

HYDRIDE DEVELOPMENT FOR HYDROGEN STORAGE

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Abstract

Gas-phase kinetic and equilibrium thermodynamic measurements, reaction modeling, and time-resolved x-ray diffraction have been performed on catalyst doped NaAlH₄. Kinetic measurements showed a distinct change in the rate of hydrogen desorption at specific pressures and temperatures. This is interpreted as due to the equilibrium pressure of the intermediate Na₃AlH₆ phase. The equilibrium pressures derived from these kinetic measurements at different temperatures are consistent with higher temperature equilibrium measurements. Equilibrium desorption pressure measurements of NaAlH₄ below 180 C were used to estimate a heat of formation of roughly -34.8 kJ/molH₂. The difference between this and reported values at higher temperatures can be accounted for by the heat of melting which occurs at about 180 C. Time-resolved X-ray diffraction measurements demonstrated this melting, clarified the reaction processes, and demonstrated the effectiveness of the added catalysts.

Introduction

The recent work of Bogdanovic and Schwickardi (1997) demonstrated that the alkali metal hydride, NaAlH₄, readily released and absorbed hydrogen when doped with a TiCl catalyst. Prior to this work, Ashby and Kobetz, (1966) had demonstrated the importance of an intermediate phase (Na₃AlH₆) in the synthesis and decomposition of NaAlH₄. The possibility of the formation of an intermediate phase had been previously suggested by Garner and Haycock, (1952) as a part of the general reaction process for the Alanates. However, slow kinetics made these materials all but impractical for hydrogen storage. Hence, the findings of Bogdanovic and Schwickardi is significant in identifying a new class of hydrides, based on the aluminum hydride complex and non-transition metals, which have great potential for use as reversible hydrogen storage media.

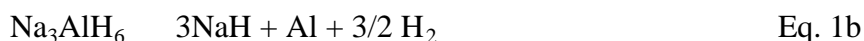
These materials are distinct from classical metal hydrides in structure and properties. Some examples of non-transition metal hydrides based on the aluminum hydride complex and their corresponding theoretical hydrogen capacities are shown in Table 1.

Table 1. Some aluminum hydride complex materials

<u>Examples</u>	<u>Theoretical Reversible Capacity</u>
Na(AlH ₄)	5.5 wt.%
Li(AlH ₄)	7.9 wt.%
Mg(AlH ₄) ₂	6.95 wt.%
Zr(AlH ₄) ₂	3.9 wt.%

Note that relatively high storage capacities are achievable. Generally, the final product contains a stable hydride phase which requires high temperatures for dissociation. The hydrogen associated with this phase is not included in the theoretical capacities shown in the Table.

The hydrogen release process is quite complex. Indeed, in the case of NaAlH₄, an intermediate phase, Na₃AlH₆, is formed before the compound decomposes to its final structure. The reactions in this case are:



This year our work has focused on three areas: (1) understanding the behavior of catalyzed NaAlH₄, (2) characterizing the materials and material processing methods, and (3) examining the performance of this material in a lab-scale hydride bed. NaAlH₄ was studied in depth for two reasons. First of all, with a reversible capacity of 5.5 wt.% H₂, this compound has merit as a potential storage medium. Secondly, a detailed understanding of the hydriding and dehydriding behavior of this compound will play an important role in the development of improved storage materials based on catalyst assisted complex-based hydrides.

In these studies, we employed gas-phase kinetic and equilibrium measurements, reaction modeling, and time-resolved x-ray diffraction measurements. The material processing and catalyst doping was performed in collaboration with the University of Hawaii (C. Jensen, R. Zidan, S. Takara). Furthermore, studies were initiated with F. Lynch, HCl, on flammability, impact resistance and other safety related properties to determine potential safety concerns in using this material in fixed or mobile hydrogen storage applications.

Results

Hydrogen desorption kinetics

Isothermal hydrogen desorption measurements on catalyst-doped NaAlH_4 were made at a number of temperatures between 80 C and 180 C. The experiments were performed by rapidly heating samples up to the desired temperature and collecting the released hydrogen in a fixed volume. The initial ramp-up in temperature generally took a relatively short time (1-2 min.) compared to the total length of the measurements. An example is shown in Figure 1.

