National Laboratories also tested samples which were mechanically milled under argon for 3 and 8 hours, as well as samples which were doped with other catalysts (specifically; Ti_3Al and $\beta\text{-TiCl}_3$).

Low temperature kinetics, plateau pressures, and capacity measurement were obtained volumetrically using samples of approximately 1.5 g of catalyzed sample. Reversible hydrogen capacity data is presented in terms of wt.% hydrogen normalized to the weight of the NaAlH_4 only and does not include the weight of the catalysts [33]. Special air-less techniques were developed at Sandia National Laboratories to be able to characterize these catalyzed alanate materials using X-ray diffraction [33,40], scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS) and Auger elemental analysis [43].

Engineering property studies were performed at Sandia National Laboratories on a "scaleup" reactor bed designed to simulate the heat transfer and gas impedance conditions that might be found in real hydrogen storage applications. The bed was loaded with 100 g of 2 mol.% each Ti/Zr-Alkoxide catalyzed NaAlH_4 (78 g of NaAlH_4 and 22 g of $\text{Ti}(\text{O}^n\text{Bu})_4 + \text{Zr}(\text{OPr})_4$) prepared in collaboration with the University of Hawaii [33].

2. Thermodynamics

Reasonably high kinetics at low temperatures allowed us to reliably determine equilibrium desorption plateau pressures down to room temperature for the NaAlH_4 phase. These data are plotted in Figure 2 in the form of a van't Hoff plot ($\ln P$ vs $1/T$) and compared to the data previously published by the Bogdanovic' and co-workers [26]. Our low temperature data is a

good agreement with the extrapolation of our previous high temperature data [41]. Thus, it has now been accurately shown that the temperature required for an equilibrium desorption pressure of 1 atma from NaAlH_4 is 33°C . This is a very convenient temperature for fuel-cell and other applications.

The Na_3AlH_6 plateau pressure is also shown in Figure 2. Because of the relatively low pressures and kinetics involved, the low-temperature Na_3AlH_6 van't Hoff data are not as reliable as the NaAlH_4 data. Be that as it may, the 1 atma van't Hoff temperature for Na_3AlH_6 is estimated to be about 110°C . This temperature is somewhat higher than desired for a PEM fuel cell and future work will aim at lowering this temperature. This can only be accomplished by direct modification of the thermodynamic properties of Na_3AlH_6 .

3. Kinetics

Combined results from our recent investigations are compared with earlier data in the desorption measurements of Figure 3 and the absorption measurements of Figure 4. Some kinetics measurements are also shown from published data of the Max-Planck-Institut für Kohlenforschung and McGill University. Measurements were performed using different sample quantities, sample holders, and techniques. As will be shown later, thermal effects such as the heats of reaction and conductivity strongly influenced the kinetics preventing any quantitative comparisons. However, some general qualitative conclusions can be made. They can be summarized as follows. First, the combined results from these four independent laboratories validate the reversibility and high capacities of these materials regardless of the specific methods of sample preparation or catalysts used. In the worst case nearly 3 wt. % of hydrogen can be desorbed at 125°C in three hours. On a weight basis this is nearly twice the capacity as current commercial metal hydrides under the same conditions. At higher temperatures (160°C) the capacity increases to nearly 5 wt. % or three times better than commercial materials. The same in general comment can be made for hydrogen absorption (figure 4). In fact, surprisingly good kinetics can be achieved; curve c ($\beta\text{-TiCl}_3$ doped NaAlH_4) absorbed over 4 wt. % in less than one hour under the reasonably moderate conditions of 90 bar H_2 and 100°C .

Another observation, which is consistent between the desorption measurements, is the appearance of a break in the curves at around 3 wt. %. This is due to the much slower kinetics of the second reaction (Eq. 1). Finally, it is apparent from these figures that both particle size and the type of catalysts used strongly influence the rates of hydrogen absorption and desorption.

Sandia National Laboratories together with the University of Hawaii initially examined the use of liquid alkoxide catalysts and the homogenization doping procedure. This has practical advantages over the "wet-chemistry" methods of doping the alanates in solution. Namely, the precipitation and drying steps are avoided and intimate mixing as well as particles reduction can be achieved through mechanical mixing and milling. However, we also found that the Ti+Zr alkoxide catalyst doping procedure has significant drawbacks. These are: 1) the alkoxide based catalysts are heavy, 2 mol. % of each catalysts results in a 22 wt.% burden on the total material, 2) the liquid organometallic catalysts contaminate the desorbed hydrogen

with hydrocarbons consisting mainly of a butane and propane, 3) oxygen from the decomposition of the alkoxide catalysts contaminates the active material, perhaps causing the less than the ideal 5.6 wt.% reversible capacity. All of these considerations lead to the need to develop non-hydrocarbon-based catalysts. For this reason, we are now investigating the catalytic properties of the titanium-halides. Recent experiments on NaAlH_4 doped with 2mol.% $\beta\text{-TiCl}_3$ have shown reversible hydrogen capacities approaching the theoretical limit with no degradation in kinetic properties and no gas impurities (curves c in figures 3 and 4) [33]. Using x-ray diffraction, it was discovered that the $\beta\text{-TiCl}_3$ catalyst precursor decomposes during the mechanical milling process to form NaCl and a dispersed titanium-based catalyst [40]. In a parallel investigation at the University of Hawaii, liquid TiCl_4 was added by homogenization milling to give a reversible capacity of _____ [34]. The nature of the titanium-based catalysts is the focus of current investigations.

