DOE Hydrogen Program

Synthesis and Characterization of Alanes for Automotive Applications

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Part of the DOE Metal Hydride Center of Excellence

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Project ID #: ST20

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Overview

Timeline

- Project start date: FY05
- Project end date: FY10
- 40 % complete

Budget

- Expected total project funding:
  - $3.00M (DOE)
- Funding received in FY06
  - $400K (DOE)
- Funding for FY07:
  - $925K (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
  - JPL, U. Hawaii, ORNL, SRNL, SNL
- Chemical Hydride Center
- IPHE and IEA collaborations
  - IFE (Norway), Polish Academy of Sciences, Russian Academy of Sciences, Academy of Sciences of Ukraine

Challenges and Objectives

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

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)
2. The key issue is regeneration (hydrogenation of Al metal)
   - Multiple regeneration pathways are being investigated

Objectives:

1. Produce aluminum hydride with 9 wt. % H_2 and 0.13 kg H_2/L
2. Develop practical and economical process for the regeneration of AlH_3 from the decomposed Al.
3. Assist in the design for an onboard fuel tank delivery system

BNL Approach

Task 1: Synthesis

Synthesize α-AlH_3 and vary particle size (0.1-50 μm) & surface coating

Task 2: Properties

Decomposition rates for α-AlH_3 as a function of particle size & morphology

Task 3: Regeneration

- Recycling: adapt synthesis to reduce/reuse byproducts
- Organometallic: Direct Al hydrogenation in organic solvents

Task 4: Tank Study

Refueling strategy - off-board (transfer of liquid/powder, tank swap,etc.)

Task 5: Management

- Coordinate MHCoE Alane subgroup
- Partnerships and reporting: supplying partners with samples (e.g. AlH_3)
- Materials characterization at unique BNL facilities (e.g. NSLS and CFN)

Why AlH_3?

– Large gravimetric & volumetric capacity

10.1 wt% (2010 S-Target = 6.0)

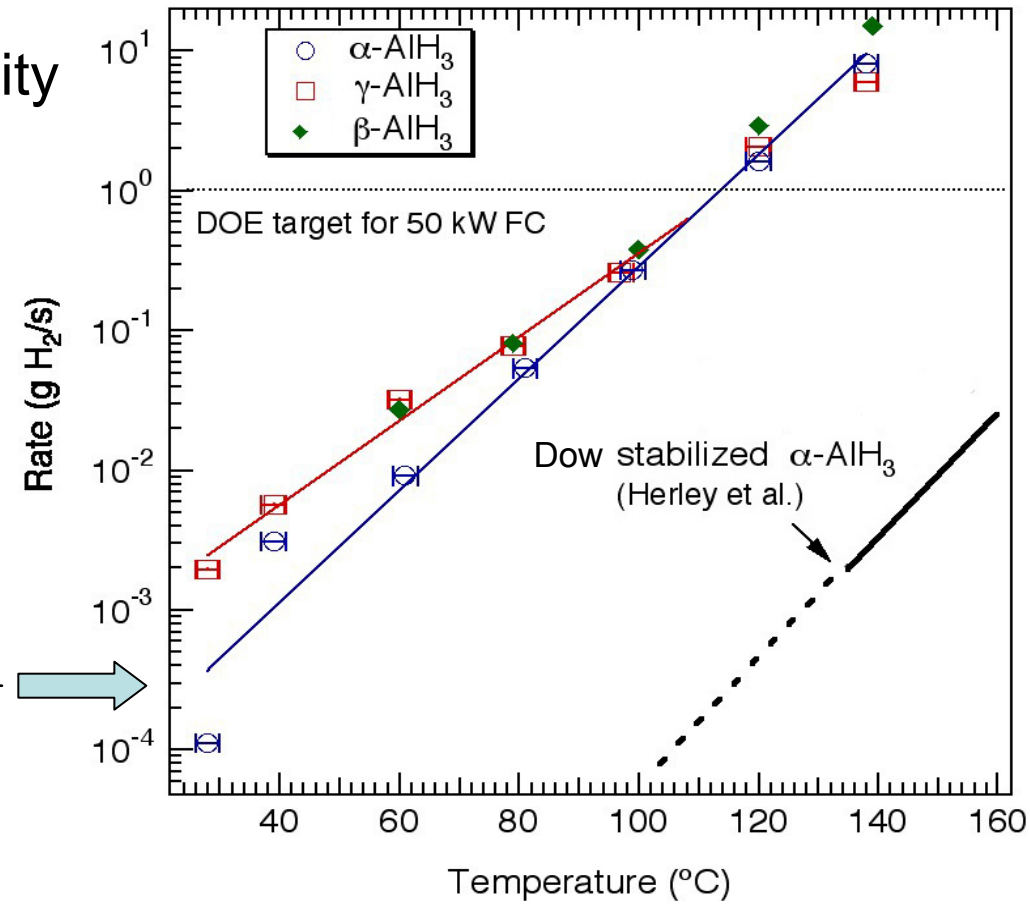
149 g/L (2010 S-Target = 45)

– Low decomposition enthalpy

$\Delta H_{\alpha AlH3} \approx$ **7 kJ/mol H_2** ($\approx 1/5\ \Delta H_{NaAlH4}$)

– Rapid H_2 evolution rates at low T

Meets DOE target (50 kW FC) at 115°C with 45% FC efficiency (120kW at 100%)



– Decomposition rates tuned through particle size and coatings

– High purity H_2 - AlH_3 decomposes to Al and H_2 (no side reactions)

