DOE Hydrogen Program

Aluminum Hydride Regeneration

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

Brookhaven National Laboratory

BROOKHAVEN
NATIONAL LABORATORY

Project ID
#st_05_graetz

Overview

Timeline

- Project start date: FY05
- Project end date: FY10
- 80 % complete

Budget

- Expected total project funding:
  - $4.00M (DOE)
- Funding received in FY08
  - $1.125M (DOE)
- Planned Funding for FY09
  - $1.25M (DOE)

Barriers

MYPP Section 3.3.4.2.1 On-Board Storage Barriers

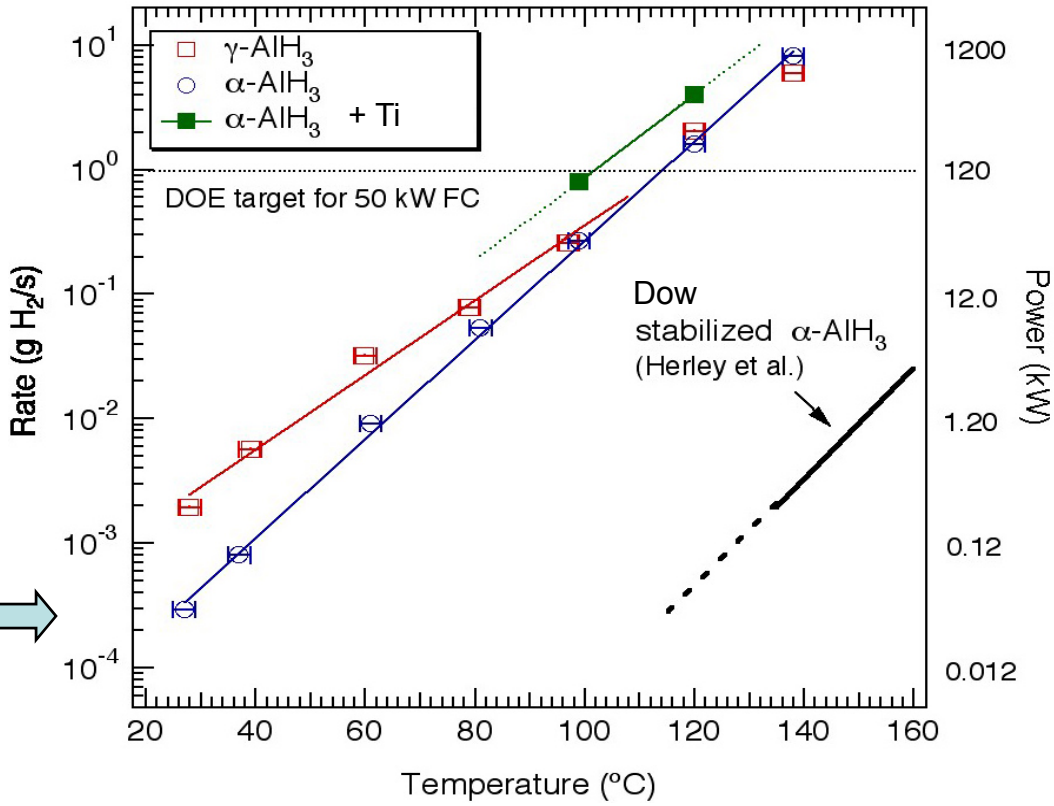
A. Weight & Volume
B. Cost
C. Efficiency
D. Durability/Operability
E. Charge/Discharge Rates
R. Regeneration Processes

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)

Relevance: AlH_3

- High capacity
  - **10.1 wt%** (2010 S-Target = 6.0)
  - **149 g/L** (2010 S-Target = 45)
- Low decomposition enthalpy
  - $\Delta H \approx 7$ **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

Collaborations

MHCoE Project D - Aluminum hydride (Lead: Jim Wegrzyn, BNL)

BNL (POC)	SRNL	U. Hawaii/UNB	ORNL
Liquid-alane harvesting	Electrochemical	Supercritical fluids	Ionic liquids

UC Davis (P. Power) – sterically crowded ligands to stabilize unusual bonding and geometries

ECKA Granules of America – Preparation of catalyzed Al

SNL – calculations of adduct stability

UIUC – studies of reaction products and catalyst distribution

ANL- Cycle life analysis (not MHCoE)

Approach

Objective: M*eet 2010 DOE technical performance targets using kinetically stabilized aluminum-based hydrides (e.g. $LiAlH_4$ and AlH_3)*

1. Develop low-energy (≤73 kJ/H_2 or 30% of fuel energy) regeneration routes to prepare kinetically stabilized hydrides from the spent fuel
2. Assist the engineering design for an off-board system based on a kinetically stabilized hydride

Challenge: Hydrides are thermodynamically unstable at 300K

1. How do we control the H_2 evolution? One solution may be a pumpable slurry but how will this impact H_2 rates and capacity?
2. Can we regenerate these hydrides from the spent material using a low cost and low energy process?