In addition to enhanced kinetics at 80-150°C, we made the rather surprising observation that desorption could be measured even down to room temperature. As would be expected, the initial desorption rate was found to be strongly dependent on particle size. While the desorption rates are low (0.016 wt.%/hr.), room temperature desorption from these high-capacity materials should prove very interesting for certain low-rate hydrogen-powered applications.

4. Cyclic Stability

The initial desorption from the alkoxide catalyzed samples gave gas capacities in excess of the theoretical 5.5 wt.% value (6 wt.%). This is believed to come from large quantities of impurities gases derive from the alkoxide catalyst precursors in addition to the desorbed hydrogen. Further cycles demonstrate a lower-than-expected capacity for all of the samples we have tested with the liquid alkoxide catalysts (both absorption and desorption capacities were about 3 wt.%). X-ray diffraction measurements clearly showed that the low capacity is due mainly to an inability to completely recharge to a composition of 100% NaAlH_4 . X-ray diffraction measurements also demonstrated that the samples could be fully desorbed to sodium hydride and aluminum. The mechanism for this incomplete recharging phenomenon is uncertain at the present time. It may involve inhomogeneous distribution of the catalysts or impurity effects. However, this capacity problem has been overcome through the application of titanium-halide catalysts.

5. Practical Studies, Applications Oriented Materials Properties

A scaleup bed containing 100g of NaAlH_4 doped with Ti- and Zr-alkoxides (2 mol.% each) was tested at Sandia National Laboratories. The bed was cycled through five absorption/desorption cycles. Absorption H_2 pressures generally ranged from 100-200 atm and nominal absorption temperatures ranged from 125-165°C. Desorption was generally performed at 150-165°C against a 1 psig (1.07 atma) backpressure. In addition to capacity and rate measurements, exothermic (charging) and endothermic (discharging) thermal effects were recorded. The desorbed hydrogen was monitored for gaseous impurities and a small sample was removed after the fourth desorption cycle for XRD and SEM/EDS analysis. The volume change of the alanate was measured over the last desorption half-cycle. Detailed results from

these tests are presented in an accompanying paper [33]. The following are some highlights of that study.

1.1. Discharge and Recharge Rates

Desorption of hydrogen occurred rapidly at 150-165°C, with about two thirds of the hydrogen (30 SL) discharging in 3 hours. For the absorption of hydrogen a range of applied pressures and starting temperatures were tried (125-165°C, 122-210 bar). In all cases charging was more rapid than we had expected. Most of the hydrogen was absorbed in the first hour or two, even for the lowest pressure and starting temperature (125°C, 122 bar). Charge and discharge curves for the scaleup bed are also included in Figures 4 and 5 (curves f).

1.2. Thermal Effects

The higher than expected initial charging kinetics, combined with limited heat transfer, resulted in exothermic temperature excursions (Figure 5), as is common with many hydrides. A hydrogen pressure of 174 bar was applied to the fully dehydrided bed which had been equilibrated to 155°C. Within one minute, the exothermic hydriding reaction resulted in an internal temperature of 234°C (the van't Hoff temperature for NaAlH₄ at this pressure). This is above the melting point of NaAlH₄ (182°C). Therefore, any NaAlH₄ produced during this high-temperature excursion forms directly into the liquid phase. After this initial excursion a thermal arrest occurs at 182°C due to solidification (Figure 5). This demonstrates that liquid NaAlH₄ was formed during the initial charge.

It is natural to ask if such melting could be detrimental to the subsequent performance of the alanate bed. Our observations indicated no negative effects of partially melting the bed at least three times. In fact, partial melting may be beneficial. We opened the reactor between cycles 4 and 5 and found the bed to be sintered into a porous, solid mass. Such a structure may have distinct advantages for actual applications. In particular, such a sintered structure should reduce particulate migration, increase packing densities, allow expansion, provide a constant internal gas impedance and enhance safety.

1.3. Hydriding Volume Changes

In the classic metal hydrides, large volume changes associated with lattice expansion during hydride formation poses significant engineering problems. Therefore, the volume change of the active material in the scaleup bed was measured from the beginning to the end of fifth desorption cycle. The volume contracted by -14.7%, which is reasonably close to the theoretical value calculated from X-ray densities for the complete dehydriding reaction (-16.5 %) [33]. Unlike the traditional hydrides, the alanates have the distinct advantage of starting with the material in its fully hydrided state. Fully packed beds can be constructed, which simplifies bed design and allows a higher volumetric density to be achieved.