– Cyclability - Offboard regeneration may reduce cycling problems

– Regeneration will be challenging, but intrinsic energy costs are low

Progress on Regeneration

- **FY06: Background studies** - regeneration requires a basic understanding of physics/chemistry of AlH_3
  - Crystallographic Structures of AlH_3
  - Thermodynamics
  - *P-T* phase diagram for α-AlH_3
  - Literature Review (selected organometallic route for exp. study)
  - Preliminary experimental design and safety review
- **Program Review Feedback**- focus on regeneration
- **FY07 - Multiple approaches to regeneration**
  - Recycling route studies (e.g. LiCl splitting)
  - Organometallic route - Experimental progress to date:
    - Retrofit 200 bar Parr reactor and purchased 340 bar PPI reactor
    - Preliminary studies on AlH_3-TEDA in THF and dodecane
    - Reduced hydrogenation pressure using activated Al powder
  - Electrochemical route being investigated at SRNL
  - Supercritical fluid route being investigated at UH (proposal submitted)

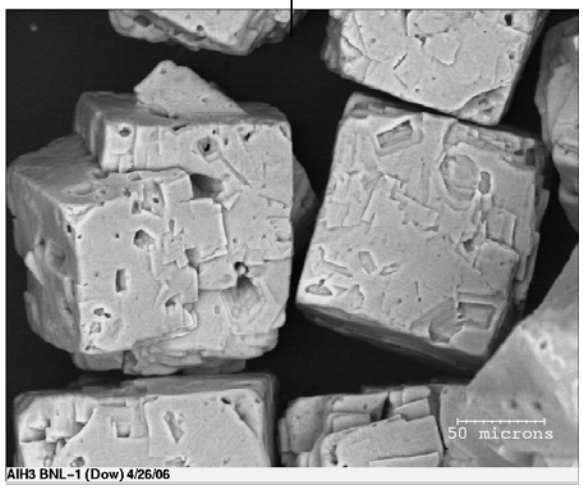
Synthesis of AlH_3

- Regeneration rate and efficiency will likely be a function of crystallite size and surface condition
- Different AlH_3 morphologies easily prepared in conventional procedure

$$3LiAlH_4 + AlCl_3 + ether \longrightarrow 3LiCl\downarrow + 4AlH_3 \bullet 1.2[(C_2H_5)_2O] + ether$$

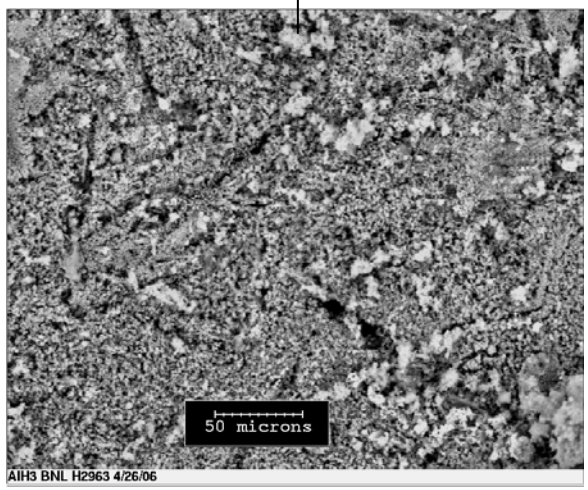
Desolvation

Batch/Continuous Reactions



α-AlH_3 (Dow) 50-100μm

Microcrystallization Reaction



α-AlH_3 (BNL) 100-200 nm

- Surface coatings (e.g. oxides) introduced through alcohol wash

Which Structure of AlH_3 is Most Stable?

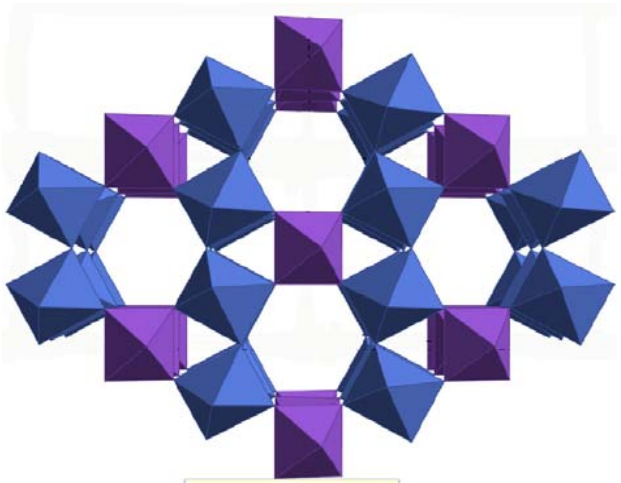
– Regeneration requires better understanding of phases and stability

– 2005 Ke et al. identified two structures of AlH_3 (orthorhombic *Cmcm* and cubic *Fd-3m*) more stable than α-AlH_3 (hexagonal) using DFT

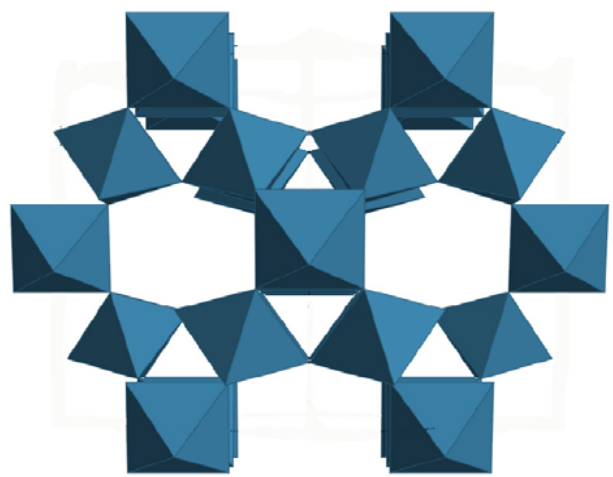
– 2006 IFE group solved the structure of α'-AlH_3 (orthorhombic, *Cmcm*)

