Aluminum Hydride Regeneration

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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 α-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

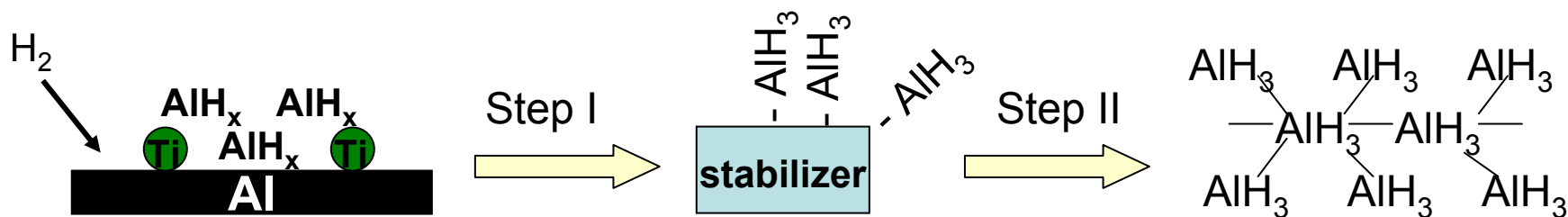**UIUC** – studies of reaction products and catalyst distribution

ANL- Cycle life analysis (not MHCoE)

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BNL Approach to AlH₃ Regeneration

Alane (AlH₃) harvesting

Step I: Form molecular AlH₃ by hydrogenating Ti-catalyzed Al and harvest/stabilize AlH₃ as a Lewis Acid/Base adduct

Step II: Remove stabilizing species and recover AlH₃

stabilizer ≡ amine (TEDA), alkali hydride (LiH), solvent (THF)

- Ti catalyzed Al (Al*) prepared by first making AlH_3 with $TiCl_3$ in ether and then decomposing the ether adduct

$$3LiAlH_4 + AlCl_3 + 0.08TiCl_3 \xrightarrow{Et_2O} 3.24LiCl\downarrow + 4AlH_3 \cdot Et_2O + 0.08Ti$$

$$4AlH_3 \cdot Et_2O + 0.08Ti \xrightarrow[2\ hrs]{100\,°C} 4Al + 0.08Ti$$

- Typical catalyst concentration was 2 mol % Ti
  - Recent results suggest reactions will work with much lower catalyst concentration

- Reactions performed in solvent medium: THF, Et_2O
  - Solvent acts as electron donor and helps stabilize AlH_x

Ti Uniformly Distributed in Al

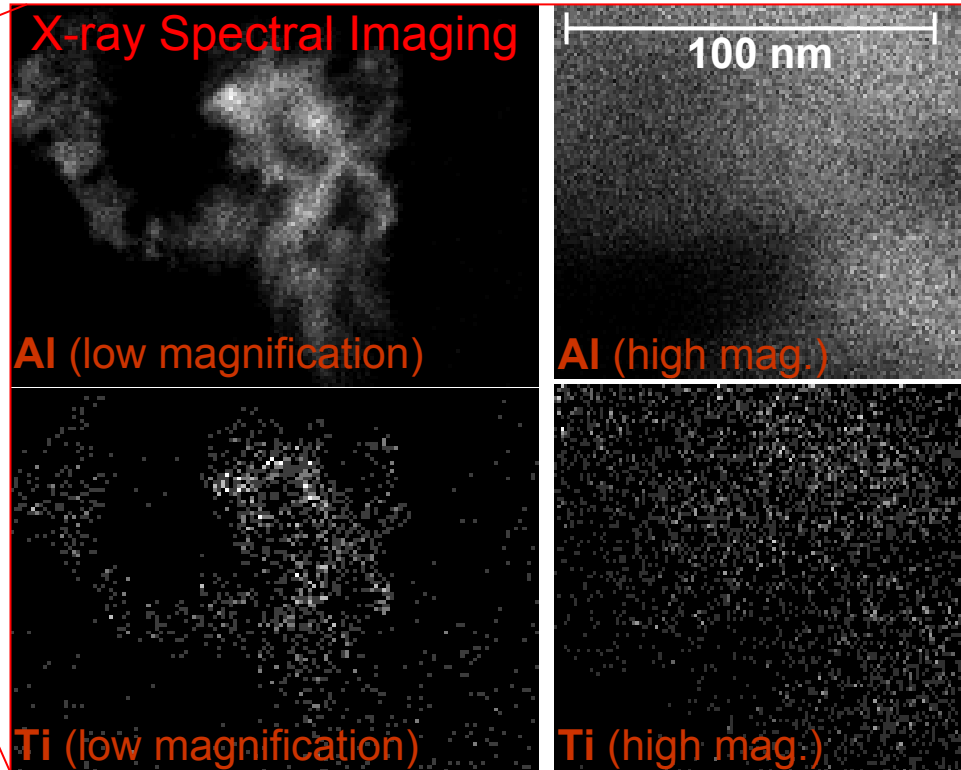TEM studies of Ti catalyzed Al at UIUC (Ian Robertson and Dennis Graham)