1.4. Impurity Gases

The composition of the desorption gases were examined regularly by RGA (Residual Gas Analysis [Mass Spectroscopy]) and occasionally using GC (Gas Chromatography). Typical RGA patterns of the desorption gasses showed not only hydrogen but also significant impurities along with the ubiquitous background RGA peaks for H₂O, CO and CO₂. GC analysis taken after the second cycle showed that butane and propane were present in the hydrogen. Thus, it appears that the liquid Ti(OBuⁿ)₄ and Zr(OPr)₄ catalysts decompose and release significant amounts of hydrocarbon impurities. PEM fuel cells are not very tolerant of impurity gases, especially hydrocarbons that lead to the formation of CO. These results led us to concentrate on the development of inorganic catalysts.

6. Fundamental Studies, Catalysis and Transport Mechanisms

The SEM images of Figure 6 show the pronounced changes in morphology that occur during the two-stage desorption of NaAlH₄ (Eq.1). This is an indication of the segregation of the constituent phases. Surface EDS analysis was also used to examine impurities effects on the samples. Measurements taken after the homogenization process also clearly showed the presence of large amounts of residual oxygen introduced by the Ti(OBuⁿ)₄ + Zr(OPr)₄ catalysts [43].

The growth of relatively narrow diffraction peaks from aluminum have been observed through in-situ x-ray diffraction measurements made during the decomposition of both catalyzed and catalyzed NaAlH₄ (Figure 7) [39]. Thus, aluminum must segregate according to equation 1 to form crystallites with dimensions on the order of 1000 Å or larger. This implies the long-range transport of metal species. Surface EDS verified this notion by showing an increasing overall aluminum concentration on the surface of the powder particles during decomposition [36]. In addition, Auger spectra analysis shows that most of the catalyst remains on the material's surface [39]. This raises the question of how aluminum hydride anions paired with sodium cations in an ionic solid could be influenced by catalytic sites that are immobilized on the particle surface. One speculation is that the transported species is a more mobile hydride such as AlH₃ [39]. The low melting point of NaAlH₄ demonstrates the weak nature of the ionic bond. It is possible that local disproportionation of 3NaAlH₄ into Na₃AlH₆ and 2AlH₃ takes place. The AlH₃ then transports to the catalytic site where it dissociates into Al and H₂. However, none of these mechanistic concepts have been verified experimentally.

Conclusion and Outlook

This overview has covered some of the recent advances in the development of catalyzed sodium-alanates as lightweight hydrogen storage materials. These materials are now realizing reversible capacities in excess of 4.2 wt.%. The current state of the art allows the desorption of 3 wt.% hydrogen in a little over one hour at 125°C. Precise plateau pressure measurements demonstrate that thermodynamically these materials are ideally suited to practical applications. The $NaAlH_4 \rightleftharpoons 1/3Na_3AlH_6 + 2/3Al + H_2$ reaction delivers 1 atm hydrogen at 33°C.

These are important achievements; however, a great deal of progress remains to be made. In particular, 1) the slow dehydriding and rehydriding kinetics remain a significant barrier to

applications such as fuel cell vehicles. Titanium-halide catalysts and dry doping procedures are showing promise, especially in overcoming the impurity and capacity related restraints of the previous alkoxide based catalysts, but the kinetics must still be improved. 2) Completing the second reaction step $1/3Na_3AlH_6 + 2/3Al + H_2 \leftrightarrow NaH + Al + 3/2H_2$ is necessary to obtain the full 5.6 wt.% theoretical capacity. Unfortunately, Na_3AlH_6 is a little too stable for many applications; releasing 1 atm hydrogen at about 110°C. Elemental substitution must be explored as a means to de-stabilize this reaction. 3) Long-term cycling studies will be needed to ensure the viability of these materials for reversible hydrogen storage. 4) Safety is an important issue that must be addressed. These compounds are highly reactive with water and air. Small amounts of water or oxygen as impurities are unlikely to be a significant problem. However, engineering solutions or material modifications will be required to reduce the hazards associated with a full exposure to air or water. 5) Finally, progress has been made in understanding the fundamental processes that take place in these solid-state reactions. Long-range transport of metal species appears to play an important role in the overall reaction kinetics. For the moment, however, the nature of the transported species and the role of the catalysts remain a mystery.

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Figure Captions

Figure 1. Thermal programmed desorption (2 °C min⁻¹) of hydrogen from NaAlH₄ doped using different catalysts and doping methods. Measurements were made following 3 full dehydriding/rehydriding cycles.

