

IV.A.4a Synthesis and Properties of Aluminum Hydride as a Hydrogen Storage Material

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Introduction

In FY 2006 work was directed at producing aluminum hydride (alane) materials, and exploring energy-efficient and cost-effective pathways for the regeneration of AlH_3 . The alane materials of interest have gravimetric system storage capacities better than 9% and volumetric system storage capacities better than 0.10 $\text{kg-H}_2/\text{L}$. Future goals are to continue studies on regeneration, and to develop a fuel tank storage system that costs less than \$133/ kg-H_2 with fuel flows greater than 0.02 g/s/kW with fuel tank holding pressures less than 4 atm(s) and operating temperatures between 90° to 100°C. Work in the last year of the project calls for an energy pathway study to be completed for delivering hydrogen to the automotive power plant with total (on-board, off-board and well-to-tank) energy efficiencies greater than 60%. To meet these aggressive storage goals by FY 2010, this work will continue to take advantage of opportunities offered through the Metal Hydride Center of Excellence under the “Grand Challenge” partnership.

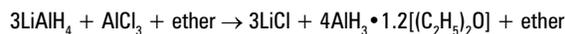
Approach

Aluminum hydride is a fascinating material that has recently attracted attention for its potential as a hydrogen storage medium for low temperature fuel cells. The approach for this year was to gain a better understanding of the strengths and weaknesses of using AlH_3 as a hydrogen storage medium by quantifying its reaction kinetics, thermodynamics, and regeneration pathways. It is known that aluminum hydride has several different polymorphs with $\alpha\text{-AlH}_3$ being the most stable and best characterized. However, little is known

about two other polymorphs (β,γ) except that they have the same stoichiometry as the α phase, but with different crystal structures. Therefore, all the AlH_3 polymorphs have the high storage capacity required for hydrogen storage, but with different thermodynamic and kinetic properties. This report describes recent work at BNL concerning the thermodynamic and kinetic properties of α , β and γ polymorphs, and reviews their possible use as hydrogen storage media for the automotive application.

Results

The procedure used in this study to synthesize the $\alpha\text{-AlH}_3$, $\beta\text{-AlH}_3$ and $\gamma\text{-AlH}_3$ polymorphs was developed by the Dow Chemical Co [1,2,3]. A more detailed discussion of the synthesis procedures has been published in a recent paper [4]. Essentially, the synthesis procedure consists of mixing lithium alanate with aluminum chloride in an ether solvent to yield a solvated form of AlH_3 in the ether solution.



The solution is then filtered and dried with excess LiAlH_4 at 60-70°C. In preparing the polymorphs of aluminum hydride, it is known that the synthesis is extremely sensitive to the de-solvating conditions (*i.e.* temperature and time), and small alterations lead to the precipitation of different polymorphs. It also should be noted that freshly prepared AlH_3 is pyrophoric and reacts violently with water. However, surface treated materials can be made very stable. In fact, BNL has safely stored samples AlH_3 (Dow) for over twenty years in a plastic container at ambient conditions with no significant hydrogen release.

Figure 1 shows a differential scanning calorimetric (DSC) plot of $\alpha\text{-AlH}_3$ over a temperature range of 35–300°C. A large endothermic peak is observed around 170° C, which is attributed to the decomposition of AlH_3 . X-ray diffraction data reveals that $\alpha\text{-AlH}_3$ is completely transformed to the face center cubic (fcc) structure of Al metal during the temperature ramp. The measured formation enthalpy is -9.9 ± 0.4 kJ/mol AlH_3 . This is similar to the enthalpy measured by Sinke [5] et al. (-11.4 ± 0.8 kJ/mol AlH_3) using calorimetry and calculated values by Wolverton [6] et al. (-6.95 kJ/mol AlH_3) and Ke [7] et al. (-12.35 kJ/mol AlH_3). The Gibbs free energy of formation at room temperature was calculated using the measured formation enthalpy and an entropy change of 130.7 (J/mol K), which is approximately the entropy associated with the transformation of hydrogen from a disordered gas to

