



Aluminum Hydride Regeneration

Jason Graetz, J. Wegrzyn, J. Reilly, J. Johnson, Y.
Celebi and WM Zhou

Brookhaven National Laboratory



Project ID
#ST 39

Overview

Timeline

- Project start date: FY05
- Project end date: FY10
- 60 % complete

Budget

- Expected total project funding:
 - \$4.00M (DOE)
- Funding received in FY07
 - \$960K (DOE)
- Funding for FY08
 - \$1.125M (DOE)

Barriers

- MYPP Section 3.3.4.2.1 On-Board Storage Barriers
- A.** Weight & Volume
 - B.** Cost
 - C.** Efficiency
 - D.** Durability/Operability
 - E.** Charge/Discharge Rates
 - R.** Regeneration Processes

Partners and Collaborators

- Project D (aluminum hydride) Lead
 - UH-UNB, ORNL, SRNL, SNL
- Other collaborations: JPL, UIUC, ANL
- Chemical Hydride Center
- International Energy Agency (IEA)

Challenges and Objectives

Objective: *Develop a material that supports the 2010 DOE technical performance targets using Aluminum Hydride (AlH_3), by fully elucidating the nature of hydrogen desorption from AlH_3 and developing an efficient regeneration method.*

1. Develop new routes to prepare pure crystalline $\alpha\text{-AlH}_3$ from Al (spent fuel) with minimal energy cost
2. Assist the engineering design for an off-board system based on AlH_3

Challenge: AlH_3 thermodynamically unstable below 7 kbar (300K)

1. In an AlH_3 system H_2 evolution controlled by T (rather than P) so the ability to tune decomposition kinetics will be critical - Various routes exist to adjust kinetics (e.g. size, coatings and catalysts)
2. The key issue is regeneration (hydrogenation of Al metal), and multiple regeneration pathways are being investigated

Routes to AlH_3 Regeneration

MHCoE Project D Lead: Jim Wegrzyn, BNL

BNL (POC)

Liquid phase
- alane harvesting

SRNL

Electrochemical

U. Hawaii/UNB

Supercritical fluids

ORNL

Ionic liquids

SNL – calculations of
adduct stability

UIUC – studies of reaction
products and catalyst distribution

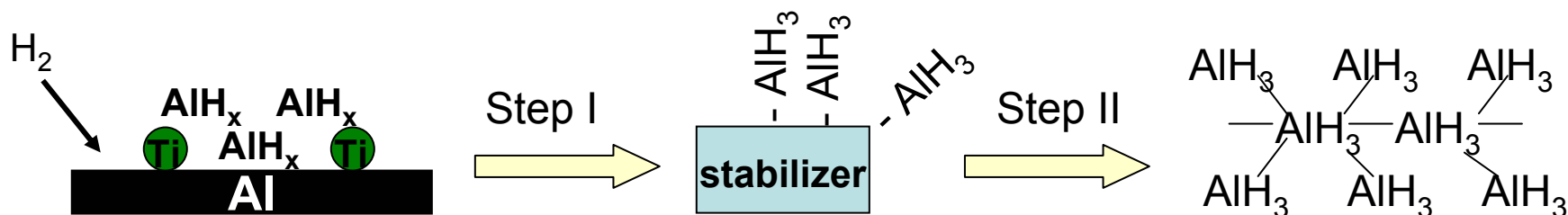
ANL- Cycle life analysis
(not MHCoE)

BNL Approach to AlH_3 Regeneration

Alane (AlH_3) harvesting

Step I: Form molecular AlH_3 by hydrogenating Ti-catalyzed Al and harvest/stabilize AlH_3 as a Lewis Acid/Base adduct

Step II: Remove stabilizing species and recover AlH_3



stabilizer \equiv amine (TEDA), alkali hydride (LiH), solvent (THF)

Methods and Materials

- Ti catalyzed Al (Al*) prepared by first making AlH₃ with TiCl₃ in ether and then decomposing the ether adduct