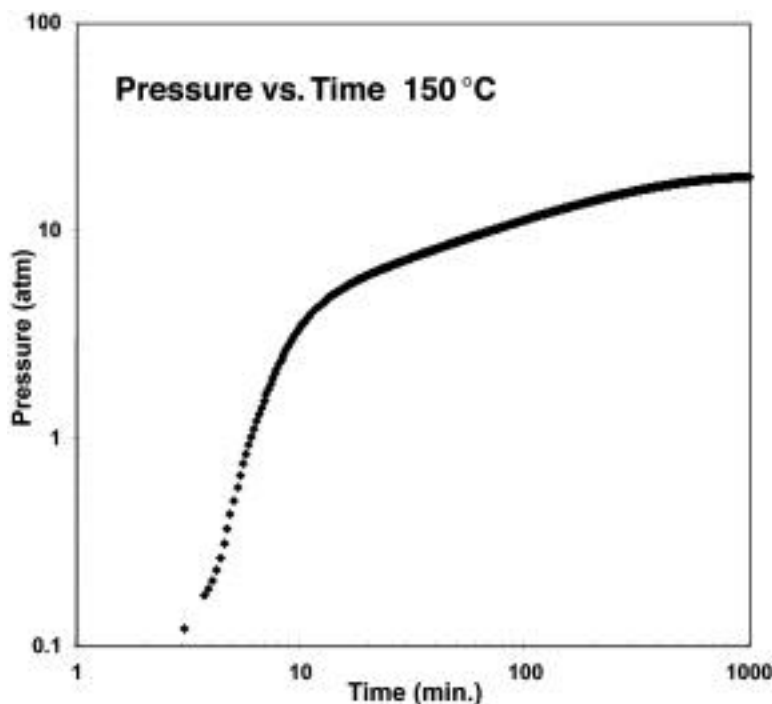


Figure 1 – Isothermal Hydrogen Desorption Kinetics Measurement at 150 C for “Sandia prepared” Ti catalyst

Hydrogen pressure is plotted as a function of time for desorption at 150 C of a sample with a Ti catalyst. A log-log plot is used to emphasize the distinct change in release rates characteristically observed in these measurements. We interpret this change in rate as being related to the plateau pressure of the low pressure intermediate phase Na_3AlH_6 . If one linearly extrapolates the high pressure and low pressure parts of the curve, the intersection of these two lines defines a pressure roughly midway through the transition. This was done for all of the temperatures measured and the values plotted in the lower curve of the van't Hoff diagram shown in Figure 2.