Two-step approach to regeneration of Al-based hydrides:

Step I: Alane stabilization - Form stabilized alane complex by direct hydrogenation of catalyzed Al and complexing agent (e.g. amine)

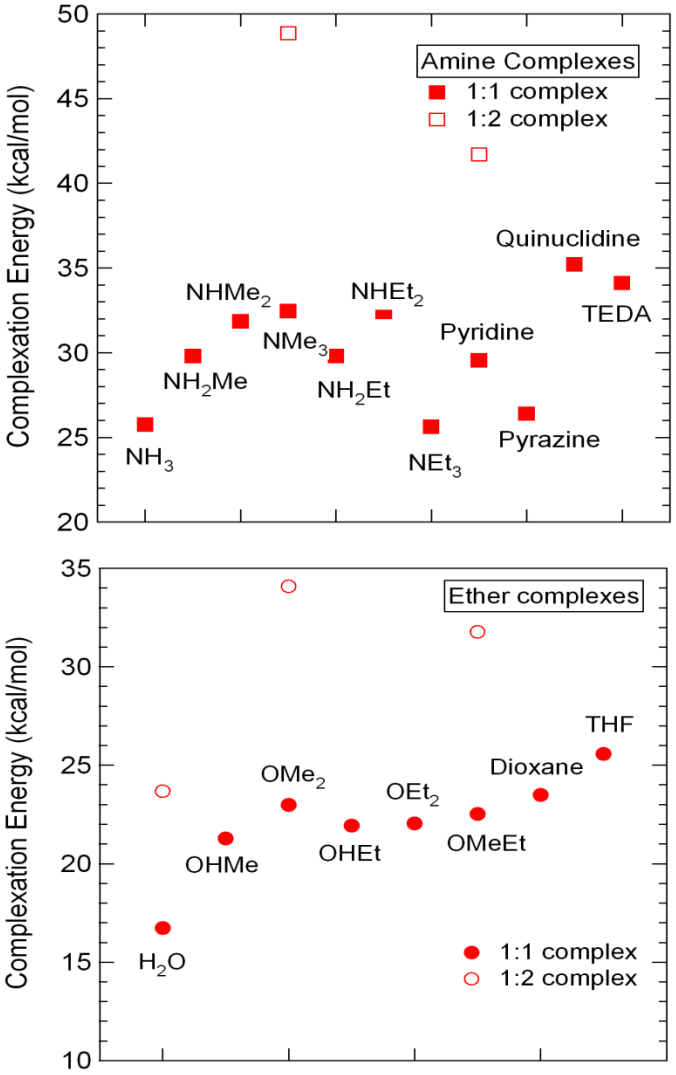
Step II: Remove stabilizing species and recover AlH_3

Approach / Accomplishments: Theory Guided Research

- High-level electronic structure calculations guide selection of alane complexation agents
- **Problem: what is the best electron donor to stabilize AlH_3 in solution?**

  Compute complexation energies

  AlH_3:(L)*n* (*n* = 1 or 2)
- **Approach:** Large complexes can't be treated with highest-accuracy methods
  - **BAC-MP2 -** Reasonably accurate and applicable to large molecules
  - G3MP2 and CCSD(T): high-accuracy methods to calibrate BAC-MP2
- **Results:**
  - Amine complexes: 25 – 35 kcal/mol
  - Ether complexes: 17 – 25 kcal/mol
  - Alternatives tertiary amines of interest: Quinulidine, TMA, pyridine



Accomplishments

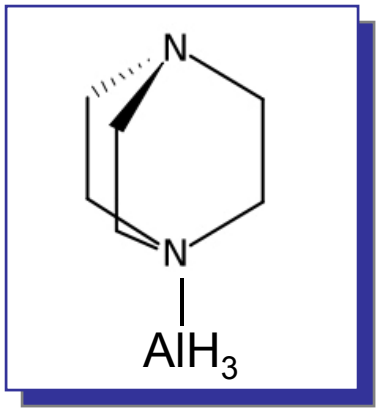
Last Year's Results

• Demonstrated a low energy regeneration route for $LiAlH_4$:

$$LiH + Al^* + 3/2H_2 \xrightarrow{THF} LiAlH_4\text{-}THF \xrightarrow[4hrs]{60^oC} LiAlH_4 + THF\uparrow$$

• Demonstrated the direct formation of AlH_3 from Al* and H_2 under mild conditions when amine used as stabilizer:

$$C_6H_{12}N_2 + Al^* + 3/2H_2 \rightarrow C_6H_{12}N_2\text{-}AlH_3$$



This Year's Results

• Step 1: Four new AlH_3 adducts identified that form by direct hydrogenation (Experiments use Al + 2mol% Ti (Al*) in solvent described previously)