Figure 2. Van't Hoff Diagram showing equilibrium pressures as a function of temperature for the $\text{NaAlH}_4 \rightleftharpoons 1/3(\alpha\text{-Na}_3\text{AlH}_6) + 2/3\text{Al} + \text{H}_2$ and the $\alpha\text{-Na}_3\text{AlH}_6 \rightleftharpoons 3\text{NaH} + \text{Al} + 3/2\text{H}_2$ reactions. Samples doped with 2 mol.% each of the liquid catalysts of Ti(OBuⁿ)₄ and Zr(OPru)₄

Figure 3. A compilation of NaAlH₄ hydrogen desorption kinetics measurements from different authors. a) 1st desorption (25-150°C) of 2 g NaAlH₄ doped by mechanical milling for three hours with 2 mol.% each of the liquid catalysts of Ti(OBuⁿ)₄, Zr(OPr)₄ and 2 mol.% solid Ti₃Al (SNL), b) 1st desorption (25-150°C) and 4th desorption (125°C) of sample processed as in a) but without solid Ti₃Al catalyst (SNL/UH), c) 3rd desorption (125°C) of 2 g NaAlH₄ doping by mechanical milling for three hours with 2 mol.% β-TiCl₃ (SNL), d) desorption (80,100,120,150°C) of NaAlH₄ milled together with 10 wt.% carbon for 2 hours [30], e) 1st desorption (120°C and 150°C) of NaAlH₄ precipitated from THF using pentane then doped with 2 mol.% Ti(OBu)₄ in toluene, filtered and dried under vacuum [26], f) 1st desorption (50-160°C) of 100 g scaleup bed NaAlH₄ doped by mechanical mixing for 30 sec. with 2 mol.% each of the liquid catalysts of Ti(OBuⁿ)₄ and Zr(OPr)₄ (SNL/UH).

Figure 4. A compilation of NaAlH₄ hydrogen absorption kinetics measurements from different authors. a) 6th absorption (125°C, 67 bar) of 2 g NaAlH₄ doped by mechanical milling for three hours with 2 mol.% each of the liquid catalysts of Ti(OBuⁿ)₄, Zr(OPr)₄ and 2 mol.% solid Ti₃Al (SNL), b) 3rd absorption (125°C, 68 bar) of sample processed as in a) but without solid Ti₃Al catalyst (SNL/UH), c) 2nd absorption (125°C, 91 bar) and 4th absorption (100°C, 90 bar) of 2 g NaAlH₄ doping by mechanical milling for three hours with 2 mol.% β-TiCl₃ (SNL), d) absorption (80,120,150°C 89 bar) of NaAlH₄ milled together with 10 wt.% carbon for 2 hours [30], e) 8th absorption (104°, 83 bar) of NaAlH₄ precipitated from THF using pentane then doped with 2 mol.% Ti(OBu)₄ in toluene, filtered and dried under vacuum [27], f) 4th absorption (160°C, 174 bar) of 100 g scaleup bed NaAlH₄ doped by mechanical mixing for 30 sec. with 2 mol.% each of the liquid catalysts of Ti(OBuⁿ)₄ and Zr(OPr)₄ (SNL/UH).

Figure 5. Temperature excursion in 100 g scaleup test bed during the fourth hydrogen absorption cycle (initial: T=160°C, P=174 bar).

Figure 6. SEM images showing changes in morphology that occur during the decomposition of NaAlH₄ doped with 2 mol.% each of the liquid catalysts of Ti(OBuⁿ)₄ and Zr(OPr)₄.

Figure 7. Dynamic *in-situ* x-ray diffraction measurements taken during decomposition of NaAlH₄ mechanically mixed with 2 mol.% each of the liquid catalysts of Ti(OBuⁿ)₄ and Zr(OPr)₄.