TEM - Ti catalyzed Al

500 nm
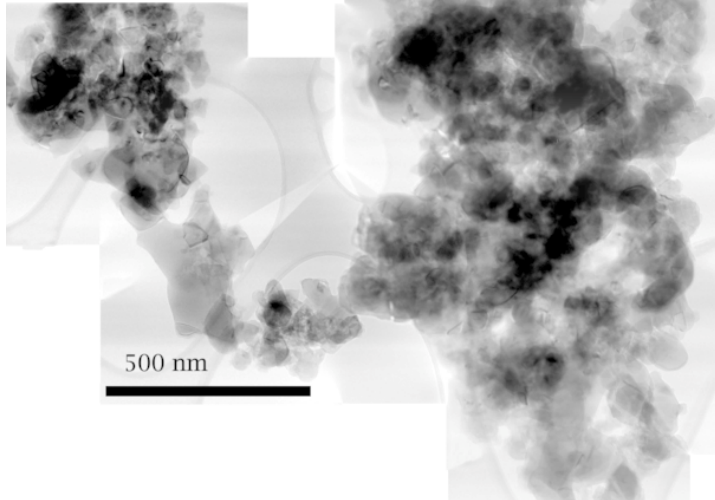
X-ray Spectral Imaging

100 nm

Al (low magnification)