• Step 2: Improvements in alane adduct separation via transamination

• Two complete regeneration pathways identified **(all steps verified!)**

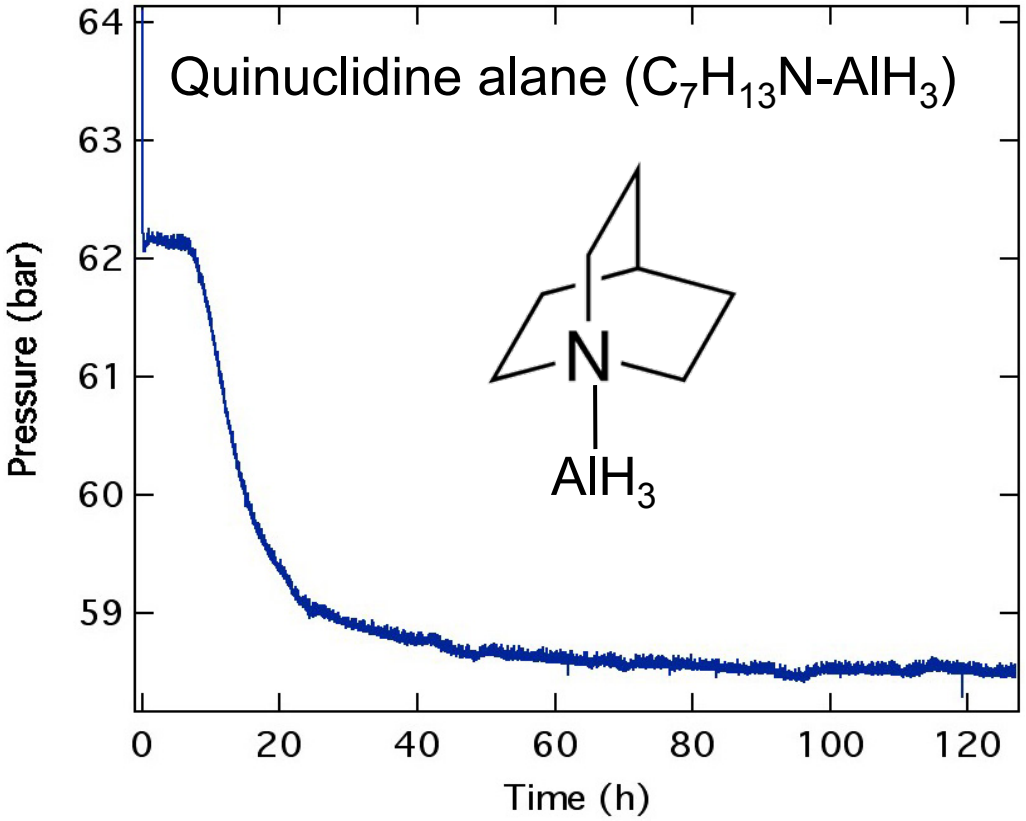
• Preliminary results on H_2 evolution rates from AlH_3 in slurries