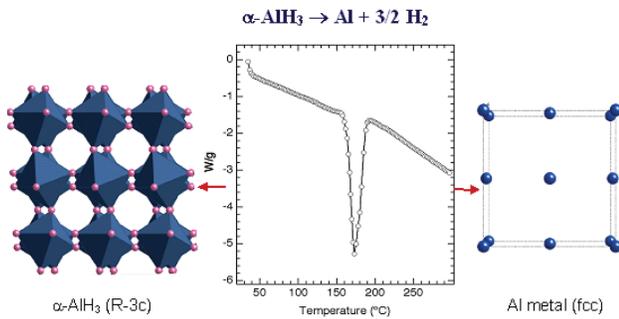


FIGURE 1. The reaction pathway & thermodynamics of α -AlH₃ showing heat flow measured during temperature ramp (10°C/min). It should be noted that the relative position of the Al atoms do not change during decomposition.

an ordered solid. The Gibbs formation energy at ambient temperature is 48.5 ± 0.4 (kJ/mol AlH₃). It is interesting to note that this value yields an H₂ equilibrium pressure of 5×10^5 bar at 298 K, which is comparable to the value predicted by Claudy et al. [8], but considerably higher than the values measured by Baranowski and Tkacz [9].

The DSC plots of β and γ -AlH₃ are shown in Figure 2. In addition to the large endothermic peak observed around 170°C, there is a significant exothermic peak that appears at approximately 100°C. X-ray diffraction patterns were acquired prior to the thermal treatment, after a ramp to 130°C, and after a ramp to 290°C and are also shown in Figure 2. Prior to thermal treatment the β sample is predominately composed of the β phase with a small amount of a γ phase impurity as shown in pattern I. After the temperature ramp up to 130°C the sample is almost entirely composed of α -AlH₃ with a small amount of Al metal and residual β -AlH₃ as shown in pattern II. As the temperature is further increased the α phase decomposes to Al metal (and H₂) as shown in pattern III. It is clear that the $\beta \rightarrow \alpha$ transition is the preferred decomposition pathway at around 100°C. However, it should be noted that at lower temperatures or faster heating rates the β phase may decompose more readily to Al + 3/2H₂. The transition enthalpy (ΔH_{trans}), total formation enthalpy (ΔH_{total}), and the Gibbs free energy ($\Delta G_{298\text{K}}$) for β -AlH₃ are -1.5 kJ/mol, -8.0 kJ/mol and 50.5 kJ/mol, respectively. The measured transition enthalpy may be slightly higher than the actual value due to the contribution from the γ phase impurity. Therefore, the magnitudes for ΔH_{total} and $\Delta G_{298\text{K}}$ may underestimate the actual values. The DSC plot of γ -AlH₃, shown in Figure 2, also exhibits a large exothermic peak around 100°C. The ex situ diffraction patterns acquired prior to the thermal treatment, after a ramp to 133°C, and after a ramp to 290°C are also shown in Figure 2. The starting material is composed of pure γ -AlH₃, which transforms to α -AlH₃ upon a temperature ramp to 133°C. Additional heating to 290°C exhibits the expected decomposition of the α

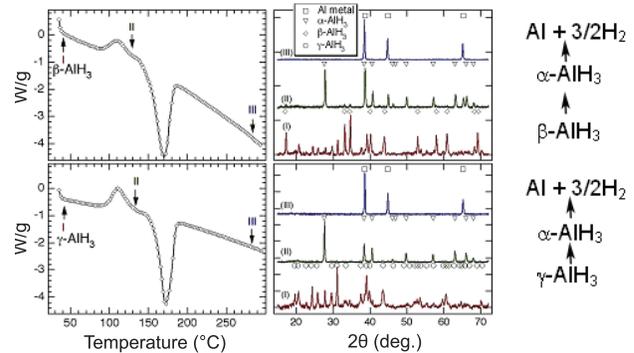


FIGURE 2. At $T \sim 100^\circ\text{C}$ γ and β -AlH₃ undergo exothermic phase transition to α -AlH₃ and at $T \sim 160^\circ\text{C}$ endothermic decomposition of α -AlH₃ to Al + 3/2H₂ as confirmed by XRD measurements.