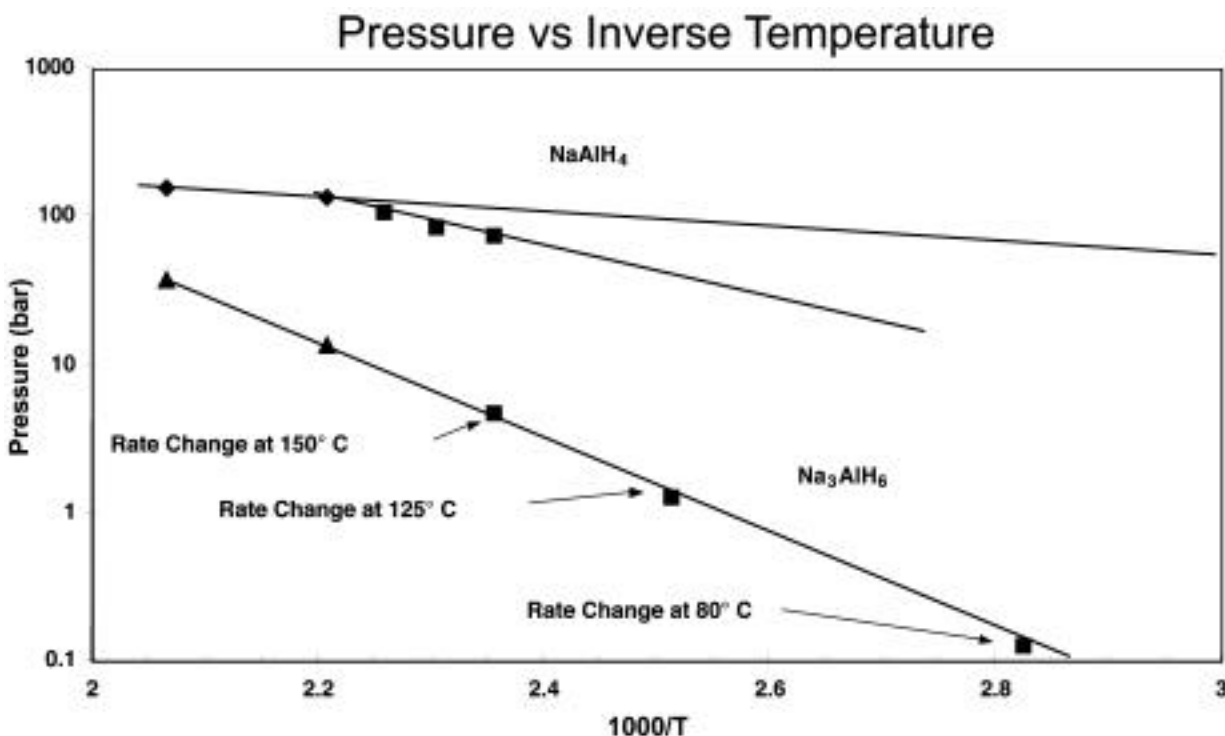


Figure 2 – Van't Hoff Diagram showing equilibrium pressures as a function of temperature for both hydride phases

Here, the log of the pressures are plotted as a function of reciprocal temperatures for desorption from both phases. Also plotted are the two plateau pressure measurements at 180 and 211 C by Bogdanovic and Schwickardi (1997) for both cases. Referring to the lower pressure curve, it can be seen that all of the values derived from the kinetic measurements agree with the extrapolated behavior from the higher temperature equilibrium results. This lends support to our interpretation of the isothermal desorption behavior. The slope of the data yields a value of about -48 kJ/molH_2 for the heat of formation of the Na_3AlH_6 phase.

The effects of two different catalysts on desorption rates were also examined. Material processing and catalyst doping were performed in collaboration with the University of Hawaii (C. Jensen, R. Zidan, and S. Takara). The starting NaAlH_4 material was prepared by one of two different methods. In the first, a commercial 1.0M solution of NaAlH_4 in THF (Aldrich Chemical) was evaporated to dryness under vacuum. This material is referred to below as "Sandia prepared". In the second process, NaAlH_4 was prepared by re-crystallizing the solid from a THF/pentane solution. In the following discussion, this material is referred to as "UH prepared". IR spectroscopy performed on these samples indicated no residual THF. The hydride was doped with catalyst using the liquid precursors: titanium butoxide $\text{Ti}[\text{O}(\text{C}\text{H}_2)_3\text{CH}_3]_4$ and zirconium propoxide $\text{Zr}[\text{O}(\text{C}\text{H}_2\text{CH}_2\text{CH}_3)]_4$ 70 wt.% in a 1-propanol solution as described in the literature (Zidan, et al, 1999). One or both of the catalyst precursors were added in 2 mole % to about 1.5 g of the dry NaAlH_4 powder. The mixture was then ground with first a mortar and pestle and finally in a SPEX mill for 30 seconds. This process caused a color change in the material from white to dark gray. All operations, including mounting of material in test cells, were performed in an argon glove box to minimize water and oxygen contamination.