– 2006 Collaboration UH, BNL and IFE synthesized and solved structures of β-AlH_3 (cubic, *Fd-3m*) and γ-AlH_3 (tetragonal, *Pnnm*)

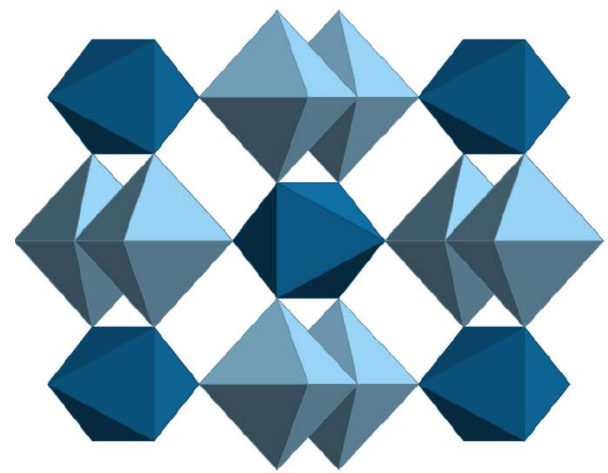
– **All three phases <u>less stable</u> than α-AlH_3 at temperatures ≥ 300K**



α'-AlH_3 [101] (1)



β-AlH_3 [101] (2)

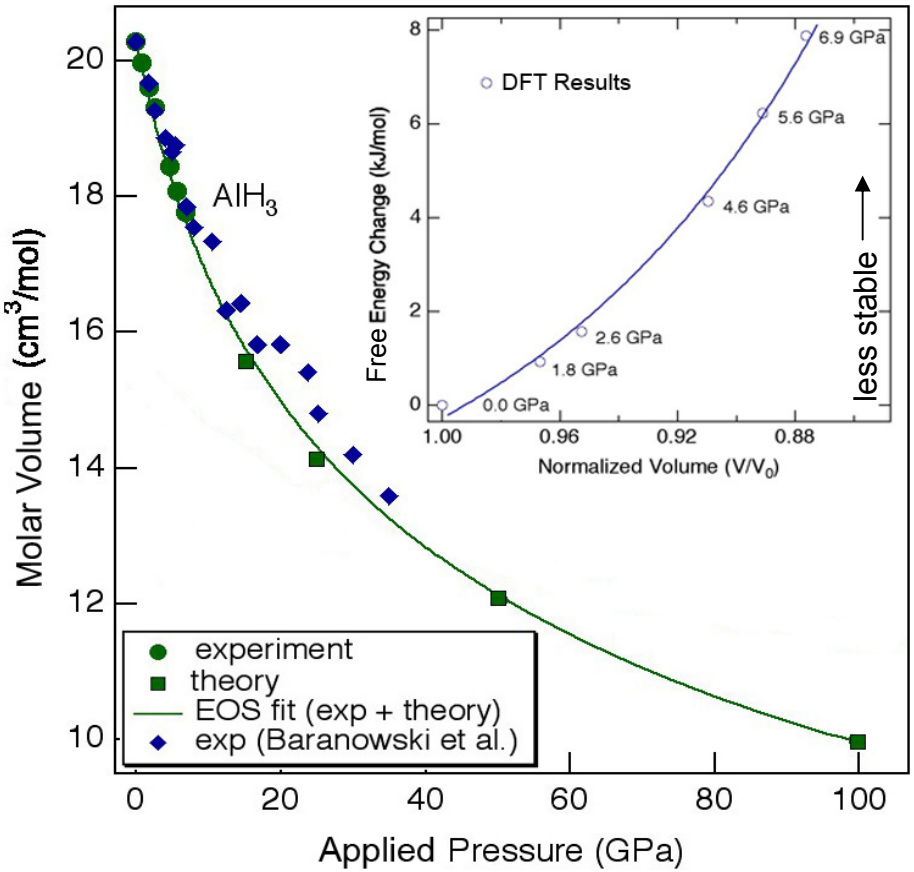


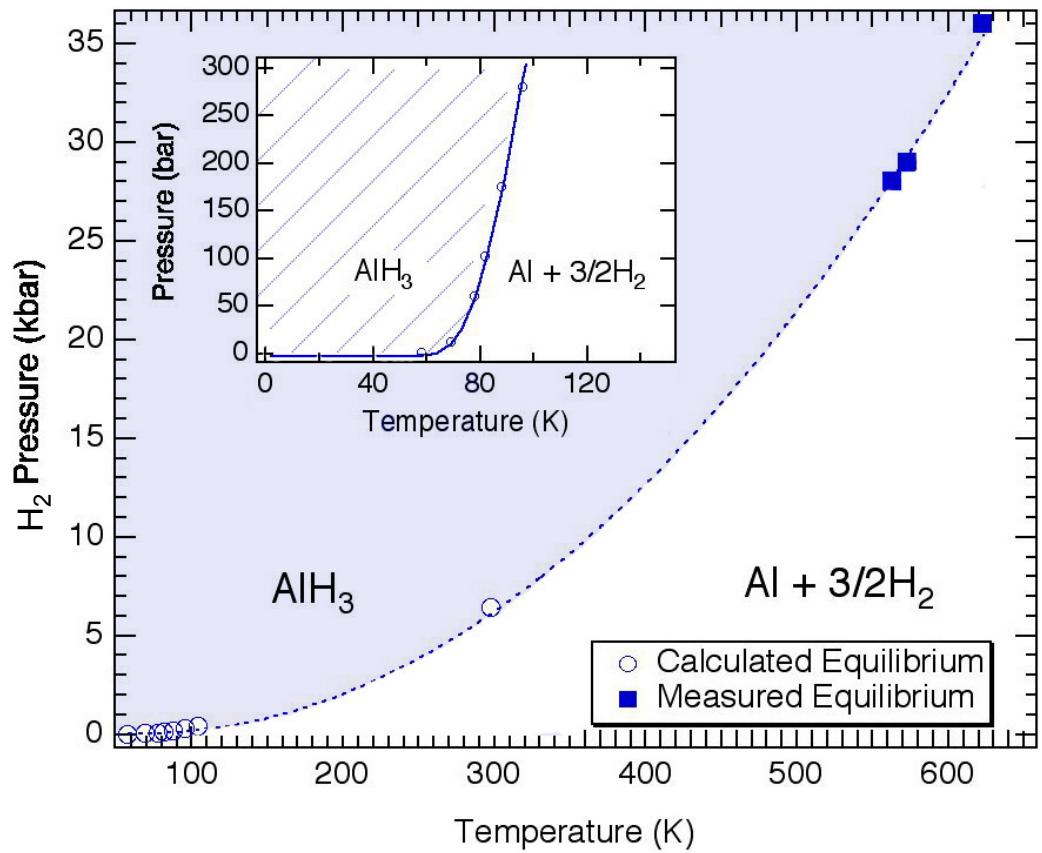
γ-AlH_3 [010] (3)