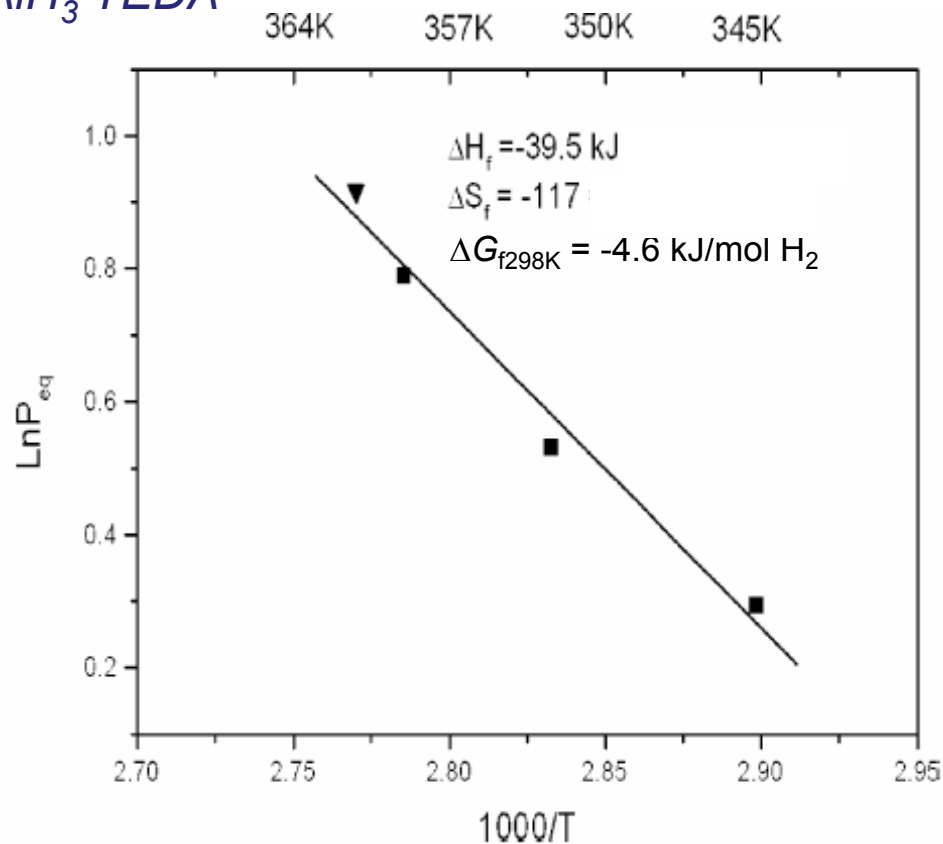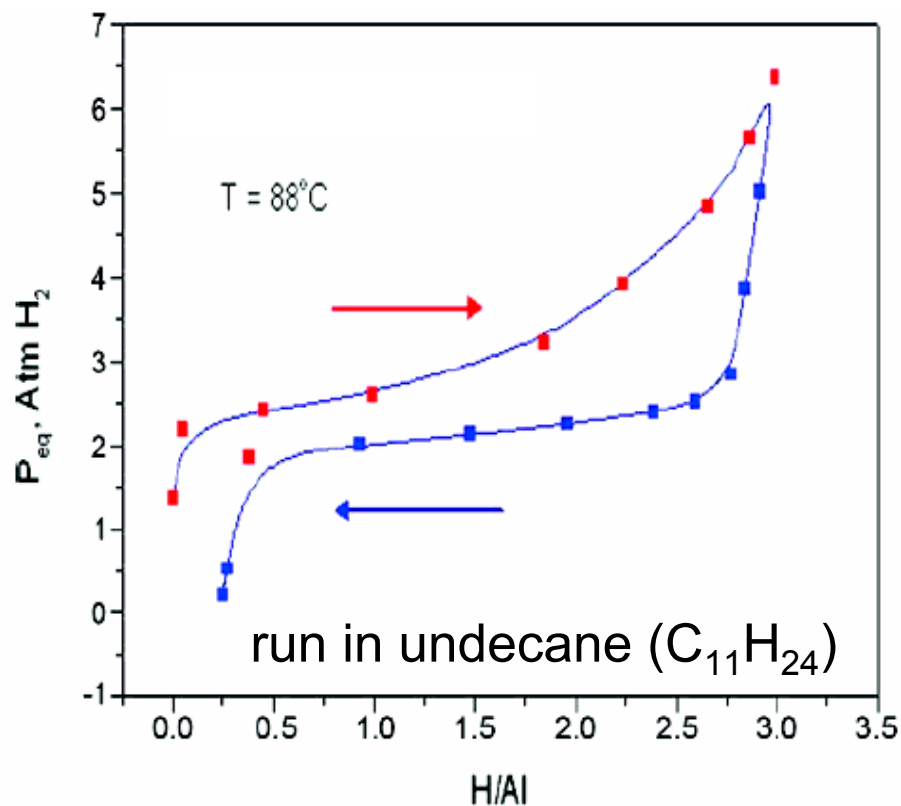Al (high mag.)

Ti (low magnification)

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

T = 88°C

run in undecane ($C_{11}H_{24}$)

