DIRECT HYDROGENATION OF ALUMINUM AT LOW PRESSURE

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Introduction

Aluminum hydride (AlH_3) is a promising hydrogen source for low-temperature fuel cells. The material has a volumetric hydrogen capacity (148 g/L) greater than twice that of liquid hydrogen and a gravimetric hydrogen capacity exceeding 10 wt.%. AlH_3 forms a number of different crystallographic phases,[1] all of which are thermodynamically unstable under ambient conditions. The decomposition of α-AlH_3 is endothermic with only a small amount of heat (7 kJ/mol H_2)[2] required to release the hydrogen. Aluminum hydride also exhibits rapid hydrogen evolution rates at low temperature (100 – 150 °C).[3] Recent kinetic studies demonstrate that 100 kg of α-AlH_3 will meet the DOE fuel flow target of 1.0 g H_2/s (50 kW fuel cell) at a temperature of 115 °C.[3,4]

One of the key challenges with utilizing aluminum hydride as a hydrogen storage material is the difficulty in regenerating the hydride from the spent Al. Although metastable under ambient conditions, AlH_3 can be prepared through a costly ethereal reaction of lithium alanate with aluminum chloride. AlH_3 can also be formed directly from the elements (Al and H_2) at a pressure of 28 kbar (300 °C).[5,6] An alternative direct approach involves a reaction of the alane with a second species to form a more stable alane adduct. One example is triethylenediamine–alane, which forms under a hydrogen pressure of 340 bar.[7] In this paper we demonstrate that amine alanes can be prepared at much lower pressures (<30 bar) using an activated form aluminum powder. This versatile hydrogenation method may be used to form new alane-based compounds with more favorable hydrogen storage properties.

Experimental

Materials. For each hydrogenation reaction 15.4 g of triethylenediamine (TEDA) was dissolved in 90 mL of anhydrous tetrahydrofuran (THF). Two batches of fine crystalline Al powder were prepared using a similar procedure. One batch of material was kept in the "neat" state and a second was activated. The activation processes are still under development and will be discussed in more detail in a future publication. In each hydrogenation experiment approximately 1.5 g of Al powder was added to the THF+TEDA solution in a stirred high-pressure reactor.

Stirred Reactor. Hydrogenation reactions were performed in a 300 mL stainless steel stirred reactor (Parr Instruments). The reactor was loaded with the reaction precursors in an Ar glove box. The sealed reactor was attached to a high-pressure gas manifold and purged with H_2 to remove the blanket of inert gas (Ar). Hydrogen gas was added to the reactor at pressures up to 115 bar and the solution was stirred at ~500 rpm at room temperature. Type K thermocouples were used to measure the internal and external temperatures and the gas pressure was monitored with a Dynisco pressure transducer.

Characterization Methods. After the reaction was complete the products were removed in the glove box and the solids were separated by filtration. Powder x-ray diffraction (XRD) was performed on the solid material before and after hydrogenation using a Philips x-ray diffractometer with Cu Kα radiation. Fourier Transform Infrared (FTIR) spectra were acquired on a PerkinElmer Spectrum One Spectrometer. Differential scanning calorimetry (DSC) measurements were performed using a Mettler-Toledo DSC822^e with a temperature ramp of 10 C/min.

Results and Discussion

Hydrogenation of a metal occurs when the fugacity of H_2 gas is greater than the equilibrium fugacity, f_{eq}. The entropy (ΔS) and enthalpy (ΔH) of hydrogenation are related to f_{eq} in the following way:

$$RT\ln(f_{eq}) = 2/x(\Delta H - T\Delta S), \qquad (1)$$

where x is the molar ratio of hydrogen to metal. Reducing the entropy difference upon hydrogenation and increasing the magnitude of the formation enthalpy can thus reduce f_{eq}. In a typical hydrogenation reaction, where a crystalline hydride is formed from a crystalline metal and H_2 gas, ΔS is dominated by the entropy of H_2 gas (130.7 $Jmol^{-1}K^{-1}$). Therefore, ΔS is high for all crystalline metal hydrides and may be reduced by forming a hydride in solution. Similarly, the equilibrium fugacity may also be reduced through the ΔH term by introducing a second metal that forms a more stable hydride. However, increasing the magnitude of ΔH increases the heat required to release the H_2 and slows the decomposition kinetics, thereby reducing the metal's usefulness as a hydrogen fuel.