(1) H.W. Brinks, A. Istad-Lem, B.C. Hauback, JPCB, **110** 25833 (2006); (2) H.W. Brinks, C. Brown, C.M. Jensen, J. Graetz, J.J. Reilly, B.C. Hauback, *JALCOM*, (2006); (3) H.W. Brinks, W. Langley, C.M. Jensen, J. Graetz, J.J. Reilly, B.C. Hauback, *JALCOM*, (2006)

Formation of α-AlH_3 From the H_2 and Al

- **Does α-AlH_3 transform to a more stable phase at high pressure?**
- **What does the α-AlH_3 phase diagram look like?**





- Structural studies of α-AlH_3 show no first-order phase transition at high pressure*
- DFT results base on exp. lattice suggest structure is destabilized at pressure**
- No hydrogenation below 573K - low T region of phase diagram calculated from ΔG
- **AlH_3 formation limited by thermodynamics <u>and</u> low temperature kinetics**

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**Funded through BES

*Performed by synchrotron x-ray diffraction (funded through BES)

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Regeneration Energy Requirements and BNL Targets

In an effort to concentrate on the most promising pathways we have established two regeneration targets:

(1) Energy required for regeneration will not exceed 30% of the fuel energy

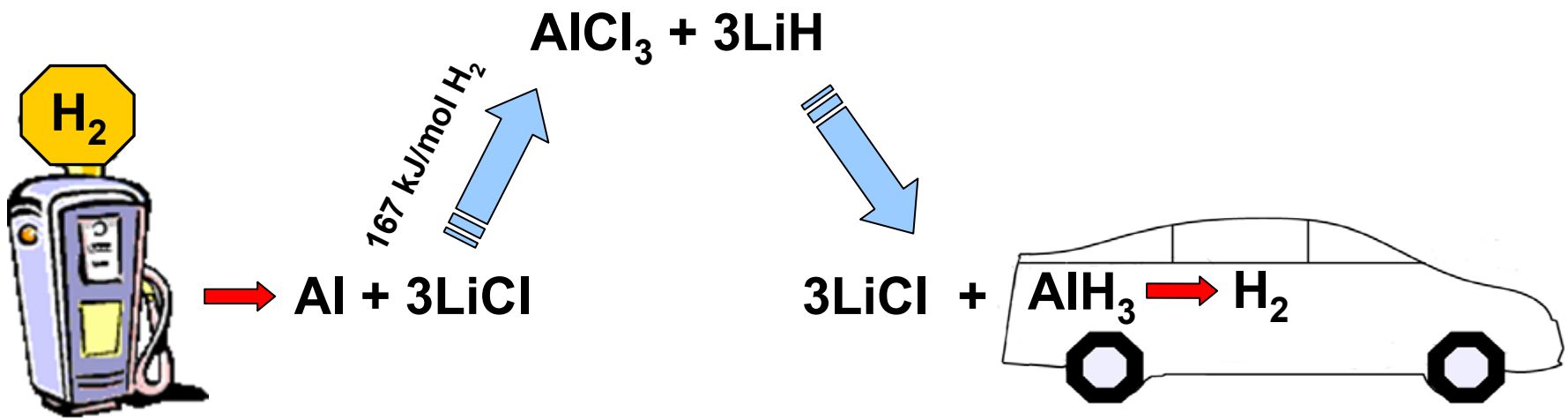
– One mole of AlH_3 contains 360 kJ of fuel energy based on the lower heating value LHV_{H2}=120 kJ/g = 240 kJ/mol H_2. Therefore, 30% energy target equivalent to $\Delta E_{regen} \leq 73$ kJ/mol H_2

– Direct hydrogenation of Al to form AlH_3 (298K) requires a <u>minimum</u> of 0.13 J for every 1.0 J of fuel energy (**13% of fuel energy needed for regeneration**)

(2) Regeneration process will produce AlH_3 with at least 90% purity

– Offboard hydrogenation will utilize spent Al

Recycling Route - LiCl splitting



<u>Synthesis</u>: $AlCl_3$ +3LiH → AlH_3 + 3LiCl

– Recycling byproducts (LiCl and Al) requires splitting 3LiCl per AlH_3:

<u>Recycling</u>: Al + 3LiCl +3/2H_2 → $AlCl_3$+3LiH

– With perfect efficiency ($AlCl_3$ & LiH formation energy not wasted):