Accomplishments: Formation of Quinuclidine Alane

Reaction: $C_7H_{13}N + Al^* + 3/2H_2 \rightarrow C_7H_{13}N\text{-}AlH_3$

Reaction conditions:
Al + 2 mol% Ti
Quinuclidine (solid) in THF
T = 298K

Product:
$C_7H_{13}N\text{-}AlH_3$
H/Al = 1.89
Yield = 63%

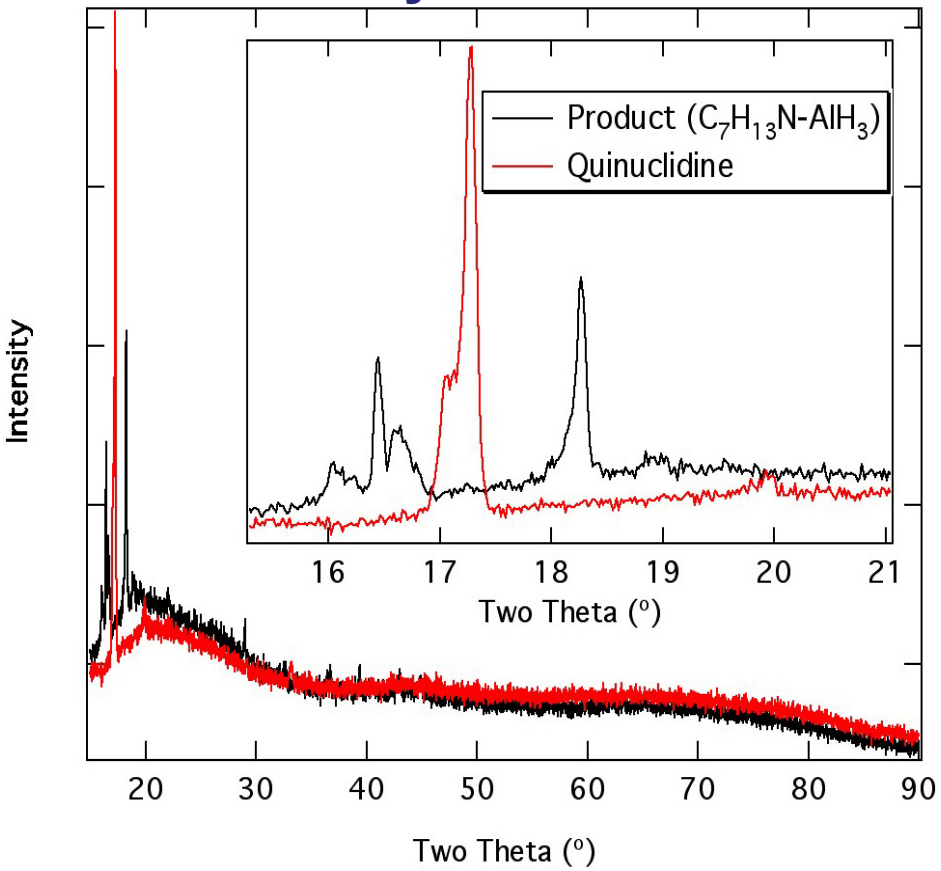


Key results:

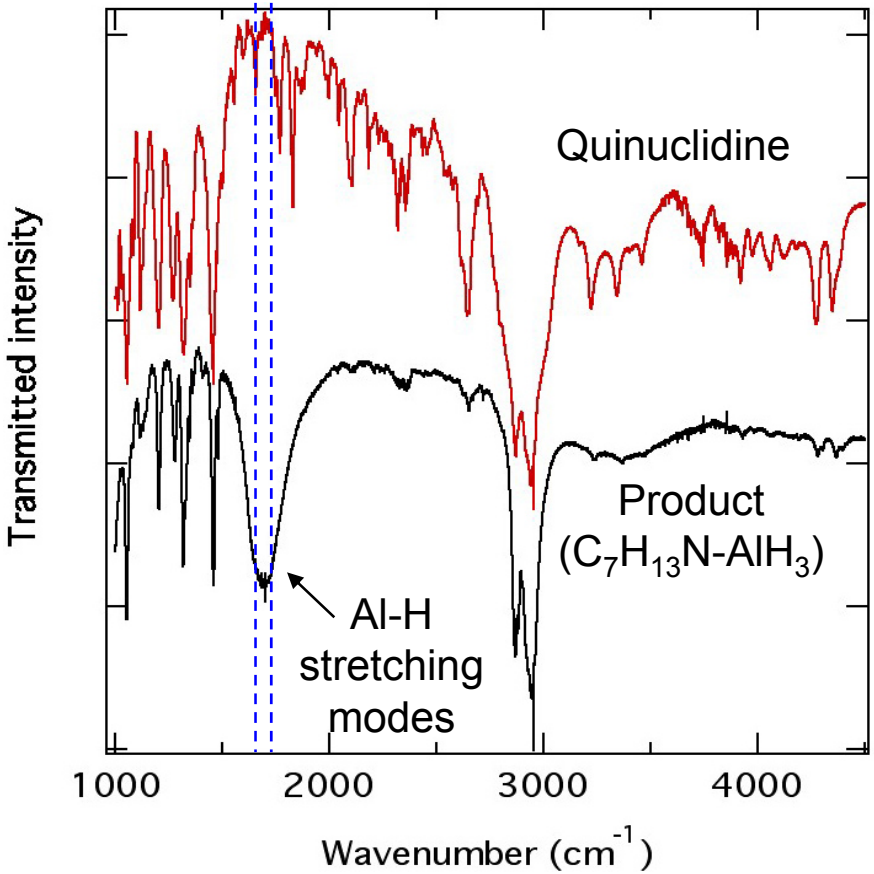
- Pressure decrease indicates hydrogenation of aluminum to form quinuclidine alane at low pressure and room temperature
- Solid product ($C_7H_{13}N\text{-}AlH_3$) precipitates out of solution