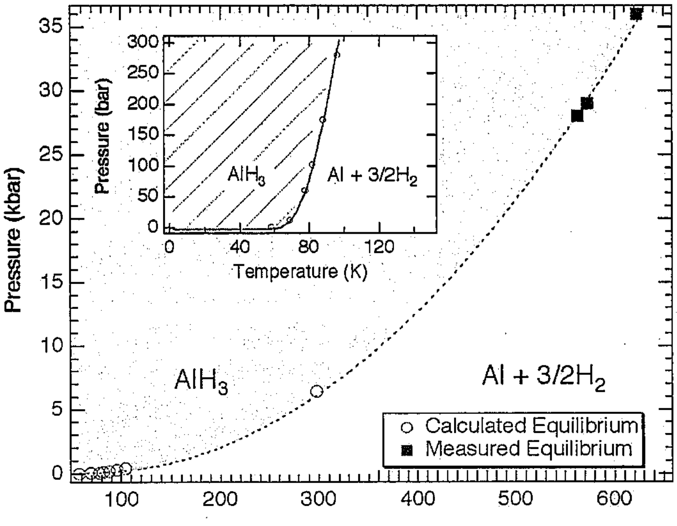

Figure 1. *P-T* phase diagram for α-AlH_3. Equilibria were determined from high pressure (≥300 °C)[5] and calorimetry (≤25 °C)[2] data.

Thermodynamic measurements of α-AlH_3 were used to calculate the equilibrium fugacities between α-AlH_3 and the elements (Al + 3/2H_2) at various temperatures.[2,8] At high pressure (>200 bar) the thermodynamic activity of H_2 gas is much greater than what is predicted from the ideal gas law. The predicted fugacities can be converted to pressure using the Beattie-Bridgeman state equation or from published tables.[9] These values, combined with high-pressure experimental results,[5] yield a pressure-temperature phase diagram for α-AlH_3, as shown in Figure 1. It is interesting to note that the equilibrium pressure at 300 K is 7 kbar and only around 100 bar at 77K, suggesting that the hydrogenation pressure can be reduced by simply lowering the sample temperature. However, previous high-pressure experiments using a H_2 pressure medium in a diamond anvil cell demonstrate that the minimum pressure and temperature required for hydrogenation is around 28 kbar at 573 K.[5,6] Although the hydrogenation condition is satisfied at lower temperatures, the hydrogen kinetics are too sluggish to fully form the hydride phase. The hydrogenation of aluminum metal is therefore limited by both the reaction thermodynamics and the hydrogen kinetics. This suggests that one method of reducing the hydrogenation pressure may be to simply enhance the low temperature kinetics, for example, by utilizing a nanocrystalline material.

An alternative approach to reducing the pressure required to hydrogenate Al involves introducing a second species to form a more stable compound. In 1964 E.C. Ashby demonstrated the direct synthesis of an amine alane using activated aluminum powder, TEDA in THF at a hydrogenation pressure of 340 bar:

$$Al + TEDA + 3/2H_2 \rightarrow TEDA{\cdot}AlH_3. \qquad (2)$$

Aluminum metal does not react with H_2 gas directly unless the reactivity of the powder is enhanced through some activation process. Although a number of procedures exist to activate Al, one example is the Ziegler procedure, where Al powder is treated with H_2 gas (135 bar) and triethylaluminum at a temperature of 140 °C.[10]