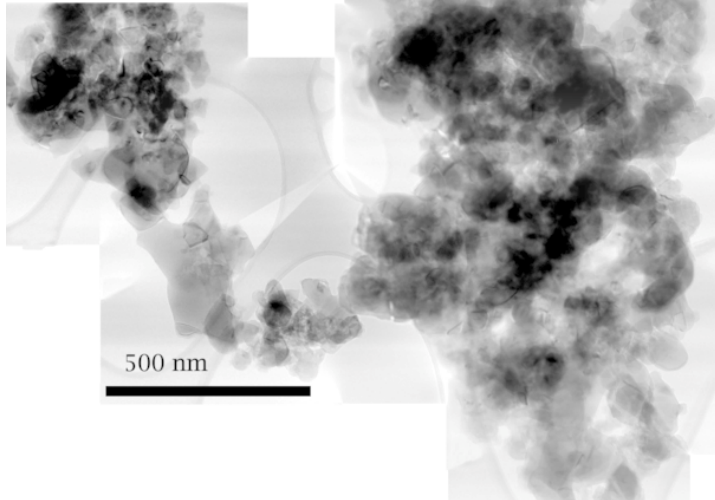


- Typical catalyst concentration was 2 mol % Ti
 - Recent results suggest reactions will work with much lower catalyst concentration
- Reactions performed in solvent medium: THF, Et₂O
 - Solvent acts as electron donor and helps stabilize AlH_x

Ti Uniformly Distributed in Al

TEM studies of Ti catalyzed Al at UIUC (Ian Robertson and Dennis Graham)

TEM - Ti catalyzed Al



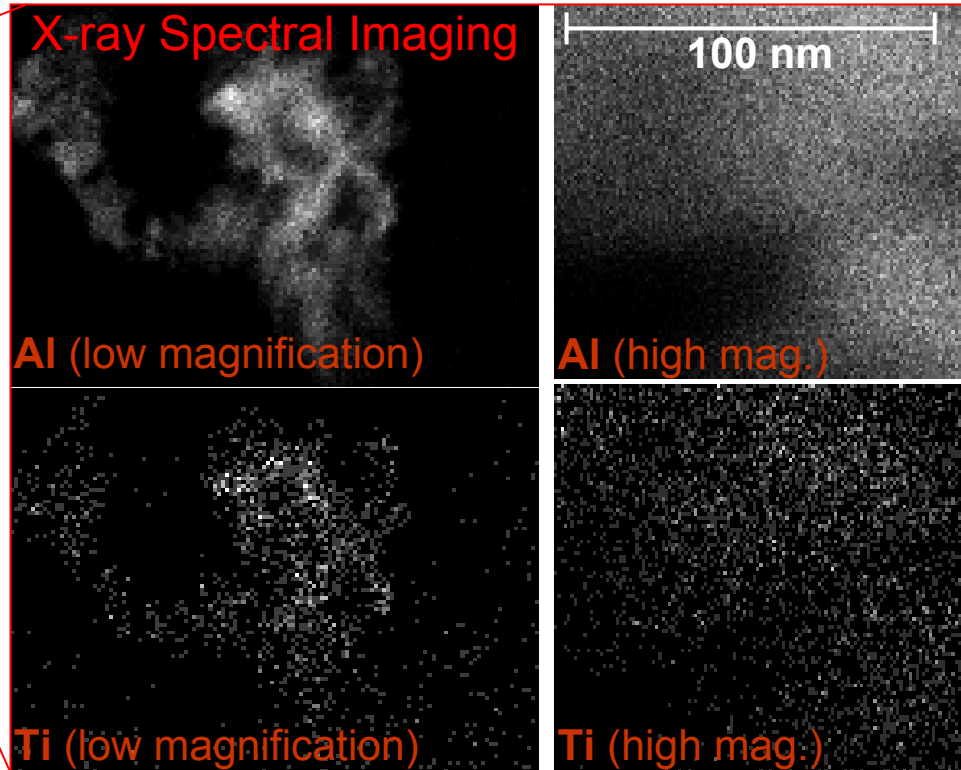
X-ray Spectral Imaging

Al (low magnification)

Ti (low magnification)

Al (high mag.)