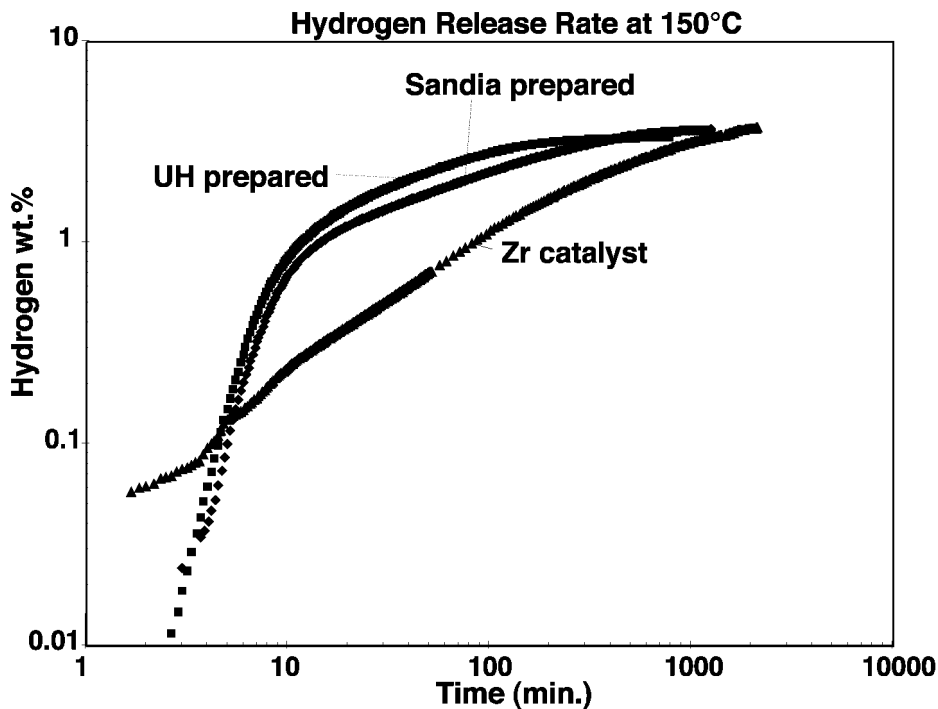


Figure 3 – Comparison of material preparation and catalysts on isothermal desorption behavior

Hydrogen desorption rate measurements at 150 C are shown in Figure 3 for two Ti catalyst samples and one Zr catalyst sample. In this case, we have plotted the fractional hydrogen release (weight percent) in order to compare samples of different masses. Note, first of all, that there is little difference between the two Ti catalyst samples which were prepared by the techniques described above. The Zr catalyst, however, displays very different desorption behavior from the Ti-doped material. One factor affecting the desorption rate is that the plateau pressure of the intermediate phase, Na_3AlH_6 , was never exceeded during the Zr catalyst measurement because the sample mass was somewhat smaller than the others. Nevertheless, the roughly constant desorption rate was less than the initial rates measured in the Ti-doped samples. TPD measurements (Zidan, 1999) at the University of Hawaii showed that both catalysts could be applied together resulting in an improved performance over single-doped material. For this reason, in the x-ray work described below and in the hydride bed studies, our initial measurements used combined catalyst (Ti and Zr) material.

Equilibrium behavior

Isothermal hydrogen pressure-composition measurements were made during desorption of the high pressure phase, NaAlH₄, at lower temperatures than reported by Bogdanovic and Schwickardi (1997). This is shown in Figure 2 (the upper curve). Here, desorption equilibrium plateau pressures at three temperatures, 150, 160 and 170 C, are plotted along with the published data. Note that the lower temperature plateau pressures show a distinct change in slope from those at 180 C and 211 C. Thus, we believe that the data reflect the equilibrium behavior of NaAlH₄ decomposition in the melted phase above 180 C and in the solid phase below 180 C. The solid phase measurements indicate a higher heat of formation (greater slope). For NaAlH₄, we obtain -34.8 kJ/molH₂ in the solid phase. These values should, however, only be considered as estimates because of the small number of points. Above 180C, the difference between this value and the reported enthalpy of melting for NaAlH₄ (23.2 kJ/molH₂, P. Claudy, 1980), is -11.6 kJ/molH₂. This value is consistent with the equilibrium measurements above 180 C reported by Bogdanovic, B. and Schwickardi (1997). The enthalpies of the solid state reactions can be formulated in terms of equations 1a and 1b:

$$H_{1a} = 1\text{molH}_2 (H_{\text{NaAlH}_4} - 1/3 H_{\text{Na}_3\text{AlH}_6}) \quad \text{Eq. 2a}$$

$$H_{1b} = 2\text{molH}_2 (1/3 H_{\text{Na}_3\text{AlH}_6} - H_{\text{NaH}}) \quad \text{Eq. 2a}$$