$\Delta H_f = -39.5$ kJ
$\Delta S_f = -117$
$\Delta G_{f298K} = -4.6$ kJ/mol H_2

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

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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
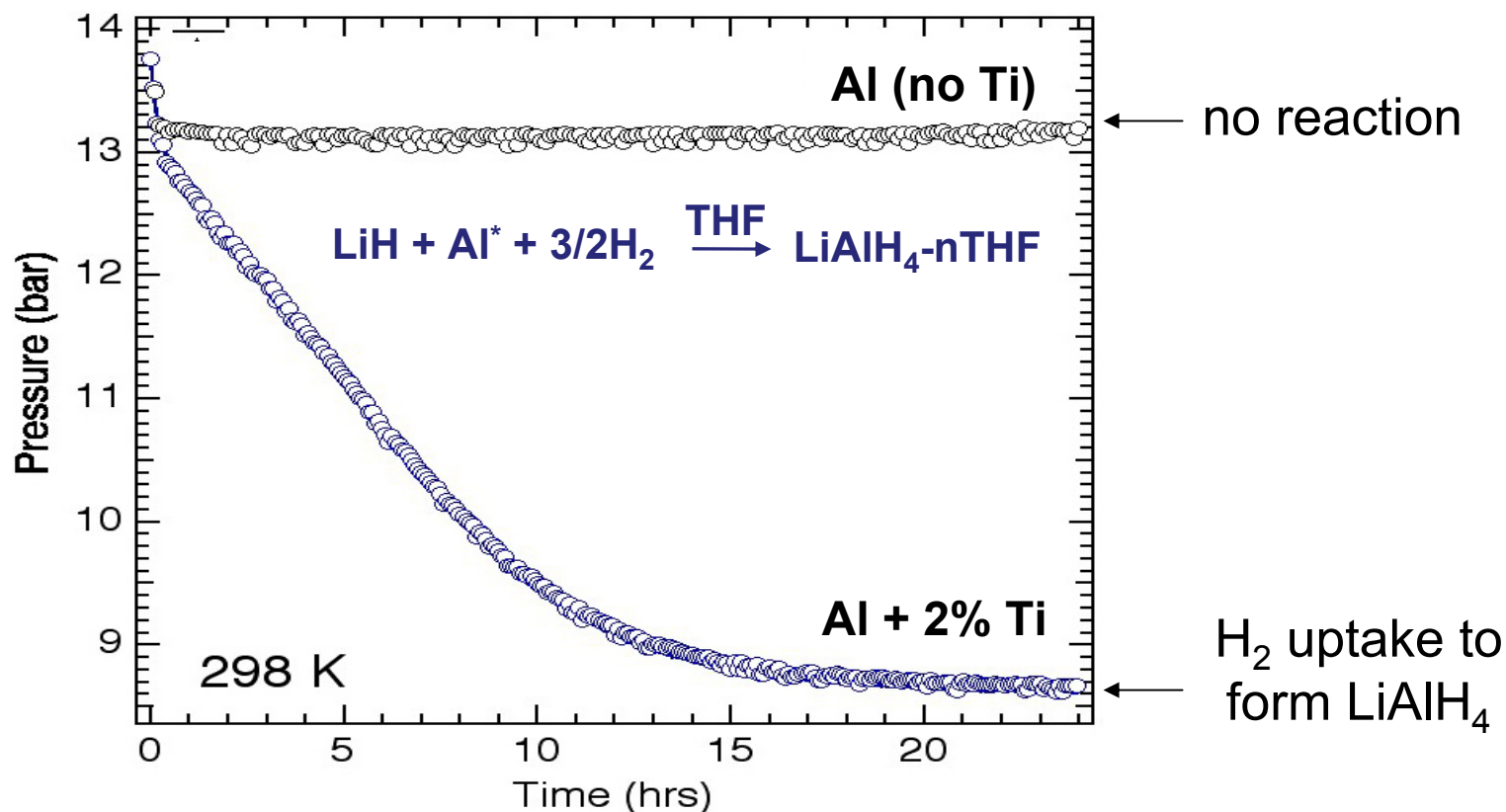
- Future efforts look at Al-O bond energies