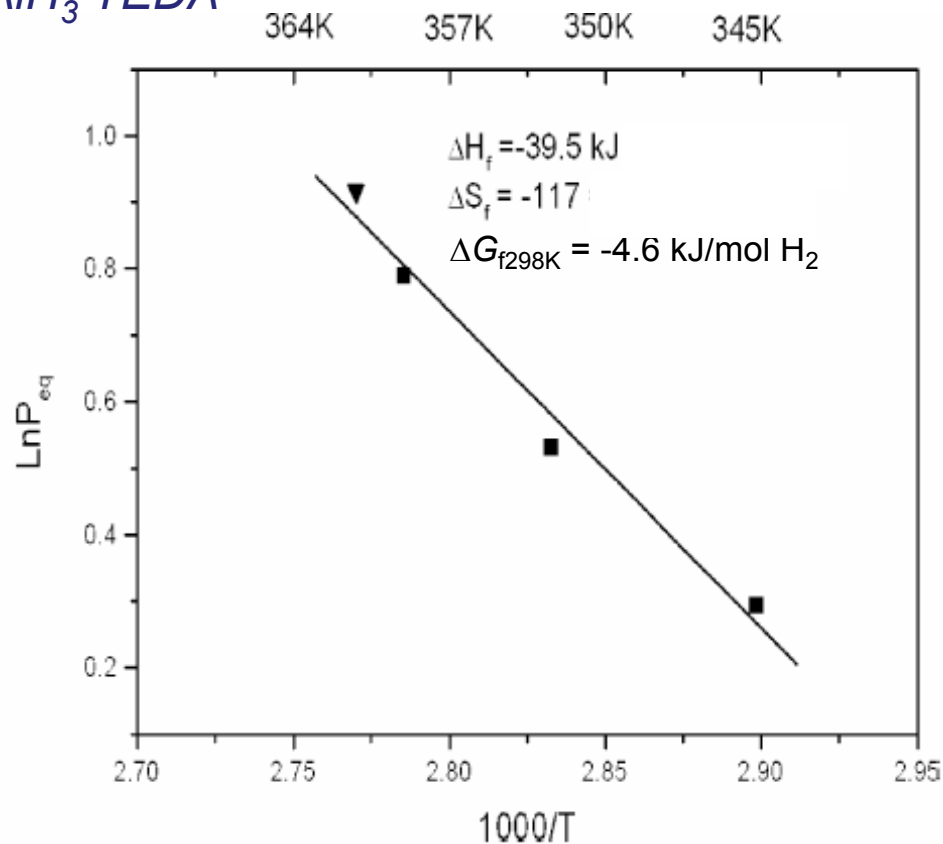
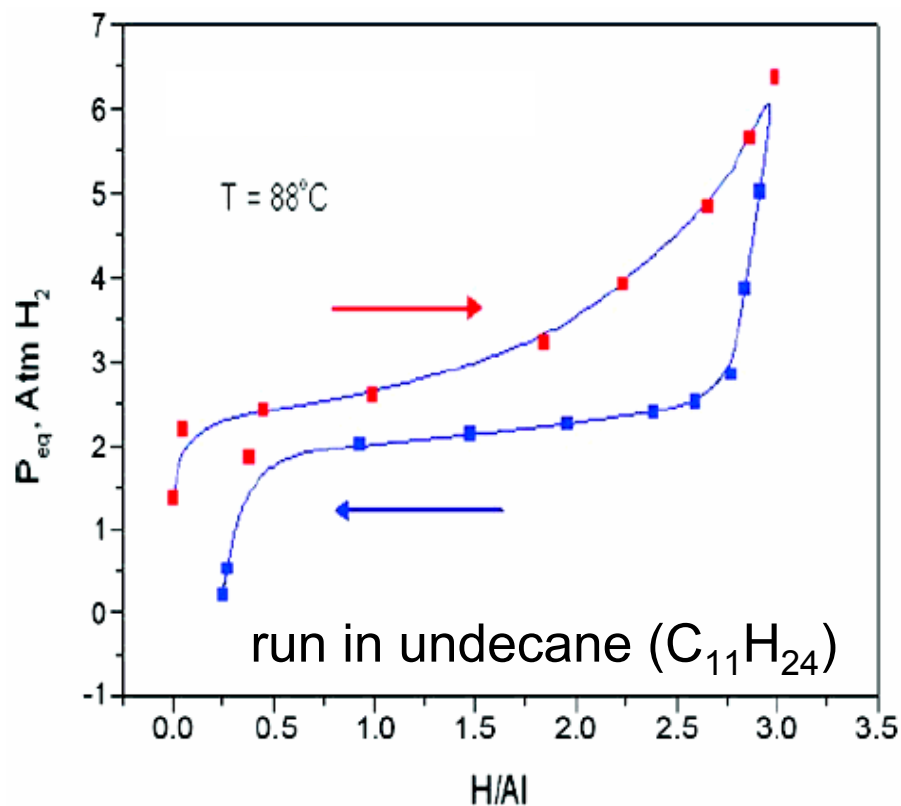
Ti (high mag.)



- Al crystals (average grain size 165 nm) show few defects
- Ti well-dispersed throughout Al matrix - no enhancement of Ti at particle edge suggests Ti not just on surface but distributed through the bulk

$AlH_3 \cdot TEDA$ Reversibly Cycles H_2

Proposed reaction: $Al + TEDA + 3/2H_2 \rightarrow AlH_3 \cdot TEDA$



- Hydrogenation reaction does **not** occur without Ti catalyst
- AlH_3 -TEDA is reversible in other solvents (THF, dodecane)
- Reversible capacity $\sim 100\%$ of theoretical (2.1 wt%)

Theory Guides Choice of Adduct

Accurate Al-N bond dissociation energies (BDE's) needed to guide optimal choice of adduct for AlH_3 regeneration ...