Combining these gives:

$$H_{1a} = 1\text{molH}_2 (H_{\text{NaAlH}_4} - 1/2 H_{1b} - H_{\text{NaH}}) \quad \text{Eq. 3}$$

Values for each of these formation enthalpies can be found in the literature. These are $H_{\text{NaAlH}_4} = -112.86$ kJ/molH₂, $H_{\text{NaH}} = -56.3$ kJ/molH₂, and $H_2 = -41.5$ kJ/molH₂ (M. Smith, 1963, and P. Claudy, 1980). Thus, the enthalpy of the solid state reaction of equation 1 determined from these values (using equation 3) is $H_{1a} = -35.8$ kJ/molH₂. This is comparable to our measured value of -34.8 kJ/molH₂.

In-situ x-ray diffraction measurements

Time-resolved x-ray diffraction measurements were made at elevated temperatures of catalyzed and uncatalyzed NaAlH₄. For these measurements, an *in-situ* sample cell with a thin Be window was devised which allows temperature and pressure control during the measurements. Loading of the cell was performed in an argon glove box to prevent oxidation of the material. Details of the cell and a more detailed discussion of these results is presented elsewhere (K. Gross, et. al, 1999). Here we will only describe some of the main findings. X-ray diffraction scans for the catalyzed and an uncatalyzed samples are shown in Figures 4a and 4b. These figures were generated by superposing periodic scans over a limited angular range. The intensity peaks correspond to specific crystallographic planes in each of the phases present in the sample. The time between individual scans is about 7 minutes, but the repeat cycle could be stopped at any time for large angle scans and phase identification. This technique allows one to follow the evolution of individual phases over the course of the experiment.