Accomplishments: Formation of Quinuclidine Alane

X-ray diffraction



Solid FTIR



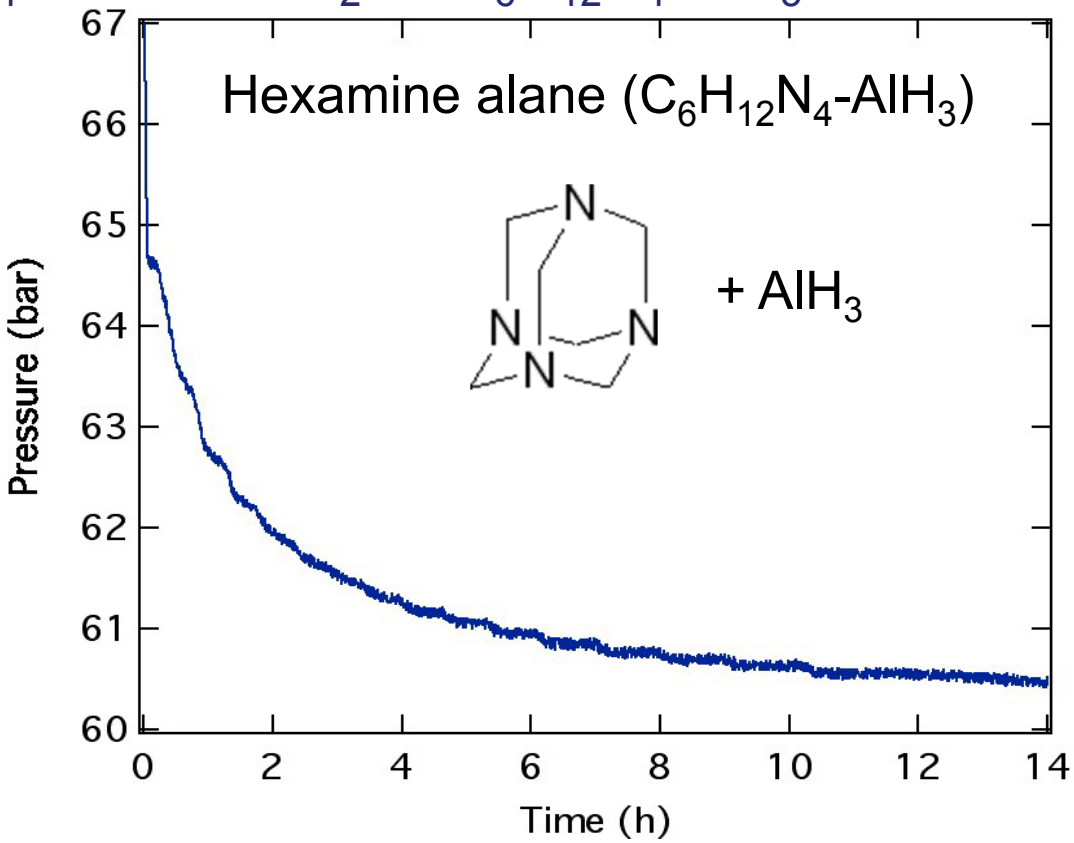
- XRD of solid product shows new peaks indicating a new phase
- FTIR of solid reaction product shows Al-H stretching modes (1700 cm^{-1}) indicating formation of alane adduct

Accomplishments: Formation of Hexamine Alane

Reaction: $C_6H_{12}N_4 + Al^* + 3/2H_2 \rightarrow C_6H_{12}N_4\text{-}AlH_3$

Reaction conditions:
Al + 2 mol% Ti
Hexamine (solid) in THF
T = 299K

Product:
$C_6H_{12}N_4\text{-}AlH_3$
H/Al = 1.6
Yield = 53%
Formation of alane product confirmed by FTIR



Key results:

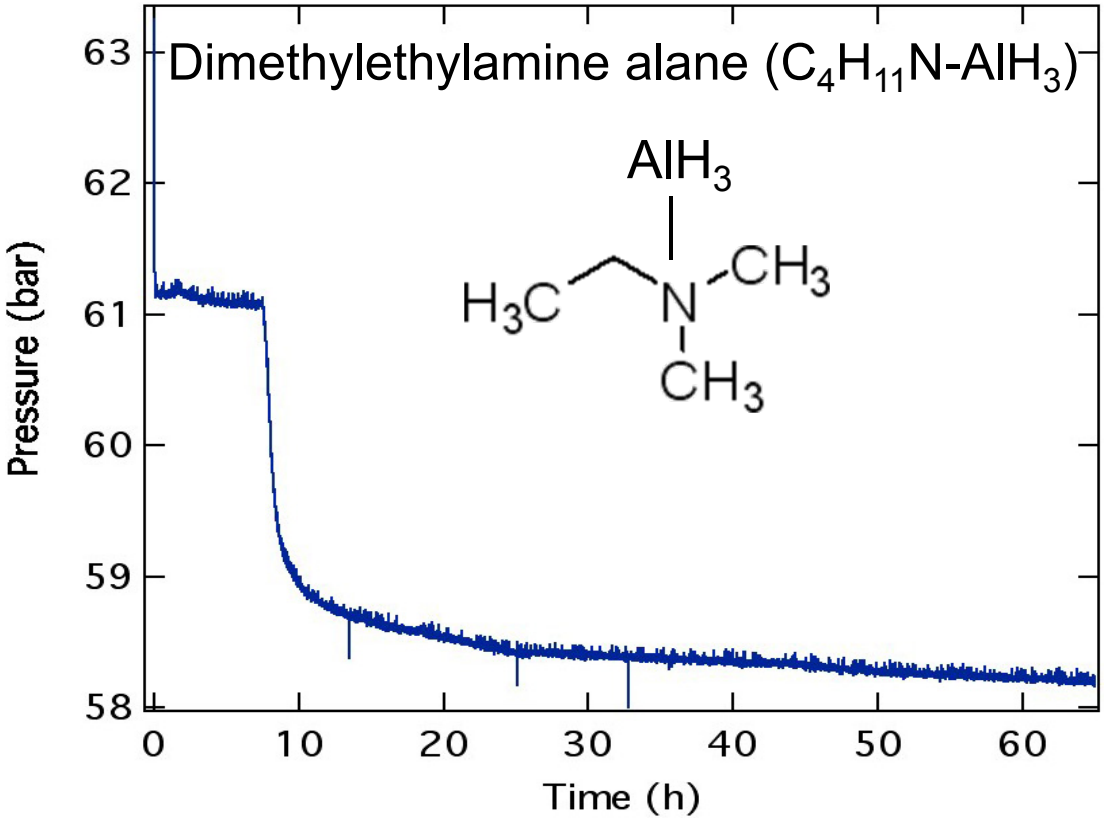
- Hydrogenation of aluminum to form hexamine alane occurs at low pressure and room temperature
- Reaction product ($C_6H_{12}N_4$-AlH_3) appears to be insoluble in THF