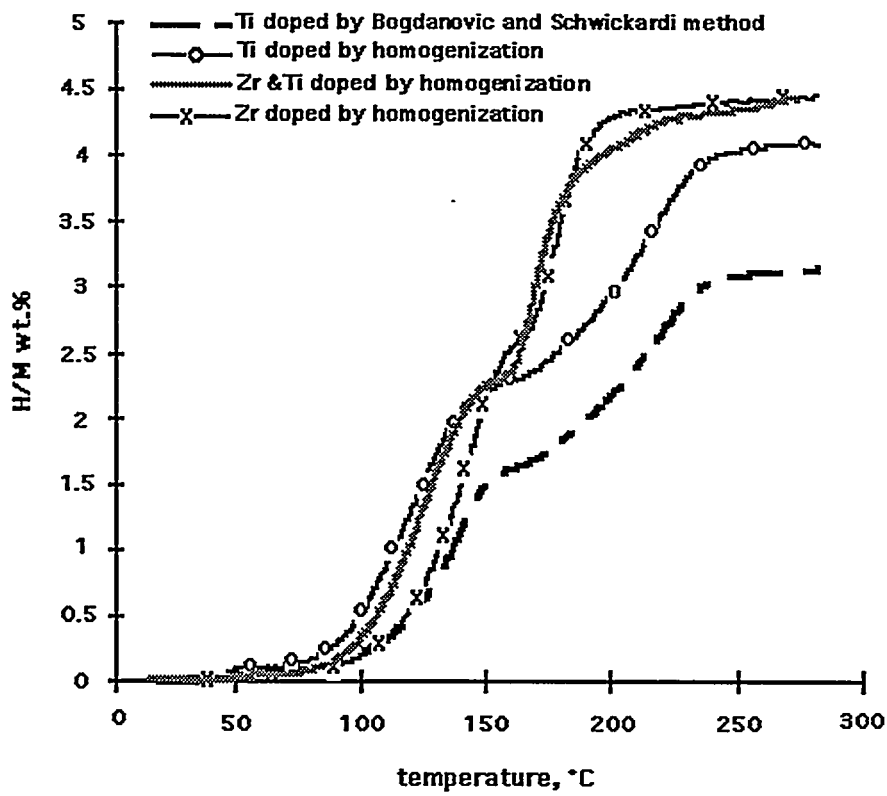


Figure 1.

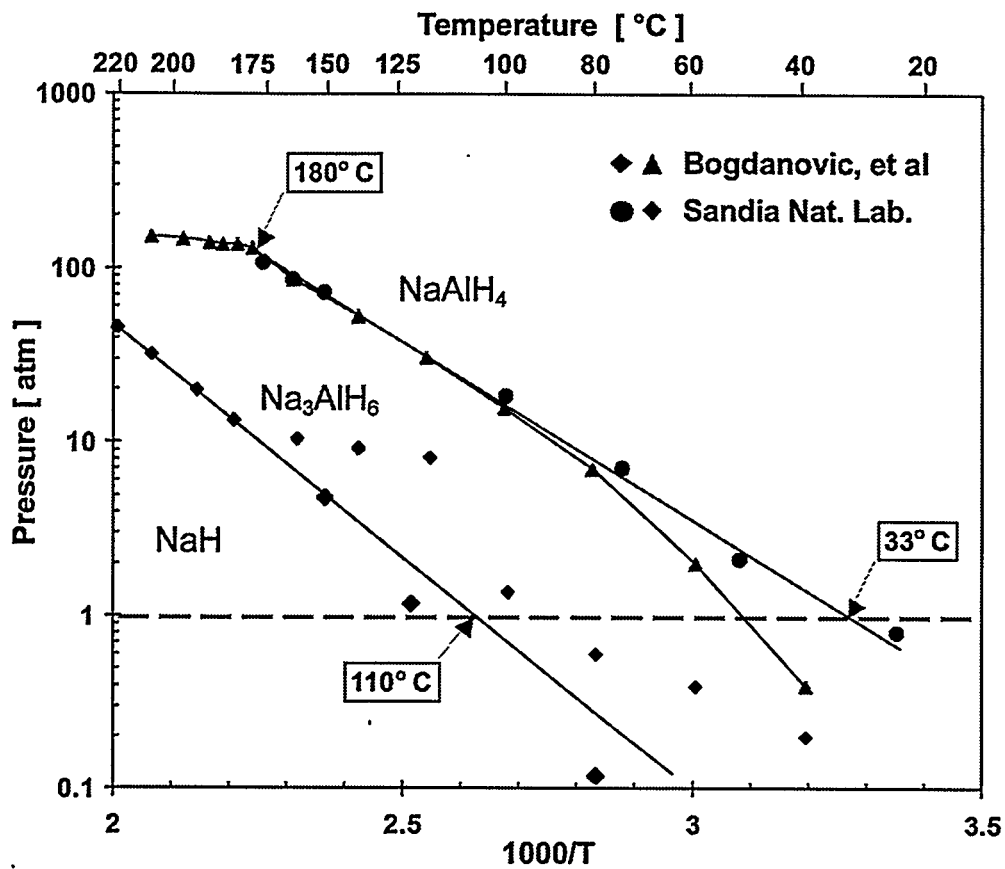


Figure 2.