- Employ “Bond Additivity Correction” to provide accurate Al-N bond dissociation energies (BDE's)
- BAC values differ from DFT predictions (S. McGrady (UNB) shown in back-up slides) , but similar trends
- AlH_3 -TEDA exhibits strong Al-N Bond while AlH_3 - NEt_3 has a weak Al-N bond
- **Pyridine and pyrazine are promising amines with moderate Al-N energies**
- 1:2 complexes (e.g. (AlH_3) -2pyrazine) are significantly less stable
- Future efforts look at Al-O bond energies

Results from gas-phase calculations:

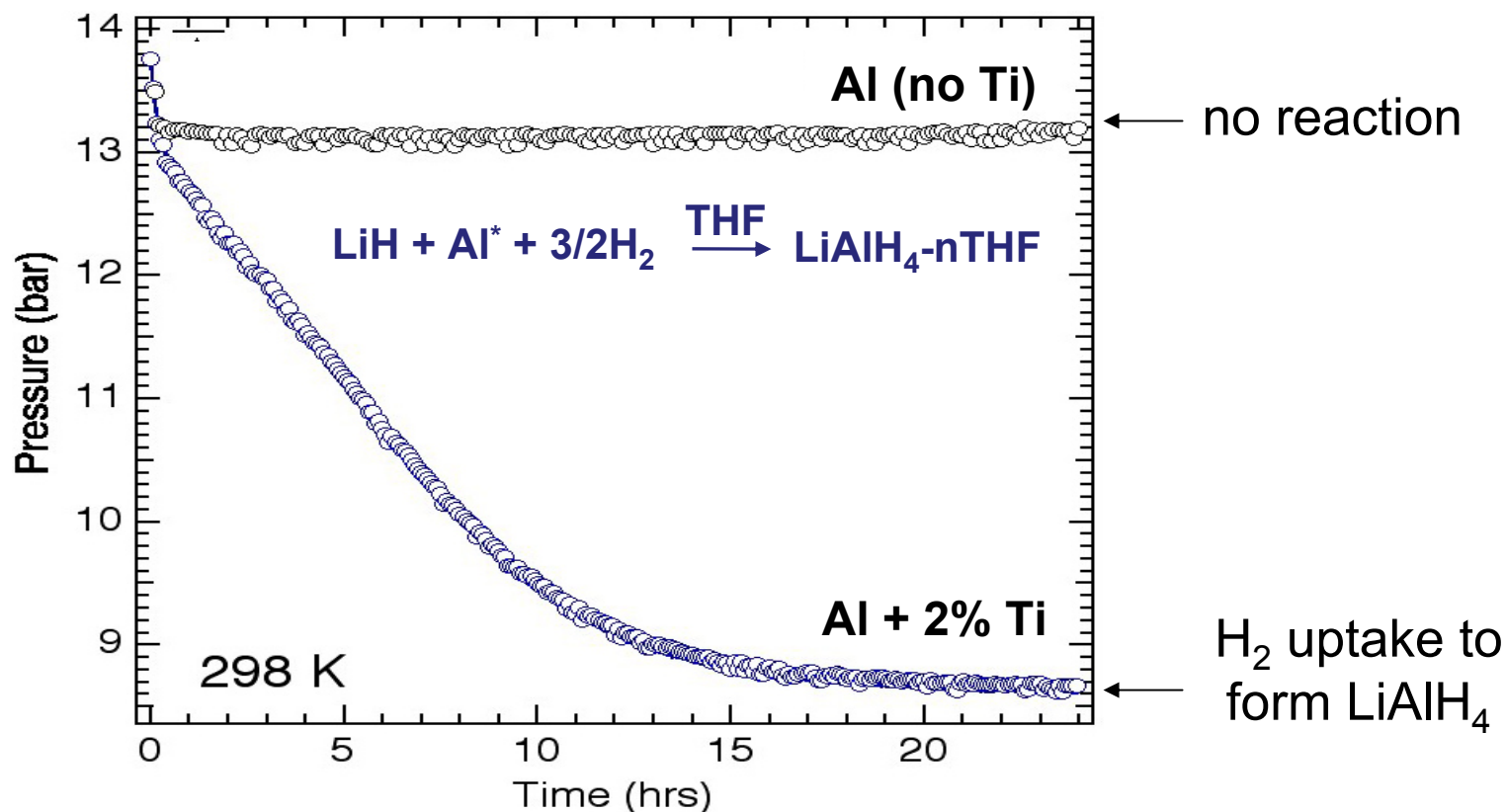
1:1 Complexes	Al-N BDE* (kJ/mole)
AlH_3 -- NH_3	142.7
AlH_3 -- NMe_3	147.6
AlH_3 -- NEt_3	118.6
AlH_3 --TEDA	156.3
AlH_3 --Quinuclidine	159.9
AlH_3 --pyridine	135.2
AlH_3 --pyrazine	125.3
AlH_3 --2TEDA	233.8
AlH_3 --2 NEt_3	158.7