Accomplishments: Formation of Dimethylethylamine Alane

Reaction: $C_4H_{11}N + Al^* + 3/2H_2 \rightarrow C_7H_{13}N\text{-}AlH_3$

Reaction conditions:
Al + 2 mol% Ti
Hexamine (solid) in THF
T = 296K

Product:
$C_4H_{11}N\text{-}AlH_3$
H/Al = 1.68
Yield = 56%
Formation of alane product confirmed by FTIR



Key results:

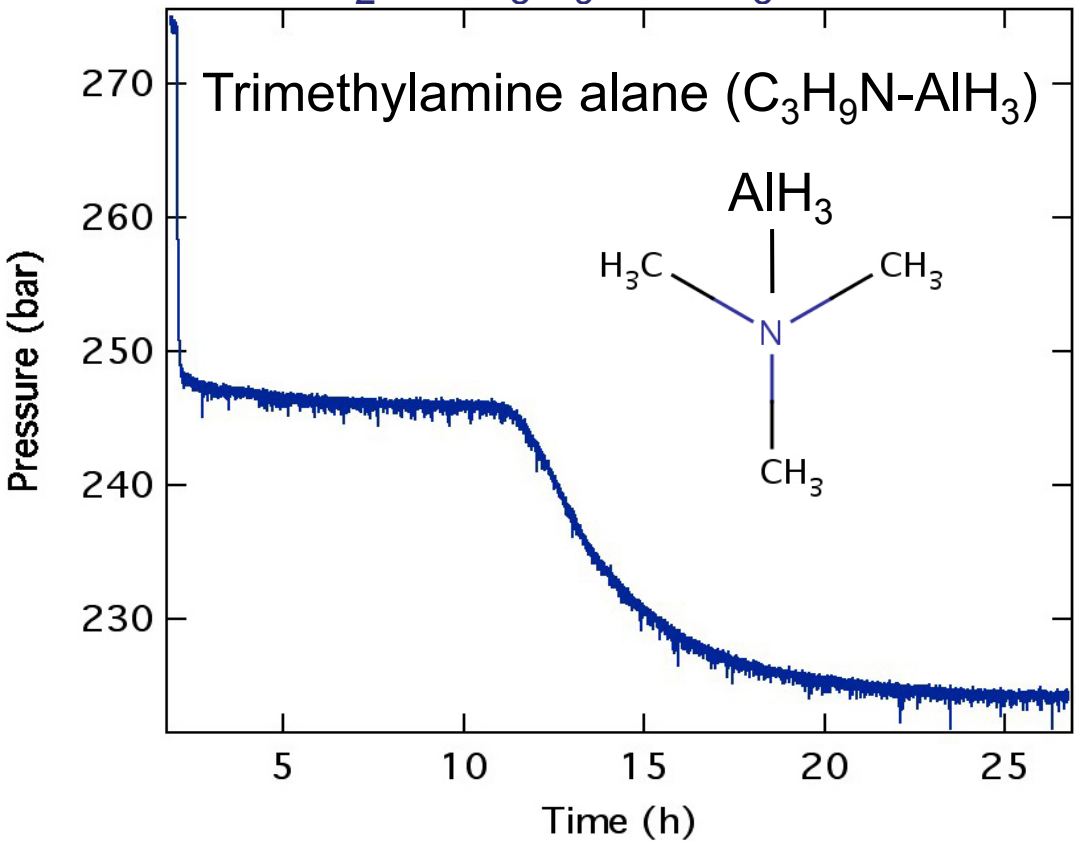
- Hydrogenation of aluminum to form DMA alane occurs at low pressure and room temperature
- Dimethylethylamine alane is a liquid at ambient P and T