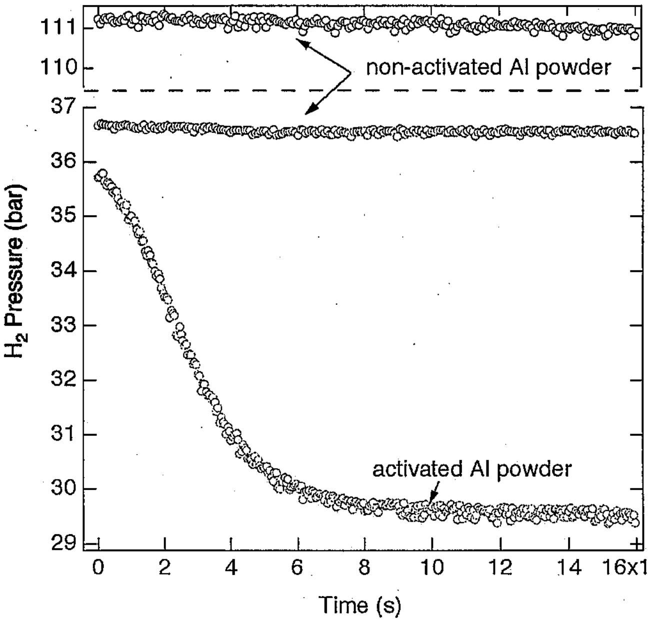

Figure 2. Hydrogenation of Al powder and activated Al powder in a solution of THF with TEDA.

We demonstrate that $TEDA{\cdot}AlH_3$ can be prepared directly at much lower pressures (<35 bar) than reported by Ashby using a different form of activated aluminum powder. Figure 1 shows the decrease in H_2 pressure within the reactor that occurs during hydrogenation of the activated Al metal. These results also demonstrate that there is no apparent reaction with the non-activated material even at a much higher pressure of 111 bar.

During hydrogenation a white/gray solid of $TEDA{\cdot}AlH_3$ precipitates out of solution. The solid reaction products were analyzed using powder x-ray diffraction and the liquids were characterized using FTIR. Preliminary FTIR results show no evidence of alane in solution. Figure 3 shows the diffraction patterns from the precursors (activated Al and TEDA), the product $TEDA{\cdot}AlH_3$ and a standard of $TEDA{\cdot}AlH_3$. The $TEDA{\cdot}AlH_3$ standard was prepared through an indirect organometallic reaction in THF at room temperature:

$$TEDA + AlH_3 \rightarrow TEDA{\cdot}AlH_3. \qquad (3)$$

The powder diffraction pattern from the solid reaction product, shown in Figure 3, is nearly identical to the $TEDA{\cdot}AlH_3$ standard and shows no trace of the original Al or TEDA. This confirms that the hydrogenation reaction (2) went to completion. Similar experiments performed with dodecane (rather than THF) showed similar results, demonstrating the reaction works with both polar and non-polar solvents. Although these are preliminary results, there are likely many other amine compounds (e.g. tetramethylethylenediamine) that will react with activated Al at low pressure to form an amine alane.

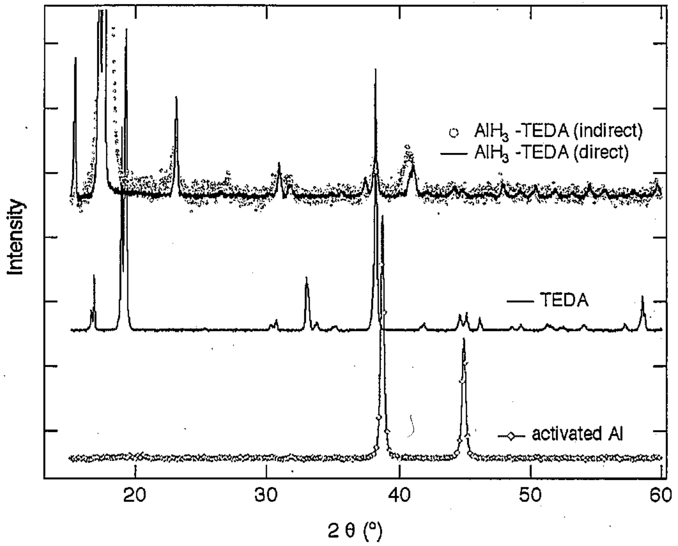

Figure 3. Powder x-ray diffraction of reactants (activated Al and TEDA) and product after hydrogenation ($TEDA{\cdot}AlH_3$). Also shown is a standard of $TEDA{\cdot}AlH_3$ prepared by an indirect method.

Acknowledgment

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