phase to Al metal (and H₂). These results demonstrate that, similar to the β phase, the decomposition of γ -AlH₃ occurs by an initial $\gamma \rightarrow \alpha$ transition followed by decomposition of the α phase. This polymorphic transition was also observed by Claudy [10] et al. Although a complete $\gamma \rightarrow \alpha$ transition occurs at 100°C, it is possible that the γ phase decomposes directly to the elements at other temperatures. The measured thermodynamic values for γ -AlH₃ are: $\Delta H_{\text{trans}} = -2.8$ kJ/mol, $\Delta H_{\text{total}} = -7.1$ kJ/mol and $\Delta G_{298\text{K}} = 51.4$ kJ/mol. It is interesting to note that γ/β transitions to the α phase are exothermic reactions and are therefore likely to occur spontaneously even at room temperature.

The isothermal fractional decomposition data for α -AlH₃, β -AlH₃ and γ -AlH₃ are shown in Figure 3. The decomposition curves are isothermal and the data acquired during the initial sample heating is not included. All three polymorphs exhibit a similar set of decomposition curves with a short induction period followed by an acceleratory period where the rate of H₂ evolution increases rapidly, and finally a decay period. At 112°C the H₂ evolution rate is 1.0 g/s, which is the DOE fuel delivery target for a 50 kW fuel cell. The reaction rate can be lowered and even stopped by decreasing the sample temperature, as shown in Figure 4. Decreasing the sample temperature to 23°C during the acceleratory period completely stops the evolution of H₂. Upon subsequent heating no induction period is observed and the decomposition reaction rate returns directly to the rate prior to reducing the temperature as shown in the inset of Figure 4.

Conclusions and Future Directions

Some of the findings reached the past year from this Alane study are the following:

1. The decomposition enthalpies of the α , β and γ forms of aluminum hydride were all measured to be between 7.1 to 9.9 kJ/mol AlH₃ (or 4.7 to 6.6 kJ/mol H₂), which indicates the need for extremely high

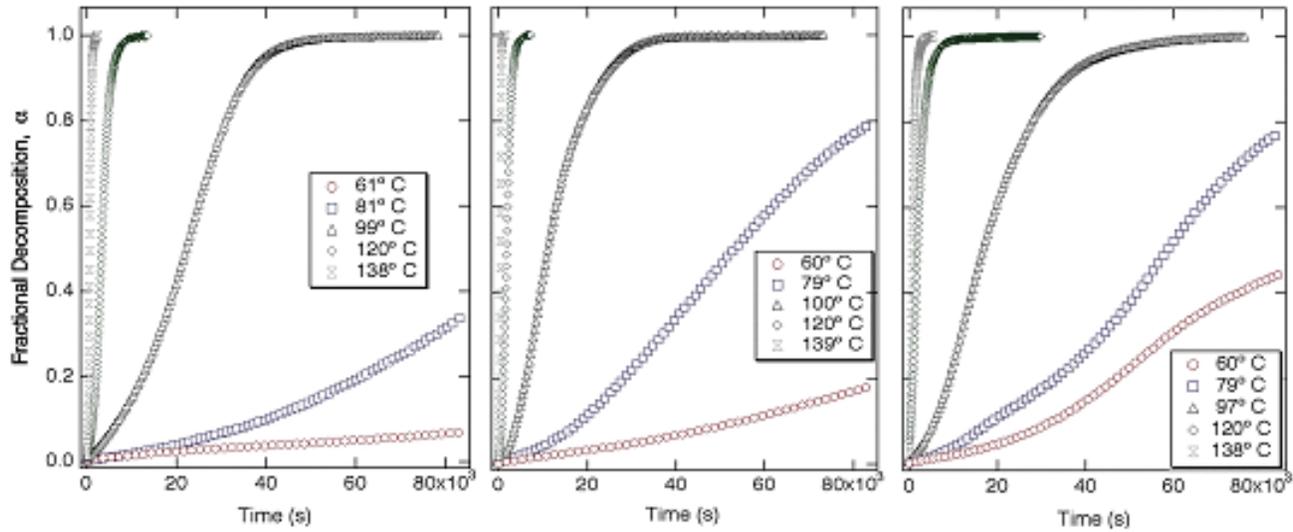


FIGURE 3. Isothermal kinetics of α , β and γ -AlH₃ polymorphs decomposed isothermally into vacuum.