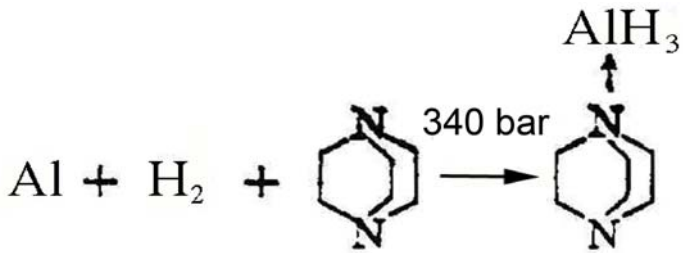
$$\Delta E_{recycle} \geq 167 \text{ kJ/mol } H_2$$

– Recycling AlH_3 by splitting LiCl (298K) requires a <u>minimum</u> of 0.7J for every 1J of fuel (**70% of fuel energy required for regeneration**)

– Recycling AlH_3 by splitting LiCl will not be investigated further

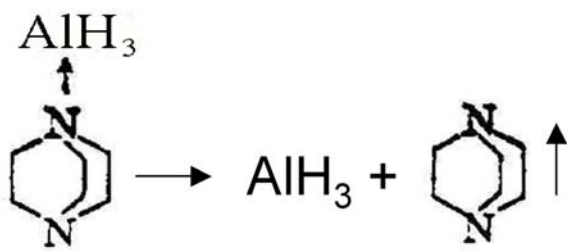
Liquid Organometallic Route - Overview

- Form AlH_3 complexes from Al and H_2 in organic solvents (THF, Et_2O)
- Reduce P_{eq} by forming a more stable intermediate phase
- Reaction between Al, H_2 and triethylenediamine (TEDA = $C_6H_{12}N_2$)

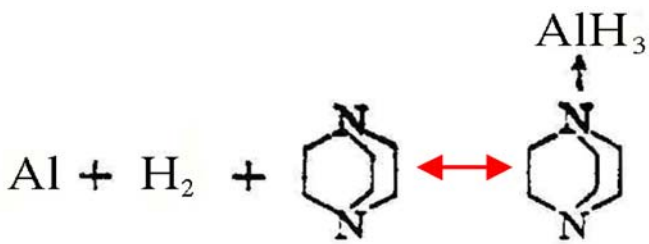


E.C. Ashby, JACS, (1964).

- **FY07 Milestone**: Improve hydrogenation kinetics & reduce required pressure
- Second step required to extract TEDA and recover pure AlH_3:



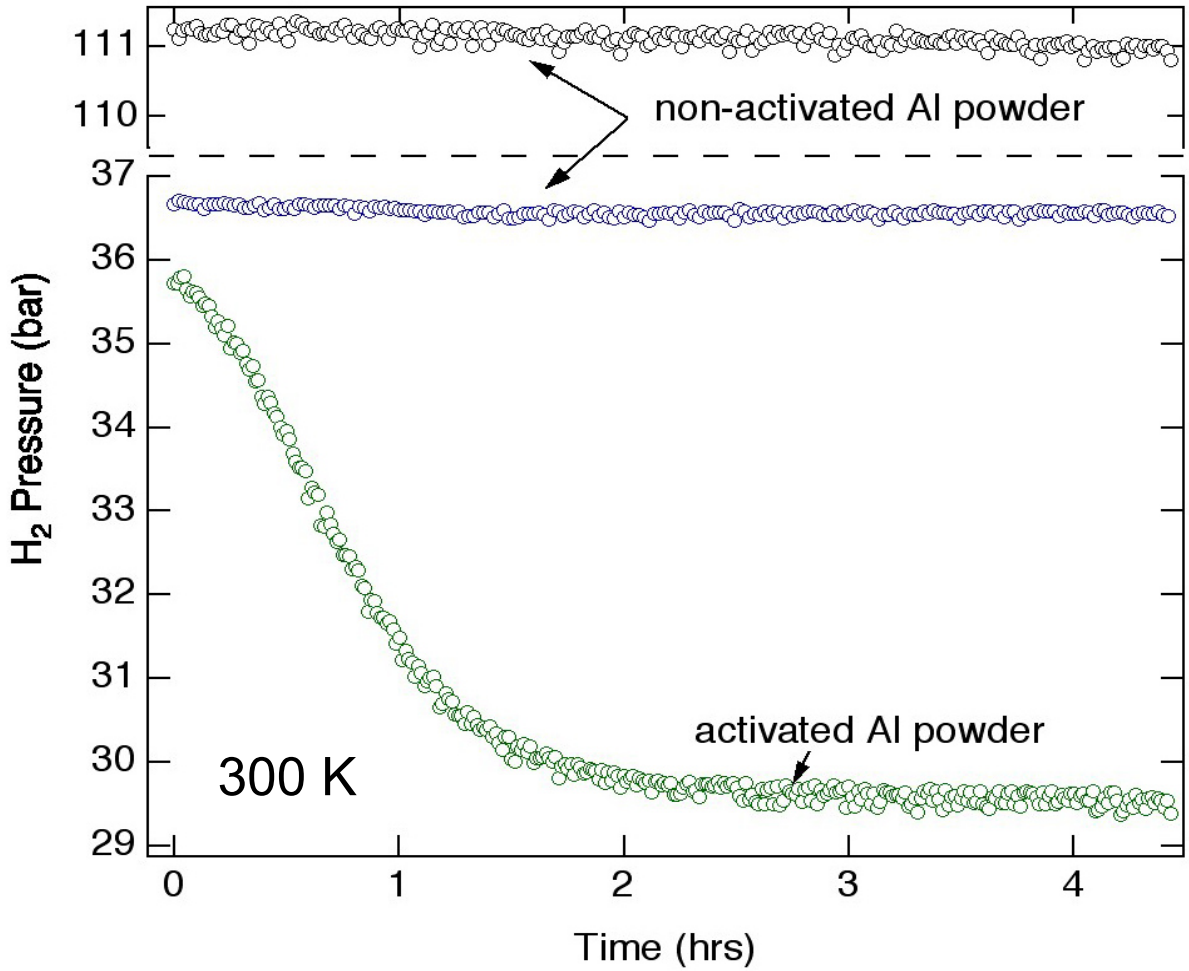
- Another route under investigation is a reversible metal-organic hydride:



2.1 wt % H_2 (theoretical)

Liquid Organometallic Route - Results

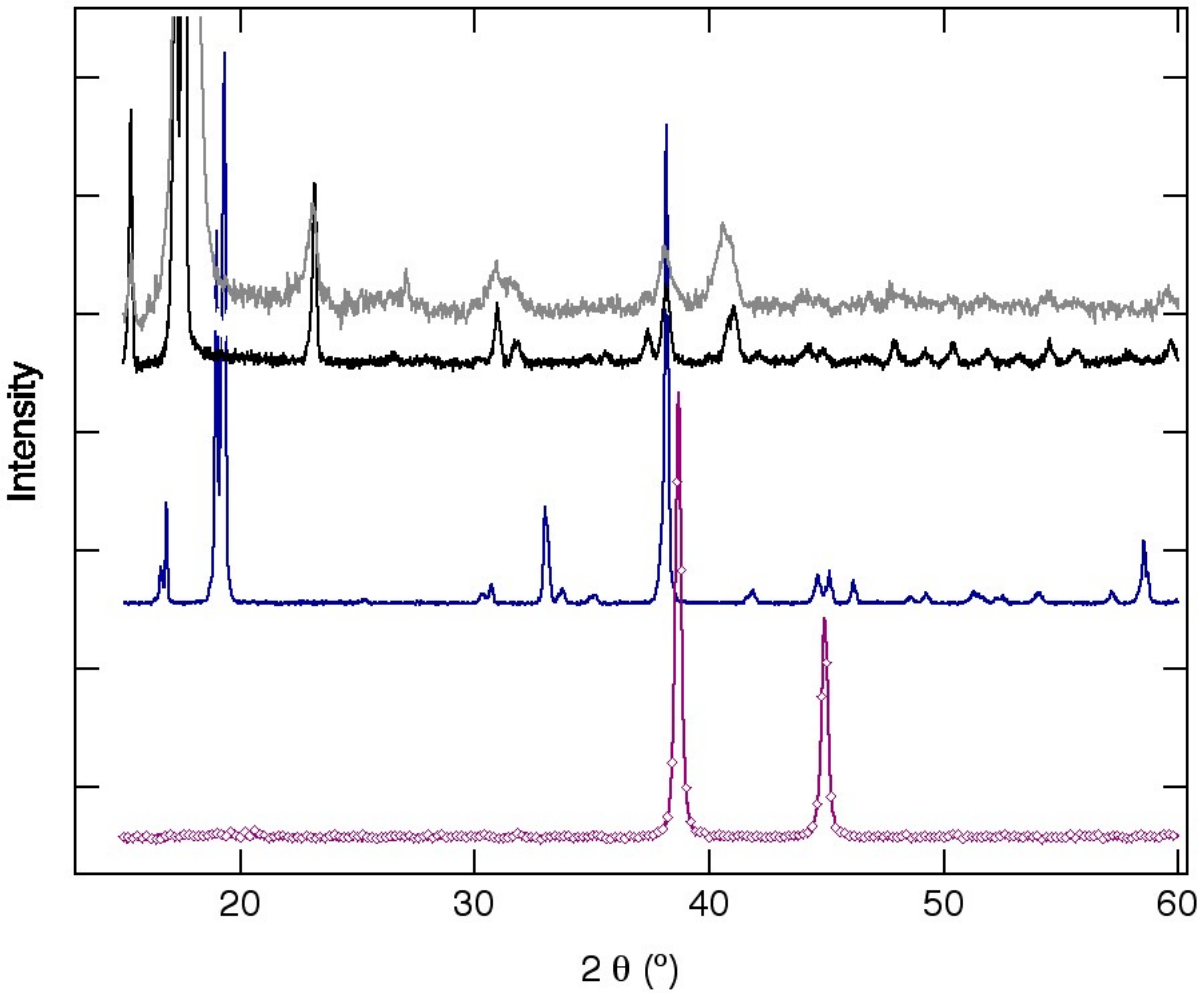
Organometallic hydrogenation of aluminum



Drop in hydrogen pressure indicates hydrogenation (~2 wt% total)

- **Hydrogenation of activated Al (Al*) at 300K occurred at much lower pressures than expected** (no reaction with non-activated Al up to 110 bar)
- Reaction is reversible: TEDA + Al* + $H_2 \leftrightarrow$ TEDA-AlH_3 (theor. 2.1 wt% H_2)