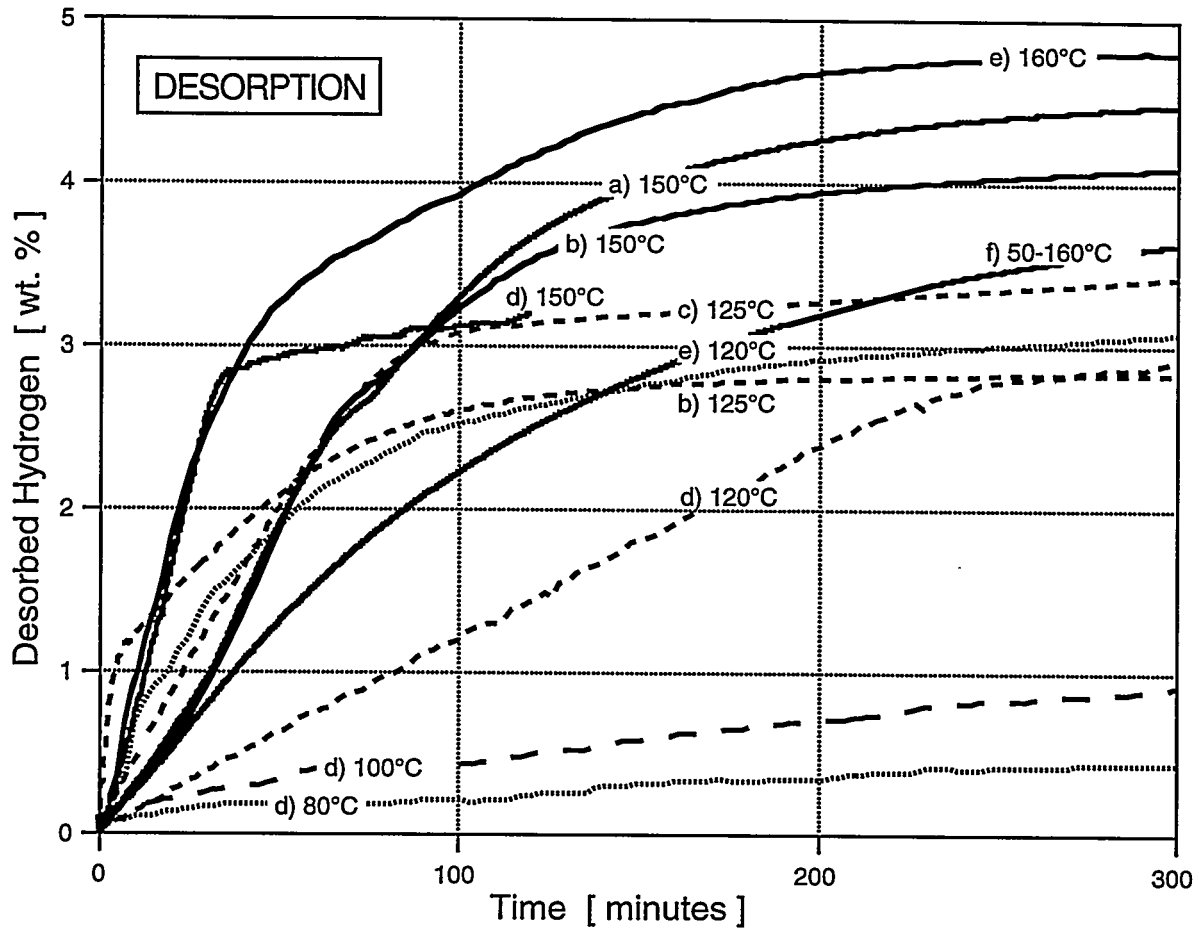


Figure 3.