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--$2NEt_3$	**158.7**

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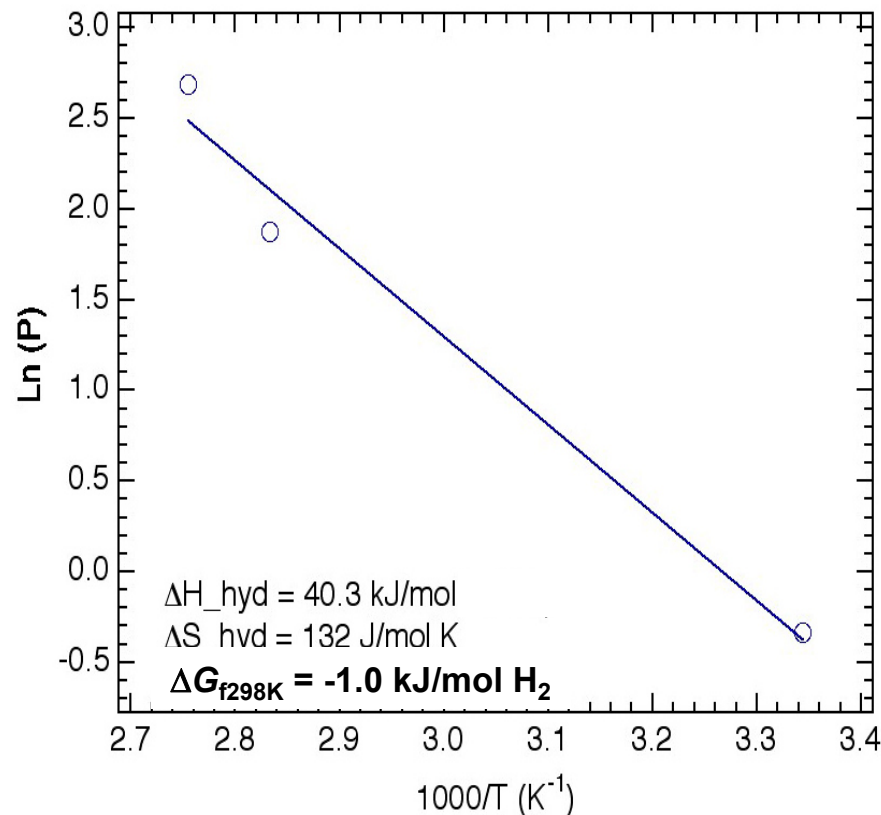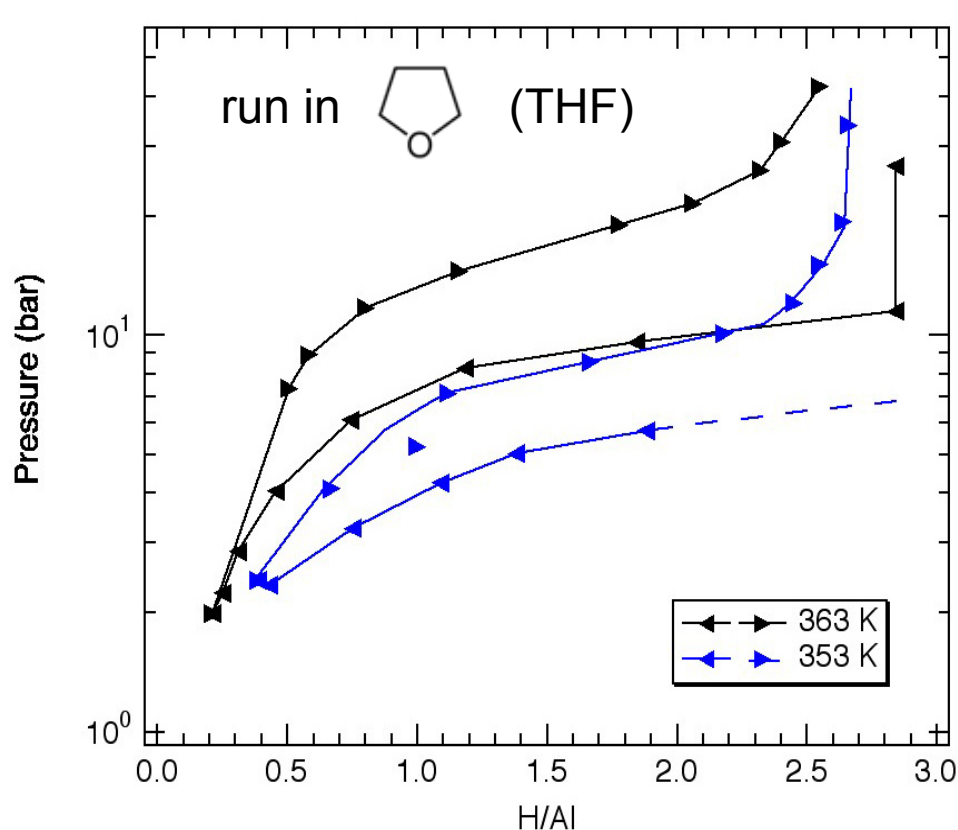**BAC-MP2** M. Allendorf (Sandia)

Sandia National Laboratories

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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?

$$LiH + Al^* + 3/2H_2 \xrightarrow{\text{THF}} LiAlH_4\text{-}nTHF$$

Al (no Ti) — no reaction

Al + 2% Ti — H_2 uptake to form $LiAlH_4$

298 K

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

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LiAlH$_4$ is not normally reversible, yet….

run in (THF)

Pressure (bar) vs H/Al

- 363 K
- 353 K

Ln (P) vs 1000/T (K^{-1})

$\Delta H\_hyd = 40.3$ kJ/mol
$\Delta S\_hyd = 132$ J/mol K
**ΔG_{f298K} = -1.0 kJ/mol H$_2$**