Liquid Organometallic Route - XRD Analysis



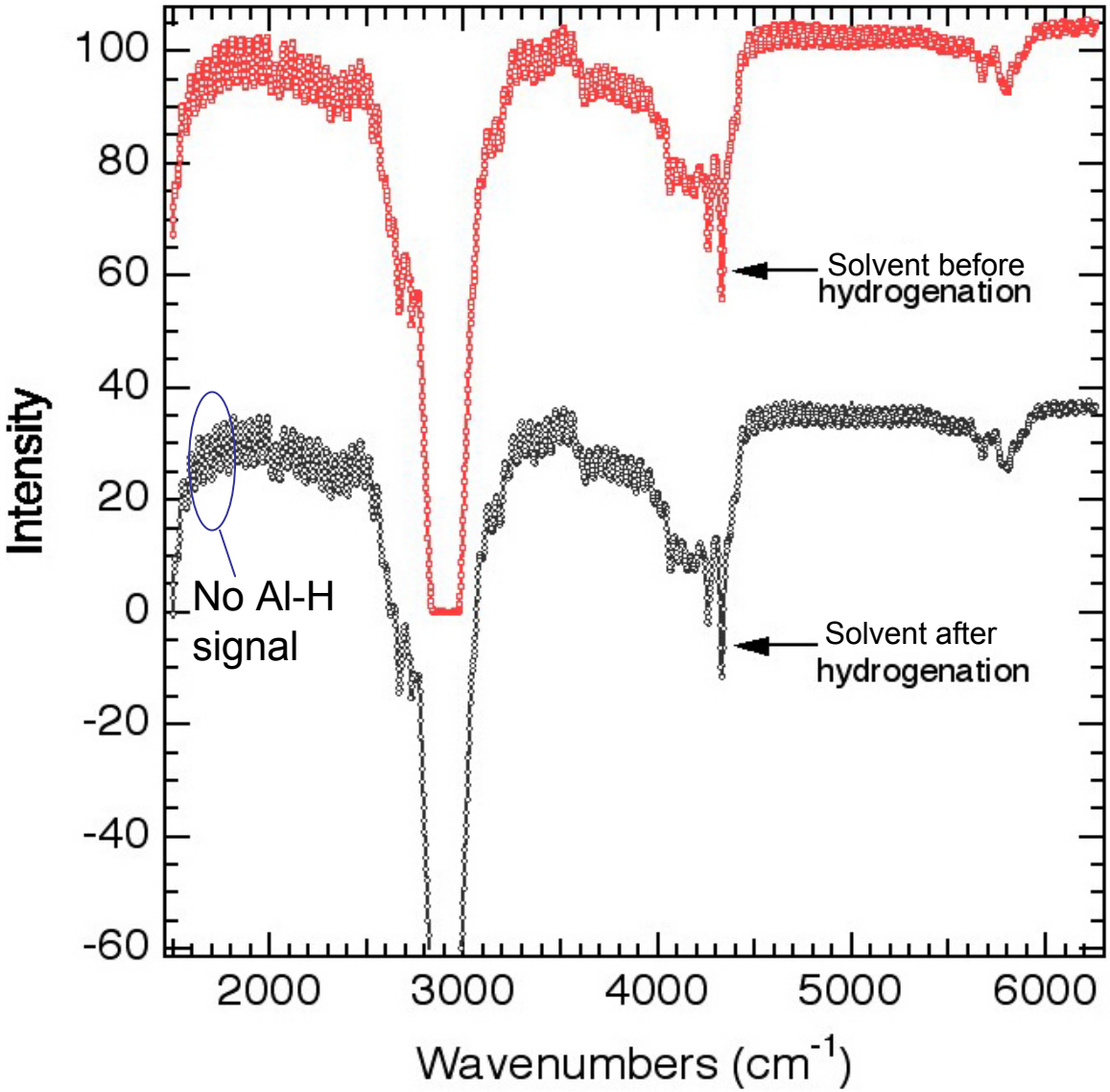
standard of AlH_3-TEDA prepared from AlH_3 and TEDA in THF

Product: TEDA-AlH_3
No trace of Al or TEDA

<u>Starting materials:</u>
TEDA (solid)
Al powder (solid)
THF solvent (liquid)
H_2 (gas)

- Powder XRD confirms 100% of Al consumed in reaction (yield near 100%)
- No evidence of any phase other than TEDA-AlH_3 (no side reactions)

Liquid Organometallic Route - FTIR Analysis



No change in solvent (dodecane) after multiple hydrogenation cycles

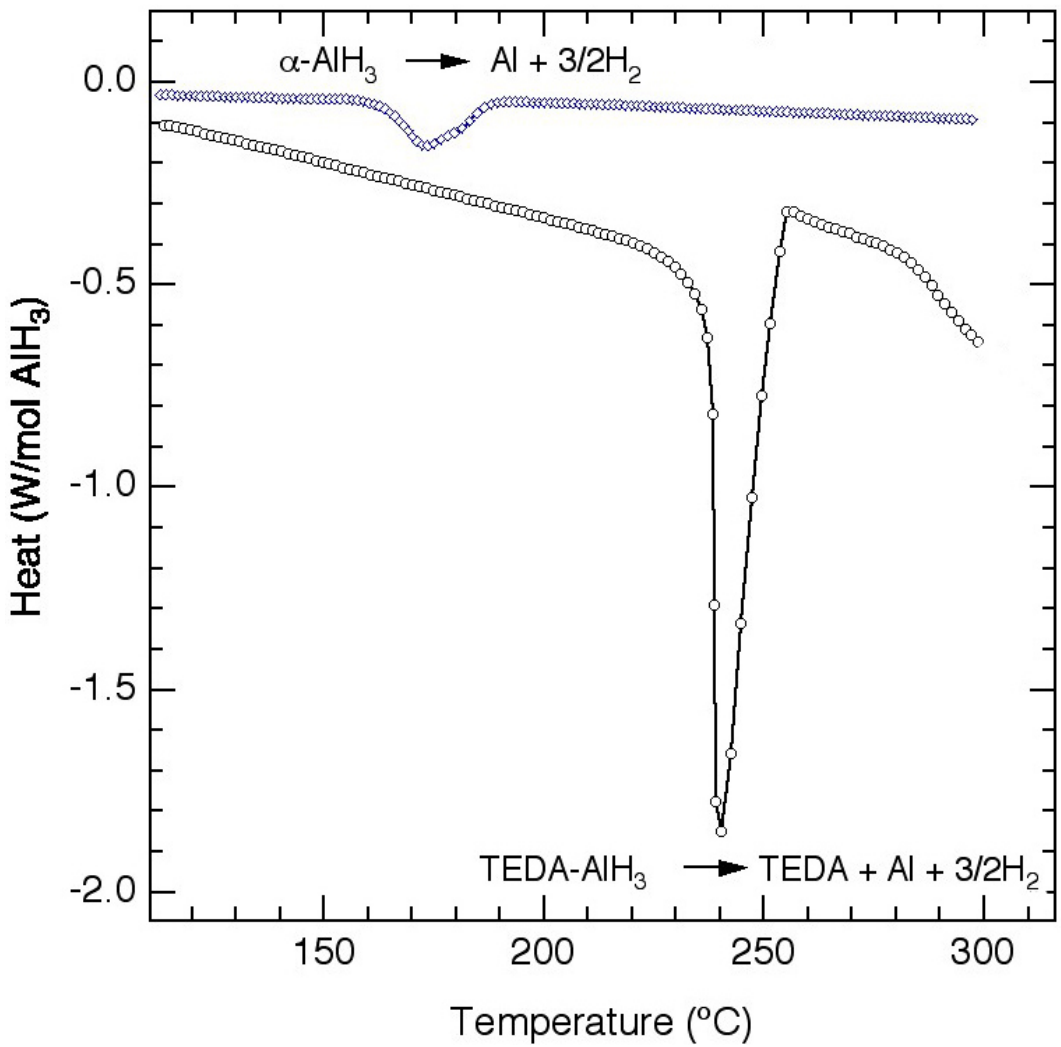
– no trace of AlH_3 in solution
– no solvent deterioration