Accomplishments: Formation of Trimethylamine Alane

Reaction: $C_3H_9N + Al^* + 3/2H_2 \rightarrow C_3H_9N\text{-}AlH_3$

Reaction conditions:
Al + 2 mol% Ti
trimethylamine (gas) in THF
T = 298K

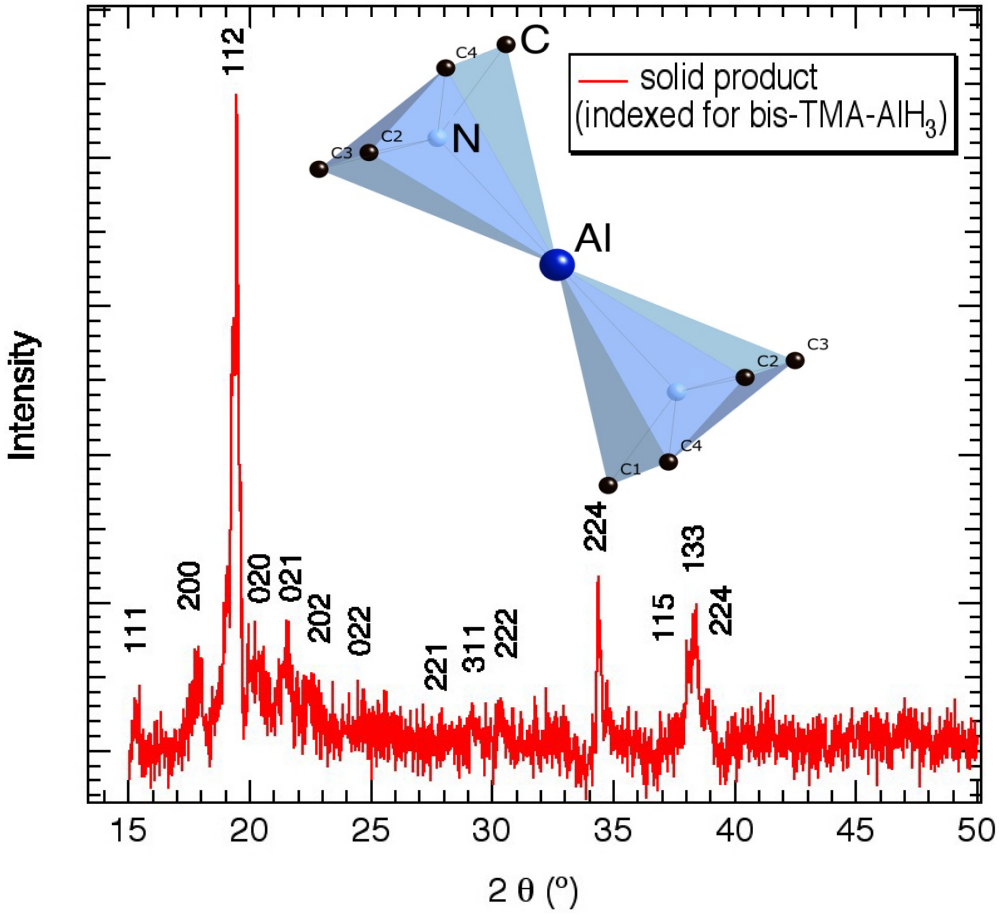
Product:
$C_3H_9N\text{-}AlH_3$
Formation of alane product confirmed by FTIR

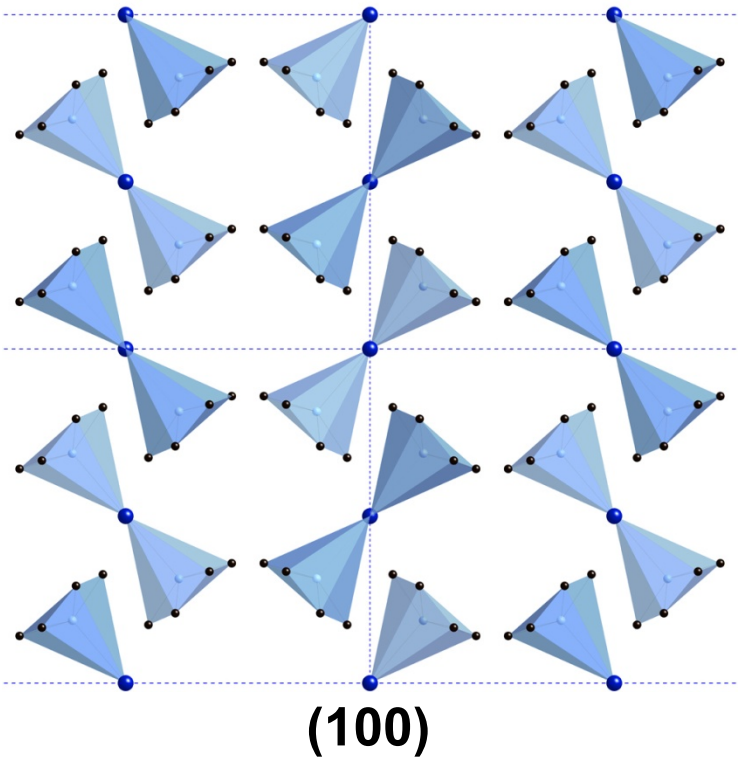


Key results:

