Accomplishments

- Determined the structural configurations, thermodynamics and kinetics of the various phases of aluminum hydride.
- Demonstrated that the decomposition of $\alpha$-aluminum hydride at temperatures 100 to 115°C meets DOE's hydrogen fuel flow targets.
- Identified the importance of titanium as a catalyst in forming various alane-amine complexes starting with aluminum powder, hydrogen and amine.
- Demonstrated the reversible uptake and release of hydrogen under moderate conditions in an alane-amine system.

Introduction

The chemistry behind hydrogen storage is essentially the chemistry of the formation and decomposition of different hydrides through reversible reactions. $\text{AlH}_3$ is a binary hydride that has been known for more than 60 years. It is a very attractive medium for on-board automotive hydrogen storage, since it contains 10.1 wt% hydrogen with a hydrogen density of 0.148 g/ml. Brower [1] prepared solvated $\text{AlH}_3$ by reacting aluminum chloride with lithium alanate in diethyl-ether. The ether was removed by vacuum distillation and heat treatment to recover the non-solvated forms of $\text{AlH}_3$. The existence of at least seven non-solvated phases was noted, with $\alpha$-$\text{AlH}_3$ being the most stable phase. The decomposition of crystalline $\alpha$-$\text{AlH}_3$ occurs in a single step:

$$\alpha-\text{AlH}_3 \rightarrow \text{Al} + 3/2\text{H}_2$$

Approach

The above decomposition reaction occurs readily at near-ambient conditions; the reverse reaction does not, however. The heat of formation, $\Delta H$, was reported by Greatz and Reilly [2] to be -11.4 kJ/mol $\text{AlH}_3$ and 46.6 kJ/mol $\text{AlH}_3$ for $\Delta G_{298}$. These results confirmed the earlier results of Sienke et al. [3]. The value of $\Delta G_{298}$ yields a room temperature equilibrium hydrogen fugacity of $5 \times 10^5$ bar, which is equivalent to a hydrogen pressure of approximately 7 kbar. In view of these data, the direct regeneration of $\text{AlH}_3$ from spent Al with gaseous $\text{H}_2$ is deemed impractical. This poses a major problem for the use of $\text{AlH}_3$ as a hydrogen fuel source since it cannot be easily regenerated.

In view of the above, we approached the regeneration problem from a different direction. Wiberg and Amberger [4] have pointed out that alane and borane form the bases of a rich organo-metallic chemistry and both will react with a variety of organic compounds. In 1964 E.C. Ashby [5] reported the direct synthesis of the $\text{AlH}_3$ adduct of triethylenediamine (TEDA) using aluminum powder and TEDA in tetrahydrofuran (THF) at a hydrogen pressure of 345 atm. We have also developed a direct synthesis of $\text{AlH}_3$: TEDA which takes place at room temperature, but at a much lower pressure; and more importantly have shown that the reaction is reversible. The key feature which enables the reaction to proceed as written below is the incorporation of a titanium catalyst in Al. The reaction may be written as follows:

$$\text{Al}_{(\text{rl})} + \text{TEDA} + 3/2\text{H}_2 \leftrightarrow \text{Al}_{(\text{Ti})}\text{H}_3\text{-TEDA}$$

The reaction can take place in an inert solvent such as tetrahydrofuran (THF) or undecane ($\text{C}_{11}\text{H}_{24}$). The $\text{AlH}_3$ adduct is insoluble and precipitates from solution as the reaction proceeds. The system can be recycled as desired.

Results

A series of Equilibrium Pressure – Composition Isotherms have been generated for the $\text{AlH}_3$:TEDA system. In Figure 1, we present 3 equilibrium absorption isotherms which were executed in a slurry of $\text{Al}_{(2/3\text{molTi})}$ powder in THF. The reactions were carried out in a 300 ml stainless steel stirred reactor (Parr Instruments) rated for 200 atm maximum operating pressure. The pressure axis in Figure 1 refers to the equilibrium partial pressure.
of hydrogen in atmospheres corrected for the vapor pressure of the liquid phase (THF + dissolved TEDA) and for H₂ solubility in the liquid phase.

A complete cycle of an equilibrium absorption–desorption isotherm was also determined using normal undecane (C₁₁H₂₄) as the solvent, as shown in Figure 2. The advantage of n-undecane is the low solvent vapor pressure; the disadvantage is that TEDA is not completely soluble. Nevertheless the reactions proceeded without difficulty but at a slower rate than in THF. The isotherms were generated at 88°C, at which point the vapor pressure of the solvent is ~0.025 atm and can be neglected. The preparation of the AlH₃ adduct and its subsequent decomposition demonstrates unequivocally that the reaction is reversible. The solubility of dissolved H₂ was determined using Henry’s constant for undecane.

A van’t Hoff plot vs. reciprocal temperature is shown in Figure 3. In some cases the isotherms are sloping, so all the points in the plot corresponded to H/Al ≈ 0.75. From these data, the thermodynamic properties for the formation of the amine-alane were determined via the van’t Hoff equation,

\[ \ln P_{\text{eq}} = \frac{\Delta H_f}{RT} - \frac{\Delta S_f}{R} \]

where \( \Delta H_f \) is proportional to the slope and \( \Delta S_f \) is calculated from the intercept. Here \( \Delta H_f = -39.5 \pm/ -4.1 \text{ kJ/mol H}_2 \) and \( \Delta S_f = -117 \pm/ -11 \text{ J/mol H}_2 \cdot K \). Thus \( \Delta G_{298K} = -4.63 \text{ kJ/mol H}_2 \). Note that for \( \alpha \)-AlH₃ \( \Delta G_{298K} = 32.3 \text{ kJ/mol H}_2 \). From theoretical calculations carried out with S. Chaudhari (Applied Sciences Laboratory and Institute for Shock Physics, Washington State University), we find that the AlH₃-TEDA bond (i.e. the Al-N bond) has a binding energy of 99 kJ/mol Al. This value is not same as the \( \Delta H \) of the reaction; it is rather an estimate of the barrier for breaking the AlH₃-TEDA bond. Nevertheless it does provide a quantitative rationale for the stability of the amine-alane.

While there are number of references in the literature describing the reaction between AlH₃ and amines to form alane adducts, we are not aware of any which reversibly absorb hydrogen. It is also very likely that Ti doped Al particles in a liquid suspension will reversibly react, in the presence of hydrogen gas, with a number of amines and perhaps other organic compounds to form AlH₃ adducts.
Conclusions and Future Directions

- AlH$_3$ is a promising hydrogen storage material for fuel cell vehicles.
- The technical barrier is regeneration of the spent aluminum back to its hydride form.
- Alane-amine adducts can be formed at moderate conditions from spent aluminum with a titanium catalyst.
- Future direction is in identifying alane-amine adducts that offer efficient pathways for separating and recovering alane from the amine adduct.

Special Recognitions & Awards/Patents Issued

1. Jason Graetz received the Ewald Wicke Award at the 2006 International Metal Hydride Symposium in Maui, HI. This award is given every two years to a young scientist for work in physical chemistry of metal hydrides.
2. James Reilly received an Outstanding Achievement Award, also at the 2006 International Metal Hydride Symposium in Maui, HI.

FY 2007 Publications/Presentations


References