BDE = Energy to dissociate to AlH_3 +ligands
BAC-MP2 M. Allendorf (Sandia)

Other compounds prepared by “alane harvesting”

Other alane compounds may be useful intermediates to forming AlH_3

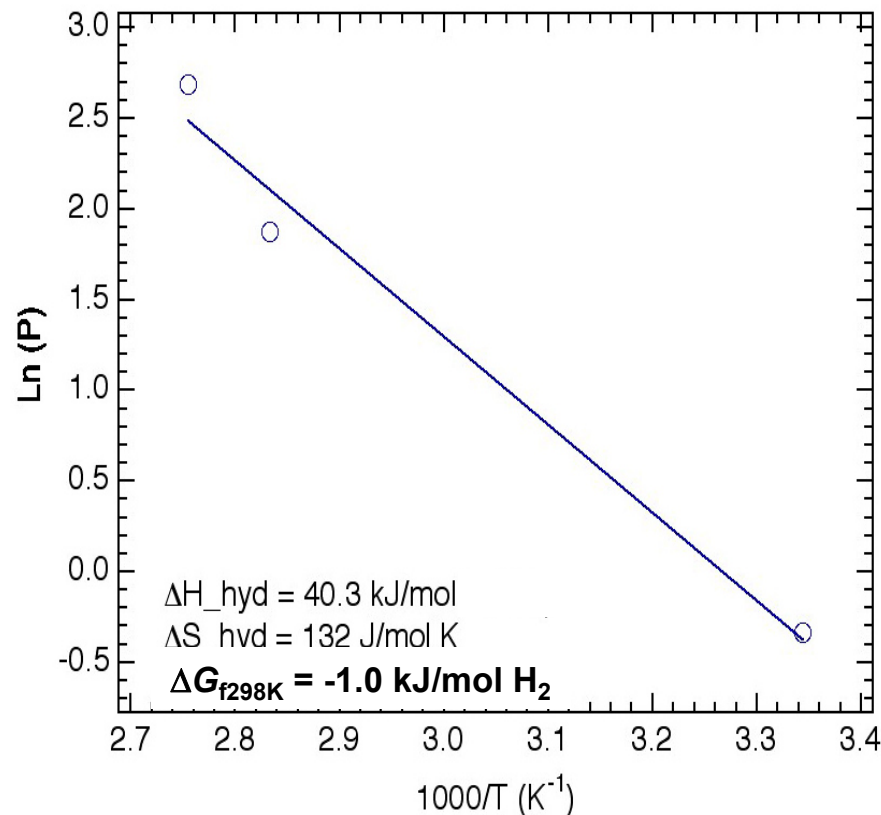
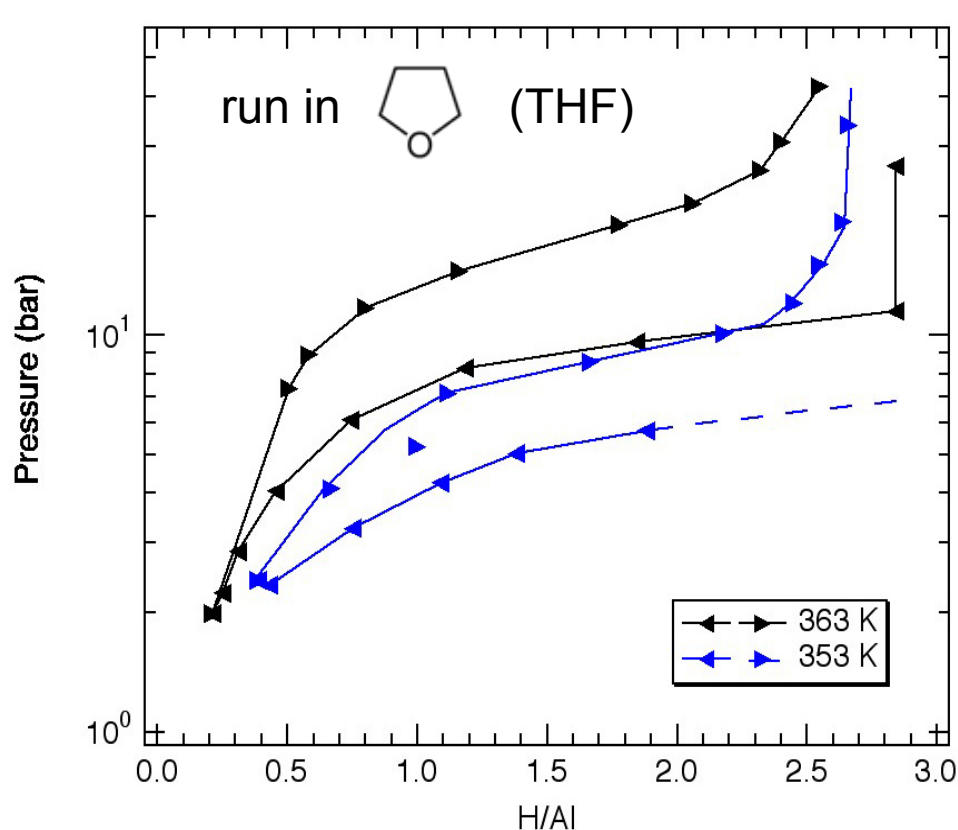
Can we make LiAlH_4 from Al^* , LiH (stabilizer) and H_2 in THF?