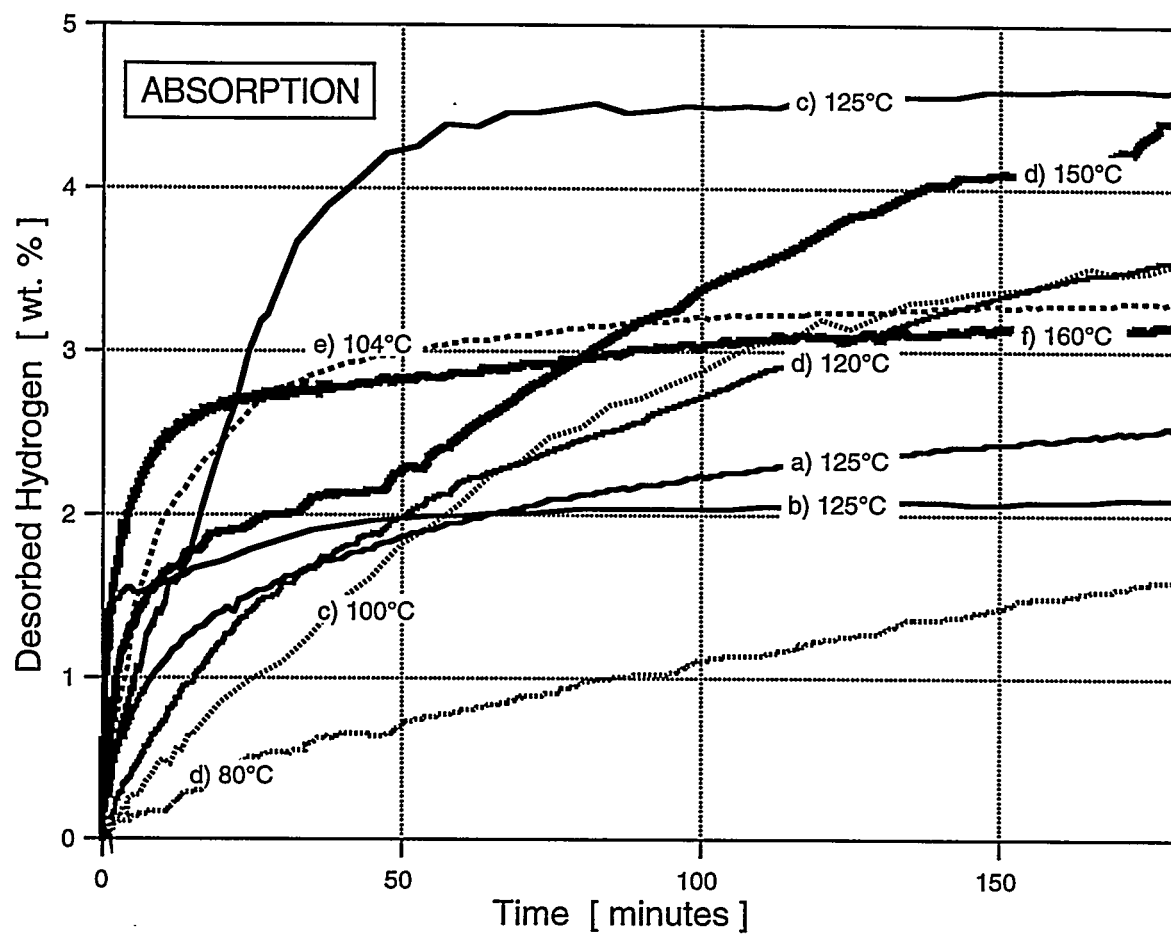


Figure 4.

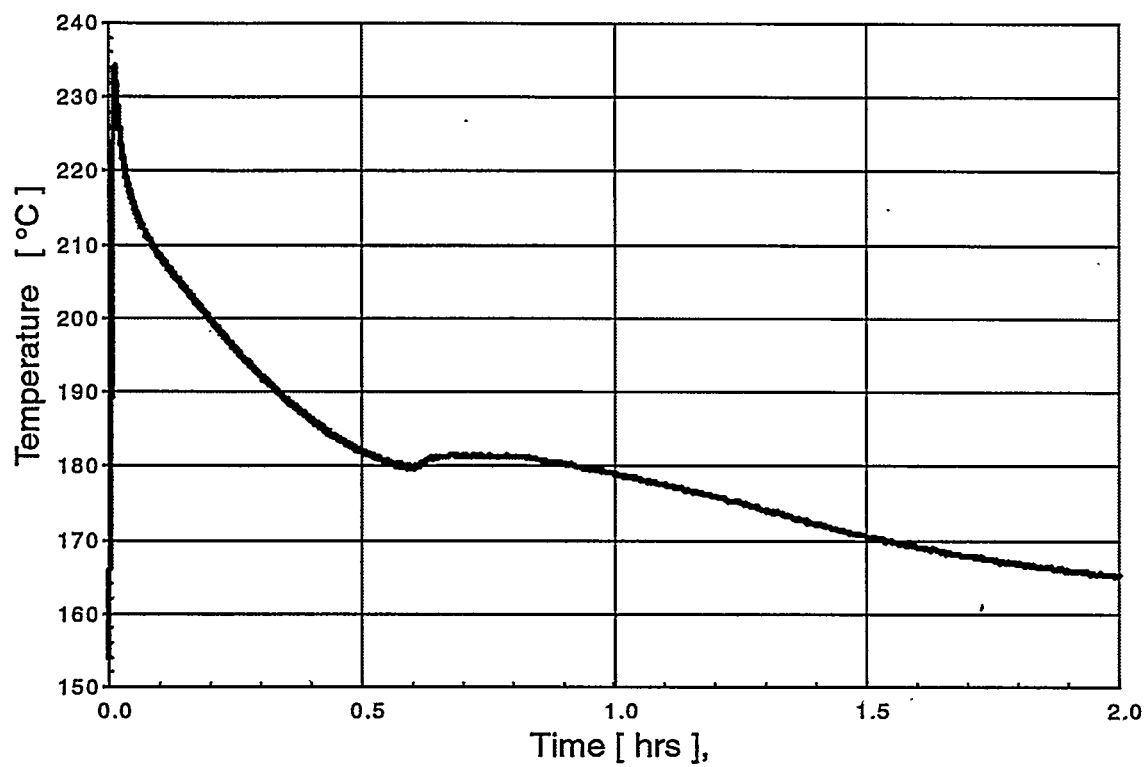


Figure 5.