➢ Reaction is reversible (~90%) at moderate pressure and temperature
➢ If we can extract THF we have a simple regen. route for LiAlH$_4$
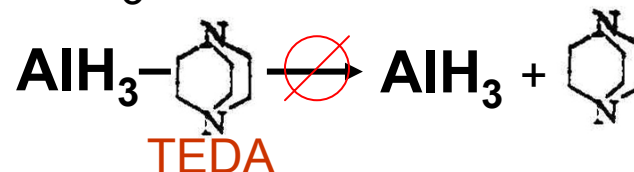➢ We may be able to use LiAlH$_4$ as step to α-AlH$_3$

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Recovering AlH₃ from Adduct

AlH_3 recovered from $AlH_3 \cdot Et_2O$ by heating 70°C under vacuum

recovered material (α-AlH₃ + Al)

starting material (TEA-AlH₃)

2 θ (°)

Legend: ▼ Al   ▼ α-AlH₃

$$AlH_3\text{-}Et_2O \xrightarrow[\text{4hrs}]{\text{70°C}} AlH_3 + Et_2O\uparrow$$
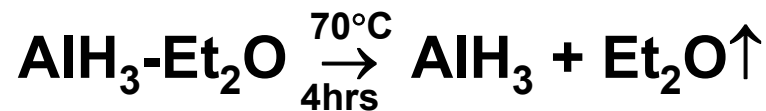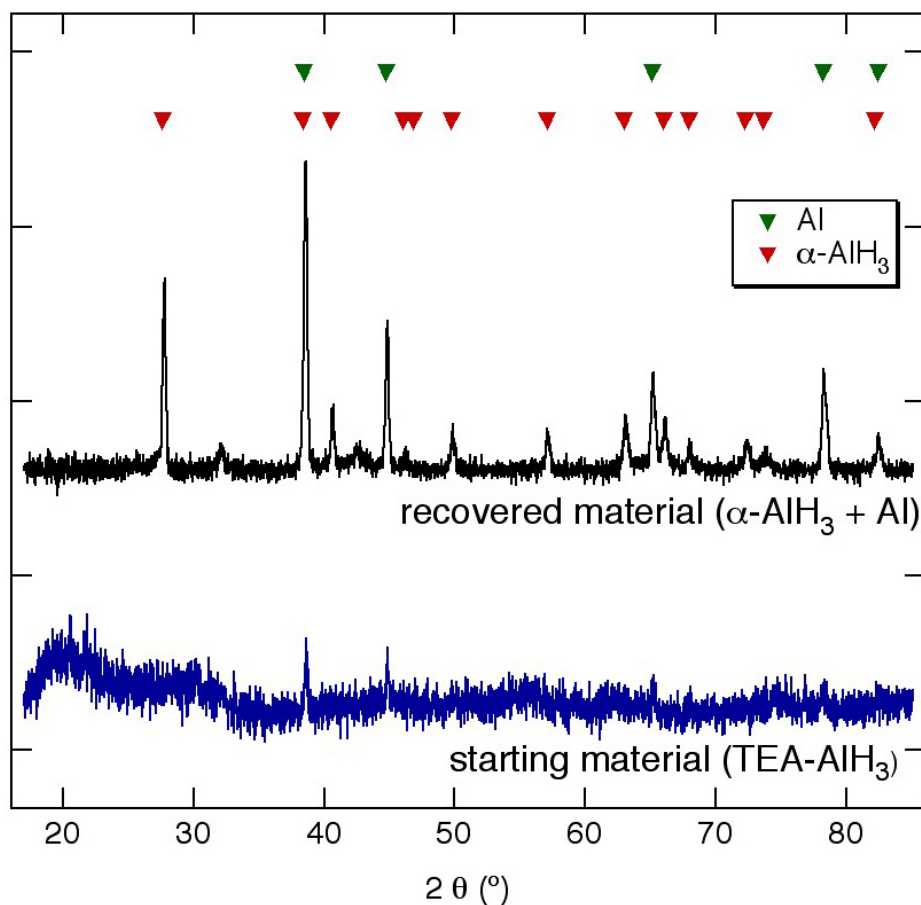
Similar method used to recover AlH_3 from alane-amine (AlH_3-TEA)