YES! Hydrogenation occurred at low pressure (<13 bar) and low temp (300K) - no hydrogenation without Ti

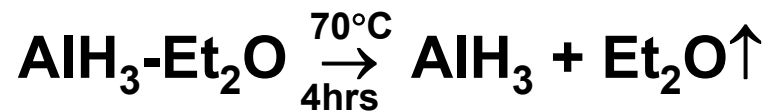
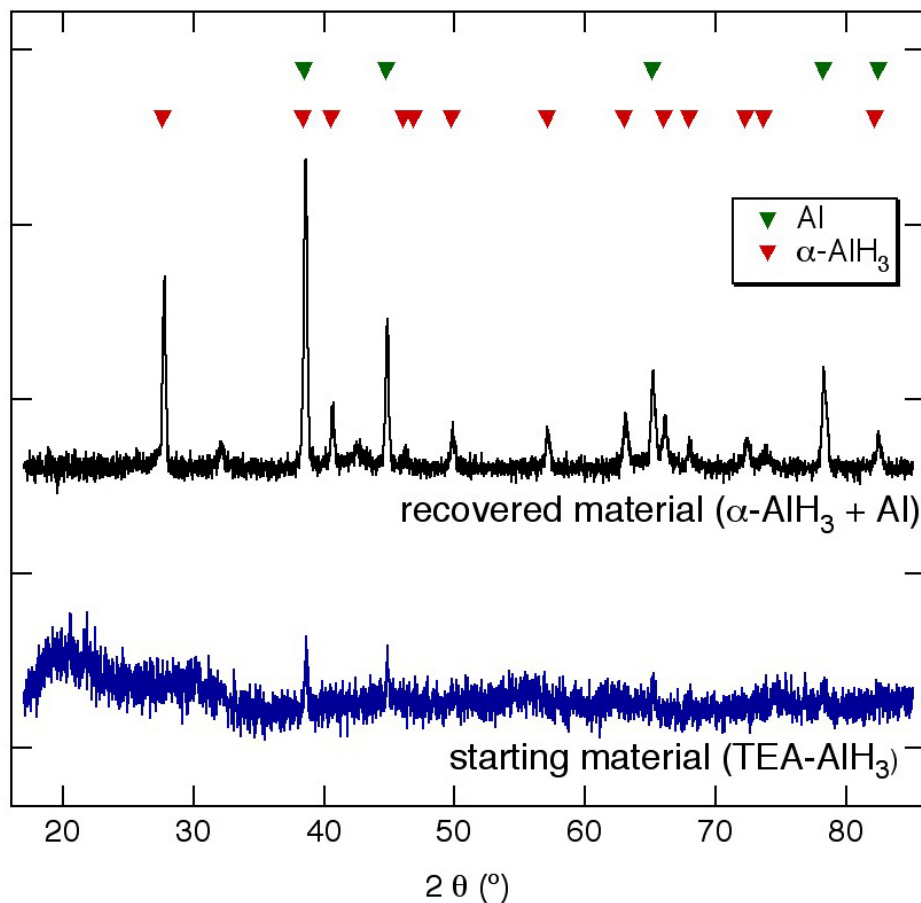
Reversible Lithium Alanate

LiAlH_4 is not normally reversible, yet....