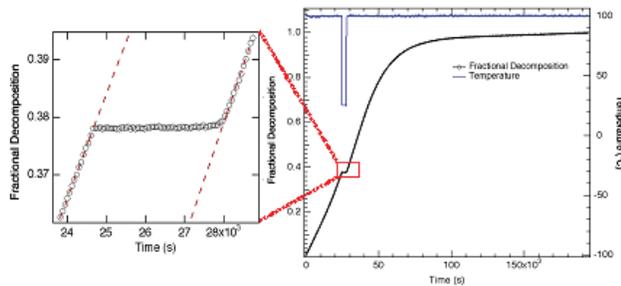


FIGURE 4. Temperature controlled decomposition where the reaction rate goes to zero as T is reduced to 23°C and returns to the same rate when T is increased back to 100°C.

pressures (100,000 atm. or higher) for the direct gas phase hydrogenation of the spent aluminum. Therefore, the direct gas re-hydriding of spent aluminum was given a no-go in FY 2006, and future research efforts at BNL are being directed to liquid phase (solvent) regeneration pathways. This is a two step wet chemical process by first solvating the spent aluminum in an appropriate solvent under a hydrogen pressure up to several thousand psia followed by separating the solvated-hydride from the solvent. If successful, this would eliminate the use of both aluminum chloride and lithium alanate in the conventional (Dow) synthesis of aluminum hydride.

- The decomposition kinetics of the α , β and γ forms of aluminum hydride all meet the DOE fuel flow target of 1.0 g H₂/s (50 kW fuel cell) at a temperature of 112°C. However, it has been shown that at the lower temperature of 40°C, β and

γ forms of aluminum hydride have higher kinetic rates than the α form. Because hydrogen release at lower temperature is of concern, the α -AlH₃ was down selected as the polymorph for continued study. Future studies include controlling the particle size and surface conditions of the α -AlH₃ in order to approach the shelf life of the Dow produced aluminum hydride, while still maintaining suitable high temperature kinetics.

- As noted herein, the hydrogen release in an aluminum hydride storage tank is temperature, not pressure, controlled. Aluminum hydride's heat of decomposition is around 7 kJ/mol H₂ at 100°C. This is less than 20% of the heat required for decomposing complex metal hydrides at ambient conditions. Future work will be the conceptual design of a temperature controlled storage system using iso-thermal aluminum hydride decomposition data. This work will allow reporting on meeting system storage targets; as well as, presenting cost/performance projections for the complete onboard storage system.

Special Recognitions & Awards/Patent Applications

- J. Reilly received the Life-Time Achievement Award from DOE at the 2006 Annual Hydrogen Program Review for his work on metal hydrides.
- G. Sandrock, J. Reilly, J. Graetz, J. Wegrzyn, "Activated Aluminum Hydride Hydrogen Storage Compositions and Uses Thereof" U.S. Patent Application Serial No. 11-192,292.

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1. Graetz J. and J. J. Reilly, "Thermodynamics of the α , β and γ Polymorphs of AlH_3 ," *J. Alloys Comp.*, (2006).
2. Graetz J., J. Reilly, G. Sandrock, J. Johnson, W.-M. Zhou, and J. Wegrzyn, "Aluminum Hydride as a Hydrogen Storage Compound", *TMS Proceedings* (2006).
3. Graetz J. and J. J. Reilly, "Solid State NMR Studies of the Aluminum Hydride Phases", *MRS Spring Meeting* 2006.
4. Graetz J. and J. J. Reilly, "Decomposition Kinetics and Thermodynamics of the α , β and γ Polymorphs of Aluminum Hydride", *MRS Spring Meeting* 2006.
5. D. Chandra, J. . Reilly and R. Chellappa "Metal Hydrides for Vehicular Applications: The State of the Art" JOM, pp26-32, Feb. 2006.

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