$$AlH_3\text{-}TEA \xrightarrow[\text{3hrs}]{\text{70°C}} AlH_3 + TEA\uparrow$$
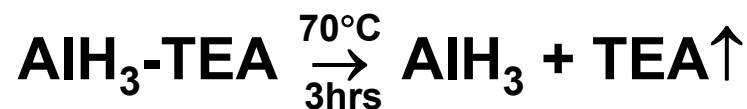
No success yet recovering AlH_3 from TEDA

$$AlH_3 - \text{(TEDA)} \not\rightarrow AlH_3 + \text{(structure)}$$

TEDA

XRD plot demonstrates AlH_3 can be recovered from alane-amines
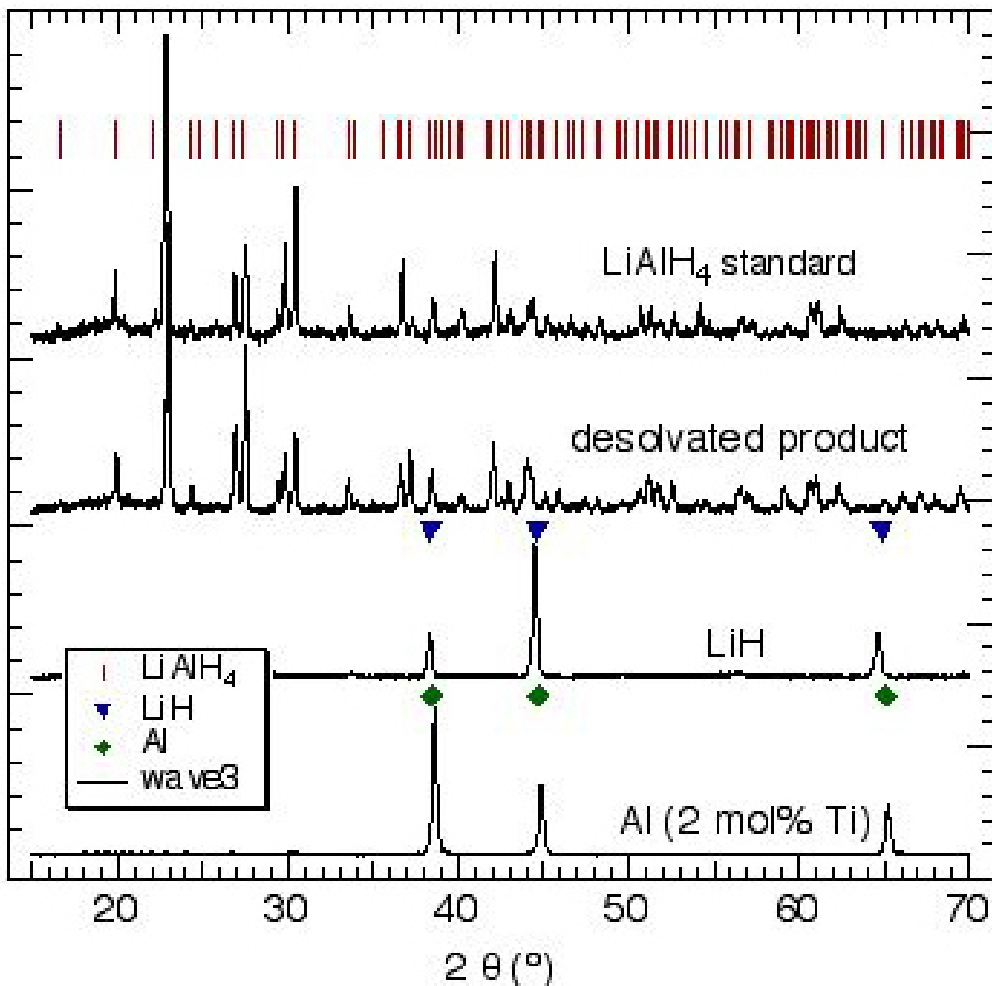
Procedure: LiAlH$_4 \cdot$THF heated ~60ºC under vacuum for ~4hrs
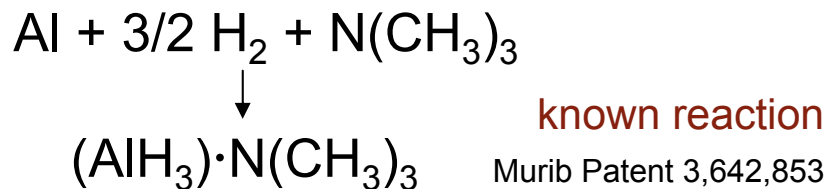
LiAlH$_4$ standard