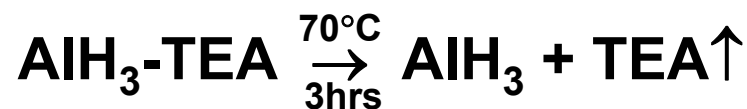


- Reaction is reversible (~90%) at moderate pressure and temperature
- If we can extract THF we have a simple regen. route for LiAlH_4
- We may be able to use LiAlH_4 as step to $\alpha\text{-AlH}_3$

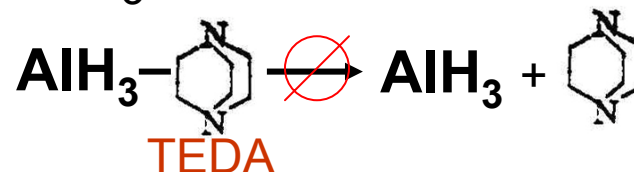
AlH₃ recovered from AlH₃·Et₂O by heating 70°C under vacuum



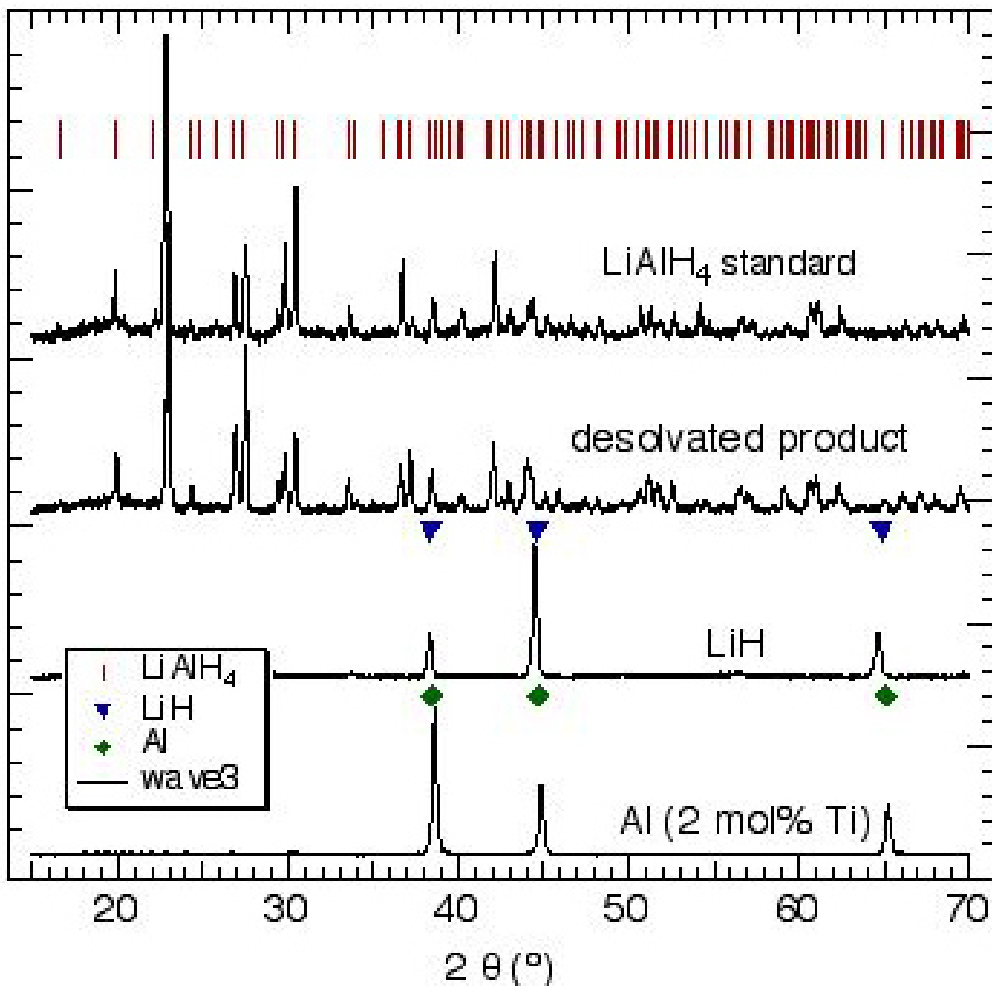
Similar method used to recover AlH₃ from alane-amine (AlH₃-TEA)