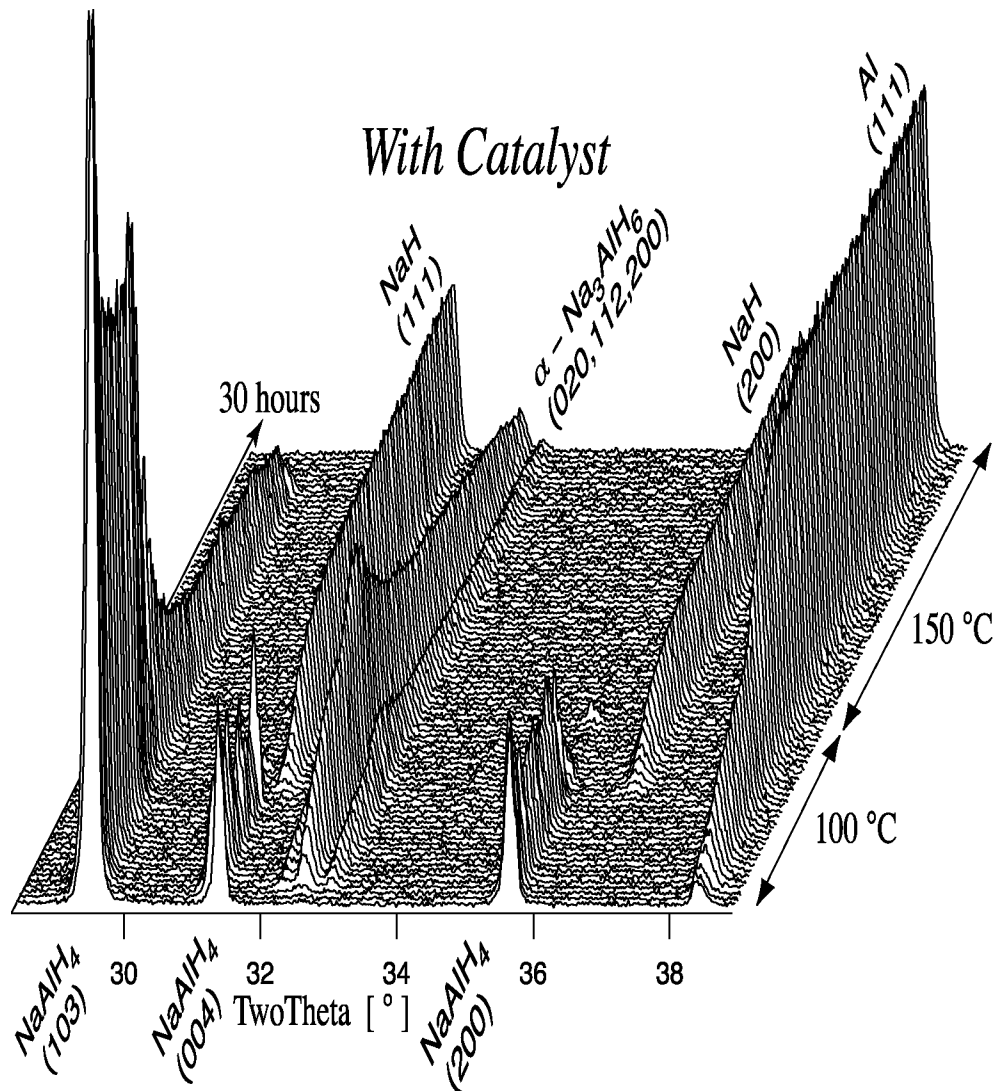


Figure 4a – In-situ x-ray diffraction of a catalyzed sample at 100 and 150 C

Figure 4a shows a series of scans taken during desorption of a sample doped with Ti and Zr catalysts. Sample temperatures are shown along the right hand side of the plot and are correlated with the time of the scans. These measurements show relative growth and decay of the different component phases (NaAlH_4 , Na_3AlH_6 , NaH , Al) which can be used to quantify the kinetics of the different reaction rates.

Several other interesting features were also observed. During the initial heating in both samples, shifts in the peak positions indicated a greater expansion of the unit cell in the c-axis due to thermal expansion. (NaAlH_4 has a tetragonal structure (Bel'skii, 1983), with the a and b axes equal and all three axes orthogonal.) Furthermore, the irregular variation in peak intensities for the NaAlH_4 reflections suggest that fairly rapid structural changes are occurring at the temperatures indicated. It should also be pointed out that the sharp diffraction profiles for Al seen in the figure are clear evidence that relatively large Al clusters are formed during the dehydriding process. Thus, some atomistic transport occurs which results in Al clustering during the decomposition of both phases, NaAlH_4 and Na_3AlH_6 .