LiAlH$_4$ +2%Ti recovered

Reaction precursors (LiH + Al*)

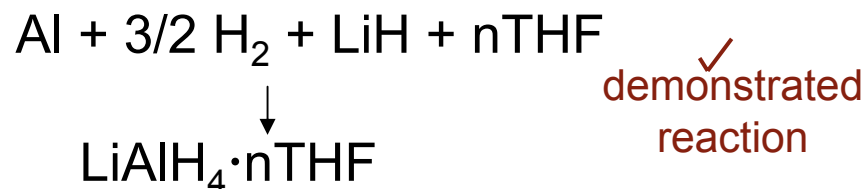- XRD confirms Ti-catalyzed LiAlH$_4$ recovered from LiAlH$_4 \cdot$THF

Multi-Step Pathways

Direct two-step approach is preferred, but a multi-step scheme may have lowest overall energy cost
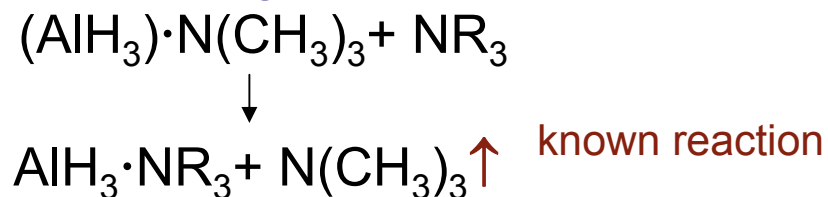
Direct formation of AlH_3-TMA:

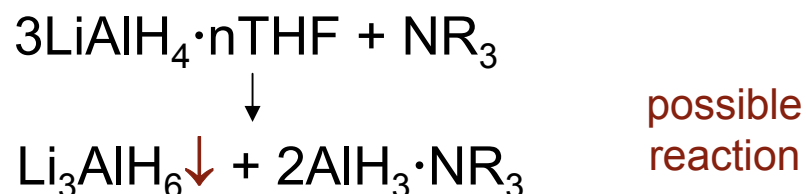$$Al + 3/2\ H_2 + N(CH_3)_3$$
$$\downarrow$$
$$(AlH_3) \cdot N(CH_3)_3$$

known reaction

Murib Patent 3,642,853

Direct formation of $LiAlH_4$-nTHF:

$$Al + 3/2\ H_2 + LiH + nTHF$$
$$\downarrow$$
$$LiAlH_4 \cdot nTHF$$

✓ demonstrated reaction

Amine exchange (transamination):

$$(AlH_3) \cdot N(CH_3)_3 + NR_3$$
$$\downarrow$$
$$AlH_3 \cdot NR_3 + N(CH_3)_3 \uparrow$$

known reaction

Exchange THF for tertiary amine:

$$3LiAlH_4 \cdot nTHF + NR_3$$
$$\downarrow$$
$$Li_3AlH_6 \downarrow + 2AlH_3 \cdot NR_3$$

possible reaction

Decomposition and recovery:

$$AlH_3 \cdot NR_3 \rightarrow AlH_3 + NR_3$$
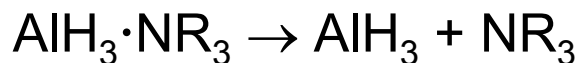
✓ demonstrated reaction

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

Overall reaction: $Al + 3/2H_2 \rightarrow AlH_3$

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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-AlH$_3$

- direct formation of alane adducts (pyridine, pyrazine, ethers, …)

- recovering hydride from alane-adducts, determine energy penalty

Continue effort on two existing pathways:

$Al + H_2 \rightarrow AlH_3\text{-}TMA \rightarrow AlH_3\text{-}TEA \rightarrow AlH_3$

$Al + H_2 + LiH \rightarrow LiAlH_4 \rightarrow AlH_3\text{-}TEA \rightarrow AlH_3$

Go/no-go on regeneration using organometallic approach

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

FY09: Regenerate AlH$_3$ with E penalty $\leq$73 kJ/H$_2$ (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