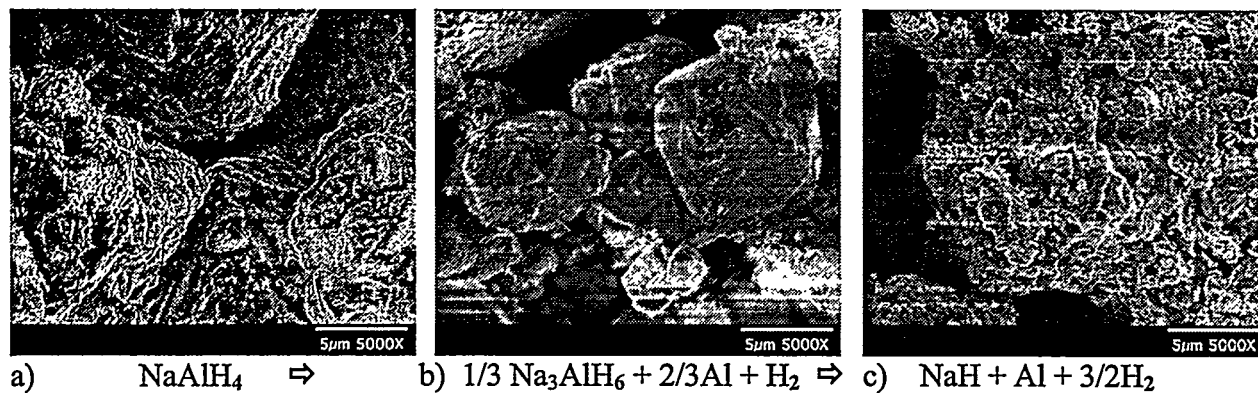


Figure 6.

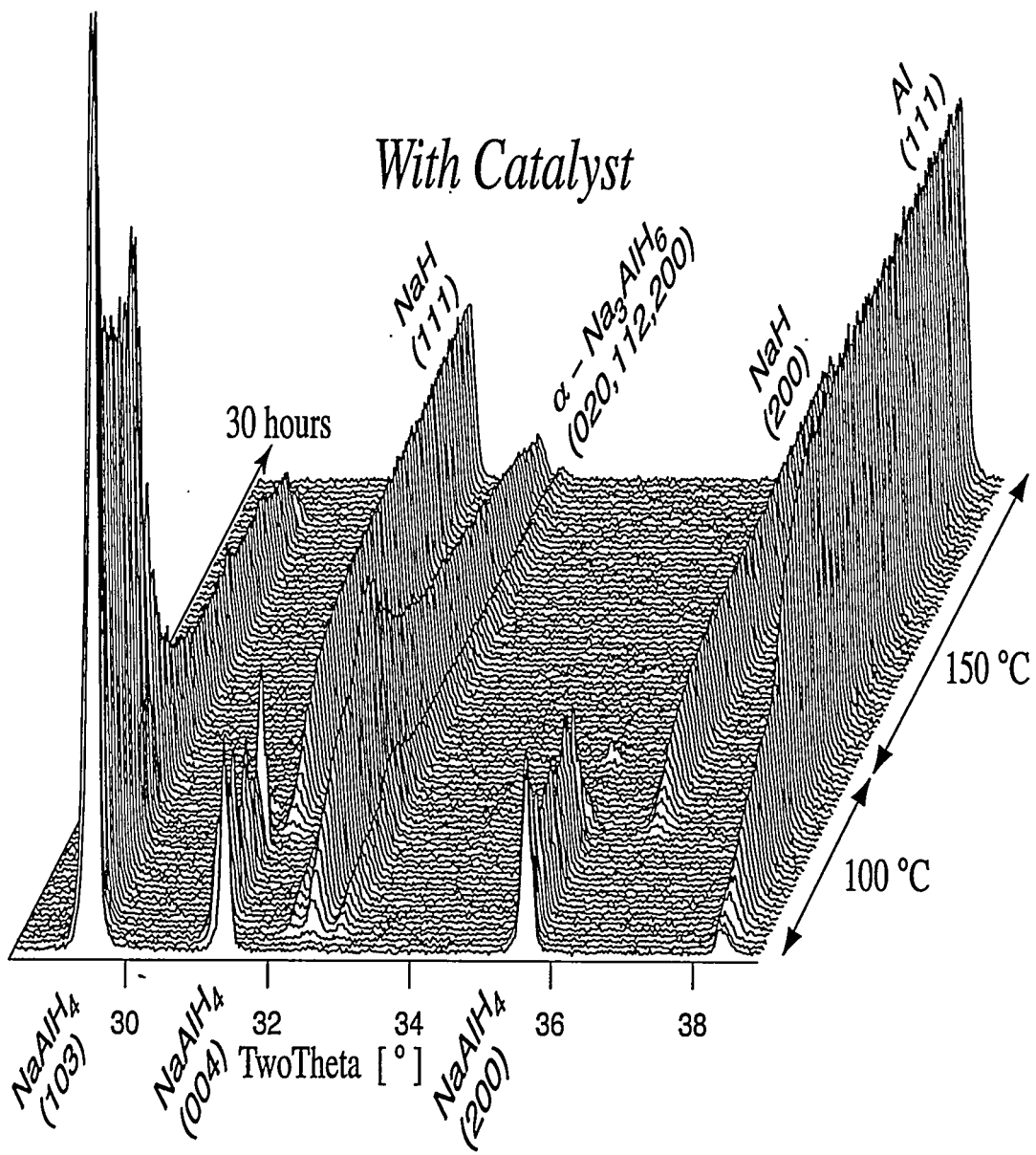


Figure 7.