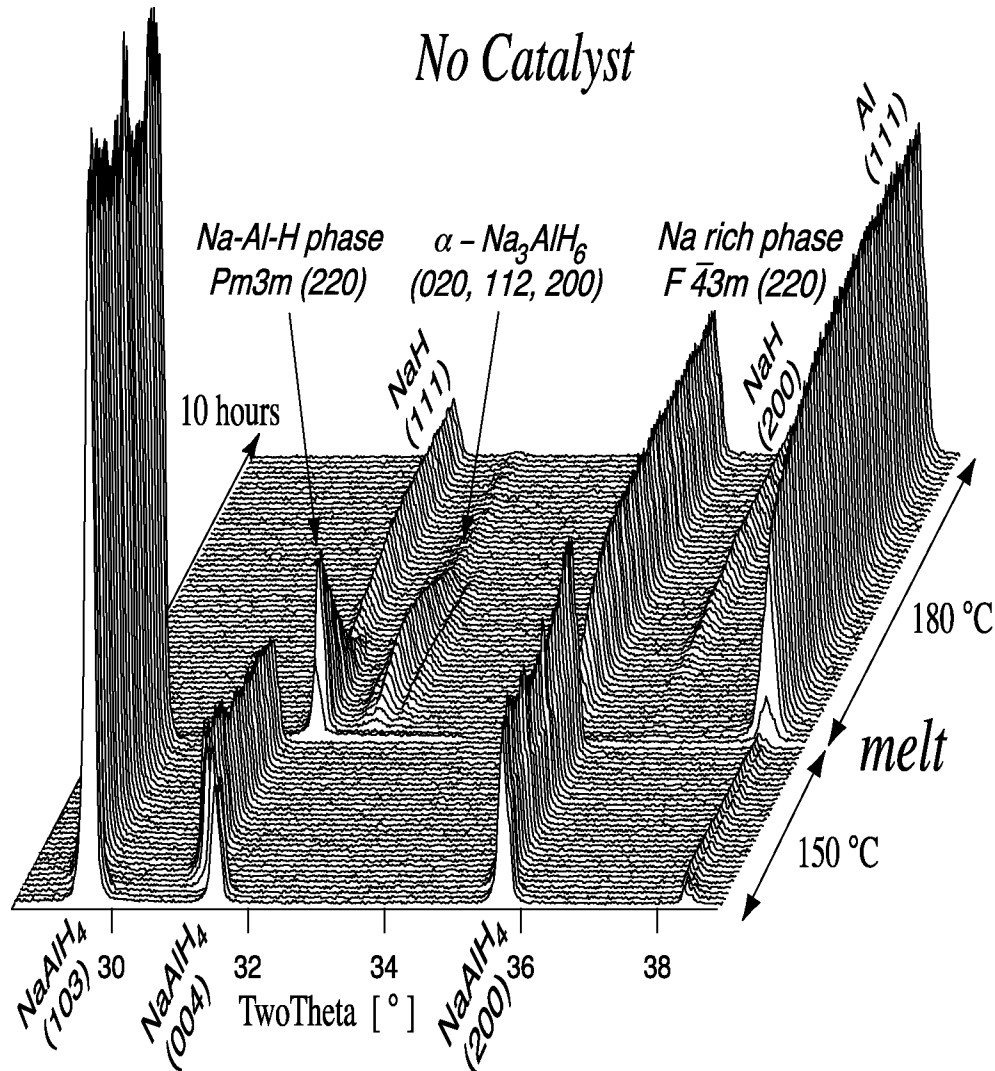


Figure 4b – In-situ x-ray diffraction of an uncatalyzed sample at 150 and 180 C

As seen in figure 4b, no decay of the initial phase, NaAlH₄, was observed for the uncatalyzed sample at 150 C. This is consistent with the lack of hydrogen release found during independent isothermal measurements. When the sample was subsequently heated to 180 C, however, all diffraction peaks associated with the NaAlH₄ phase abruptly disappeared, indicative of rapid and complete melting of the sample. This is in agreement with published values of the melting temperature for this material and was also verified by differential scanning calorimetry. The time interval at which this occurred is indicated in the figure 4b. Immediately following the melt transition one can see a corresponding increase in Al content and the formation of other phases. Since free Al was observed and the hexahydride phase is known to have a higher melting temperature, the formation of the intermediate phase was expected. However, it was found that a new Na-Al-H phase, with a structure different from alpha- Na₃AlH₆, precipitated first from the melt. This phase then rapidly decayed to form the expected alpha-NaAlH₆ structure. The stoichiometry and structure of the new phase are not known at this time. However, the Space-group with the highest symmetry which satisfies the observed peak positions has been identified as Pm-3m (No. 221).