– Reaction works equally well in polar (THF) and nonpolar (dodecane) solvents

Liquid Organometallic Route

Energy Requirements

Energy required to form TEDA-AlH_3 is small, but how much energy is required to break AlH_3 from TEDA to recover pure AlH_3?



$TEDA\text{-}AlH_3 \rightarrow TEDA + Al + 3/2H_2$

$\Delta H_{TEDA\text{-}AlH3} = 53$ kJ/mol H_2

$AlH_3 \rightarrow Al + 3/2H_2$

$\Delta H_{AlH3} = 7$ kJ/mol H_2

From these values we can approximate the heat required to release AlH_3:

$TEDA\text{-}AlH_3 \rightarrow TEDA + AlH_3$

$\Delta H \approx 46$ kJ/mol H_2

– Regeneration will require a minimum of 20% of the AlH_3 fuel energy

– Although energy requirement is <u>not</u> prohibitive the challenge will be extracting AlH_3 without decomposition

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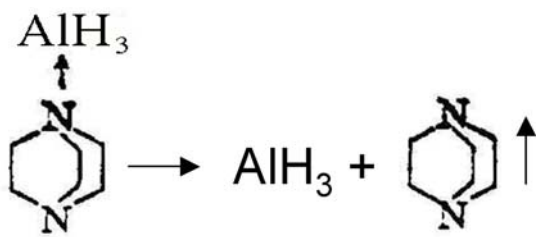
Path Forward - Regeneration

Preliminary Studies:

- Crystal structures and phase stabilities (**complete**)
- Reproduce Ashby's reaction (**complete**)
- Reduce hydrogenation pressure and temperature (**complete**)
- Explore Activated Al powder (**ongoing**)

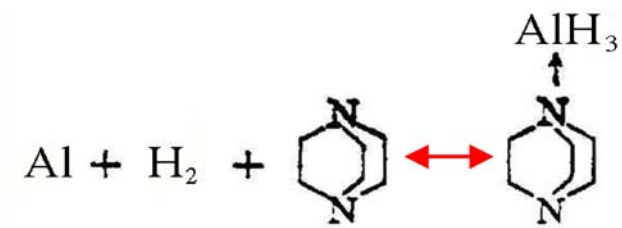
Regeneration Routes To Be Investigated:

Preparation of pure AlH_3 by isolating from alane-adduct



– Examine amine/adduct substitutions that form less stable compounds
– Evaluate energy requirements

Reversible metal organic hydrides:



– Examine solvent and adduct substitutions to determine if capacity can be improved
– Evaluate thermodynamics

Path Forward - Regeneration

Collaborations:

MHCoE Theory Group - Identify possible adduct substitutions; Search for lighter adducts that accommodate multiple AlH_3 units; amine-alane chemistry

Chemical Hydride Center of Excellence - Information exchange; Synergisms between amine-borane and amine-alane investigations

IPHE/IEA - Fundamental high pressure studies; high pressure hydrogenation; decomposition kinetics, insitu synchrotron XRD

Decisions and Milestones:

- FY07 Milestone: Hydrogenate Al at low temp and pressure (P<70 bar)
- FY08 Go/no-go: Regeneration using organometallic approach
- FY09: Overall objective to regenerate AlH_3 with energy penalty ≤73 kJ/H_2 and a yield of ≥90% and (2) Determine mass/energy balance over 100 cycles on 5g samples

Project Summary

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

Significant accomplishment: **Direct hydrogenation of activated Al powder at P<35 bar (ten-fold reduction in pressure) with a yield near 100%**

Storage Parameter	Units	2010 System Target	FY07 materials*
Gravimetric Capacity	kWh/kg wt. % H_2	2.0 6.0	3.17(3) 9.5(1)
Volumetric Capacity	kWh/L Kg H_2/L	1.5 0.045	4.75(4)[x] 0.143(2)
Desorption Temperature	ºC	85	<100
Rate**(114 ºC)	g/s/kW	1.0**	0.14(1) / 1.0(1)
BNL Regeneration Target	kJ/ mol H_2	73	—

* Data is based on material only, not system value; ** Based on 50kW FC with 45% efficiency for 100kg AlH_3; [x] Does not account for packing density (a conservative estimate for packing density is 50%)