No success yet recovering AlH₃ from TEDA



XRD plot demonstrates AlH₃ can be recovered from alane-amines



Procedure: LiAlH₄·THF heated ~60°C under vacuum for ~4hrs

LiAlH₄ standard

LiAlH₄ + 2%Ti recovered

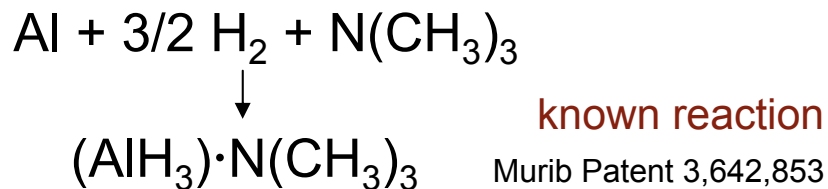
Reaction precursors (LiH + Al*)

- XRD confirms Ti-catalyzed LiAlH₄ recovered from LiAlH₄·THF

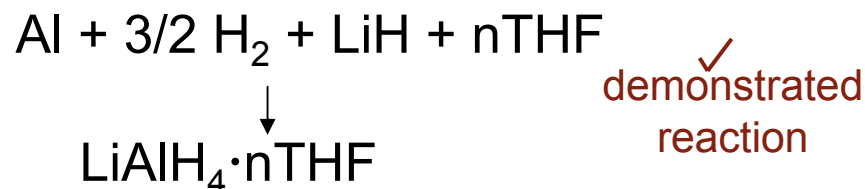
Multi-Step Pathways

Direct two-step approach is preferred, but a multi-step scheme may have lowest overall energy cost

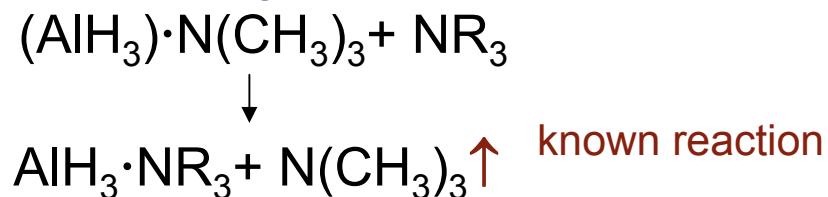
Direct formation of $\text{AlH}_3\text{-TMA}$:



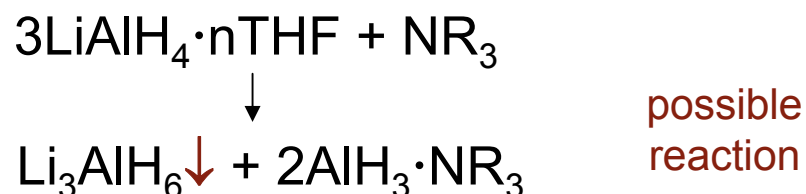
Direct formation of $\text{LiAlH}_4\text{-nTHF}$:



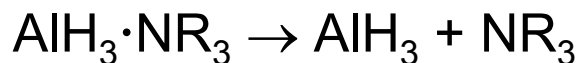
Amine exchange (transamination):



Exchange THF for tertiary amine:



Decomposition and recovery:



✓
demonstrated reaction

Note: Li_3AlH_6 may be decomposed to $\text{LiH} + \text{Al}$ or possibly regenerated directly to LiAlH_4

Overall reaction: $\text{Al} + 3/2\text{H}_2 \rightarrow \text{AlH}_3$

Summary of Accomplishments

Goal: Develop and demonstrate a storage system that meets DOE targets using aluminum hydride as hydrogen fuel source.

Four major accomplishments:

- (1) Developed a simple method to prepare Ti-catalyzed Al for Al hydrogenation reactions, Ti uniformity confirmed by TEM/EDS
- (2) Demonstrated reversible hydrogenation of spent Al* and TEDA to form AlH_3 -TEDA in solution at low P and T
- (3) Developed preliminary method based on TEA and Et_2O to separate stabilized alanes and recover α - AlH_3
- (4) Demonstrated reversible hydrogenation of spent Al* and LiH to form LiAlH_4 in solution at low P and T

FY08: Demonstration of complete regeneration cycle

Identify new pathways to α -AlH₃

- direct formation of alane adducts (pyridine, pyrazine, ethers, ...)
- recovering hydride from alane-adducts, determine energy penalty

Continue effort on two existing pathways:



Go/no-go on regeneration using organometallic approach

Down select (FY08) type(s) of alane adduct(s) for further study

FY09: Regenerate AlH₃ with E penalty ≤ 73 kJ/H₂ (30% of fuel energy)

Work with partners to determine mass balance & energy cost

Begin investigation of alane slurries and liquid carriers

Work with group(s) in Engineering CoE on alane system