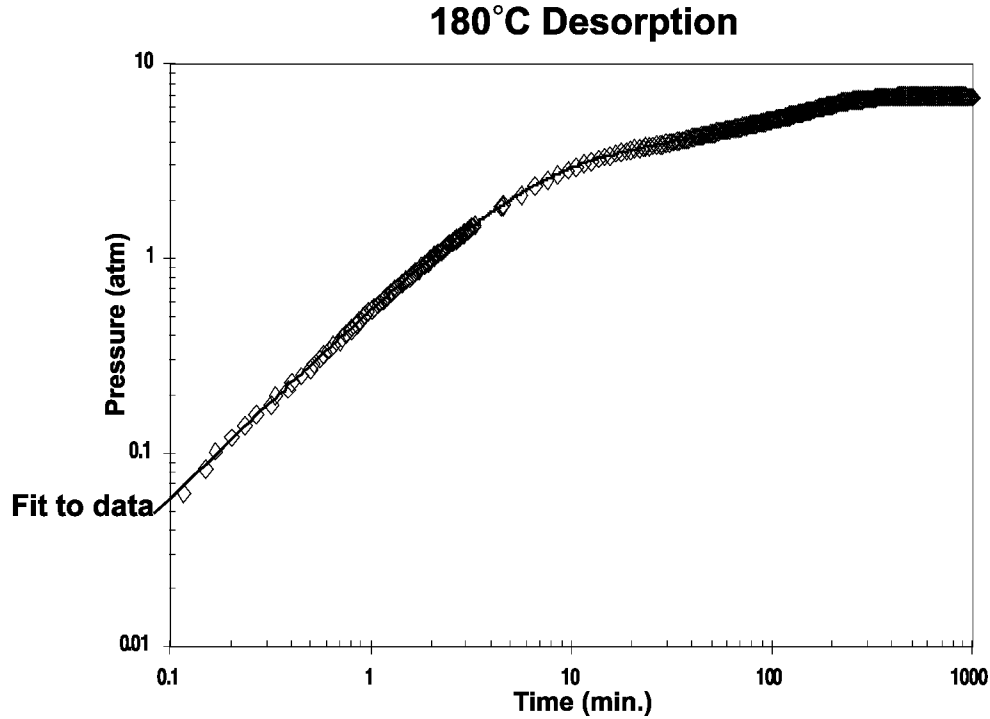


Figure 5 – Fit of desorption data with a numerical model of first-order chemical reactions

Kinetic modeling

Classical chemical kinetic models suggest that the isothermal results might be described by first order reaction rates; that is, for the reactions defined in Eq.'s 1a and 1b:

$$dN_1 = -3r_1N_1dt$$

$$dN_2 = r_1N_1dt - (1-a)r_2N_2dt + ar_3N_3dt$$

$$dN_3 = -ar_3N_3 + (1-a)3r_2N_2$$

$$dH_1 = -dN_1dt \quad dH_2 = -3dN_2dtdH_3 = -dN_3dt$$

where: subscript 1 refers to NaAlH_4

subscript 2 refers to Na_3AlH_6

subscript 3 refers to NaH , and

$a = 1$ when $P > P_e$ and $a = 0$

when $P < P_e$ for the intermediate phase

A numerical model containing the forward and back reactions of the initial, intermediate and final phases, as shown in the above equations, was constructed and compared to the experimental data. It was found that this approach can simulate the observed behavior extremely well when applied to release data at 180 C, that is, at the melting temperature of the starting material. This can be seen in figure 5. For the simulated curve, actual experimental quantities of starting materials and gas free volume were used. Rate constants for each of the reactions were obtained and subsequent fitting to measurements at other

temperatures should yield activation energies for the decomposition reactions. As might be expected, however, this straightforward approach does not accurately predict the experimental desorption results when applied at temperatures below the melting point of the initial phase. Other mechanisms, such as solid state diffusion, appear to be the rate limiting steps in the desorption process. This work is being continued at this time.

Conclusion

This study focused on elucidating some of the physical properties and mechanisms involved in the enhanced hydrogen sorption kinetics of catalyst doped NaAlH₄. Above 180C, the melting of NaAlH₄ changes the equilibrium thermodynamics of hydrogen sorption as well as creating a complex series of decomposition reactions involving several phase transitions. Below 180C, the thermodynamics of the decomposition - reformation reactions are well described in terms of solid state reactions.

Acknowledgements

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