- Hydrogenation of aluminum to form TMA alane occurs at moderate pressure and room temperature
- Solid reaction product ($C_3H_9N\text{-}AlH_3$) precipitates out of solution

Accomplishments: Bis-trimethylamine alane structure





C. W. Heitsch et al., *Inorg. Chem.* **2**, 508, 1963

- Solid product recovered by vacuum drying at room temperature
- Solid TMA alane forms a “bis” structure with two TMA ligands on each AlH_3 and appears to be highly soluble in toluene and Et_2O

Accomplishments:

Separation - Recovering AlH_3 from Adduct

AlH_3 can be recovered from AlH_3-TEA (TEA=triethylamine)

$$AlH_3\text{-}TEA \xrightarrow[3hrs]{70^\circ C} AlH_3 + TEA\uparrow$$

AlH_3-TEA does not form by direct hydrogenation but may be exchanged with another amine in a **transamination** step:

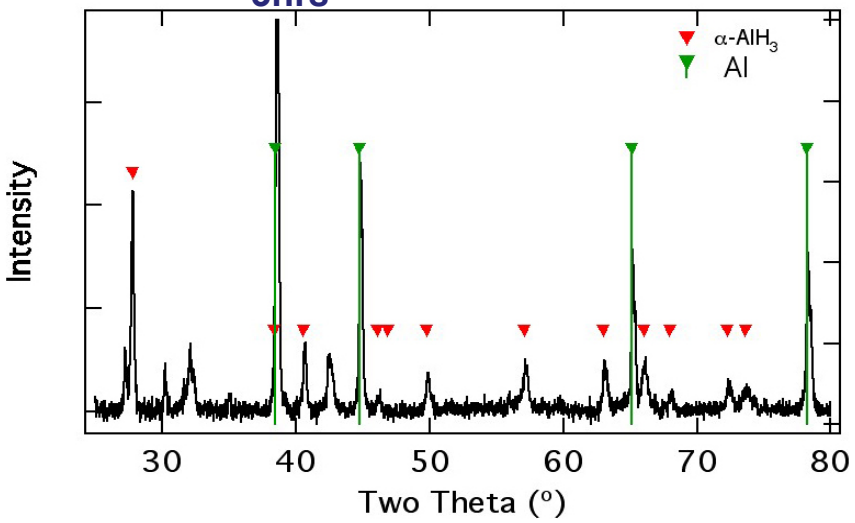
$$AlH_3\text{-}NR_3 + TEA \xrightarrow[3hrs]{50^\circ C} AlH_3\text{-}TEA + NR_3\uparrow$$

(Direction and rate of any reversible reaction is a function of concentration)

Full separation procedure:

$$AlH_3\text{-}NR_3 + TEA \xrightarrow[3hrs]{50^\circ C} AlH_3\text{-}TEA + NR_3\uparrow \xrightarrow[3hrs]{70^\circ C} AlH_3 + TEA\uparrow$$

DMEA alane separated using this procedure - XRD of recovered material shows AlH_3 + Al indicating further optimization is necessary



Accomplishments: Multi-Step Pathways

Two low energy pathways identified for complete regeneration of AlH_3 (each step verified independently)

Direct formation of AlH_3-DMEA:

$Al^* + 3/2\ H_2 + N(CH_3)_2\ CH_5 \rightarrow AlH_3 \cdot N(CH_3)_2CH_5$ ✓ demonstrated

Direct formation of AlH_3-TMA:

$Al^* + 3/2\ H_2 + N(CH_3)_3 \rightarrow (AlH_3) \cdot N(CH_3)_3$ ✓ demonstrated

Murib Patent 3,642,853

Amine exchange (transamination):

$AlH_3 \cdot N(CH_3)_2CH_5 + N(C_2H_5)_3 \rightarrow AlH_3 \cdot N(C_2H_5)_3 + N(CH_3)_2CH_5\uparrow$ ✓ demonstrated

Amine exchange (transamination):

$(AlH_3) \cdot N(CH_3)_3 + NR_3 \rightarrow AlH_3 \cdot N(C_2H_5)_3 + N(CH_3)_3\uparrow$ ✓ demonstrated

Decomposition and recovery:

$AlH_3 \cdot N(C_2H_5)_3 \rightarrow AlH_3\downarrow + N(C_2H_5)_3\uparrow$ ✓ demonstrated

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

Why Use AlH_3 in Slurry Form?

Motivation: Off-board regeneration and repeated refueling will be challenging with a powder delivery system. Some of these challenge may be mitigated with a slurry system, but how will a slurry impact the capacity and H_2 rates?

Definition of "Slurry": a pump-able solid/liquid mixture for a 3 minute refill

Advantages to Slurry Delivery:

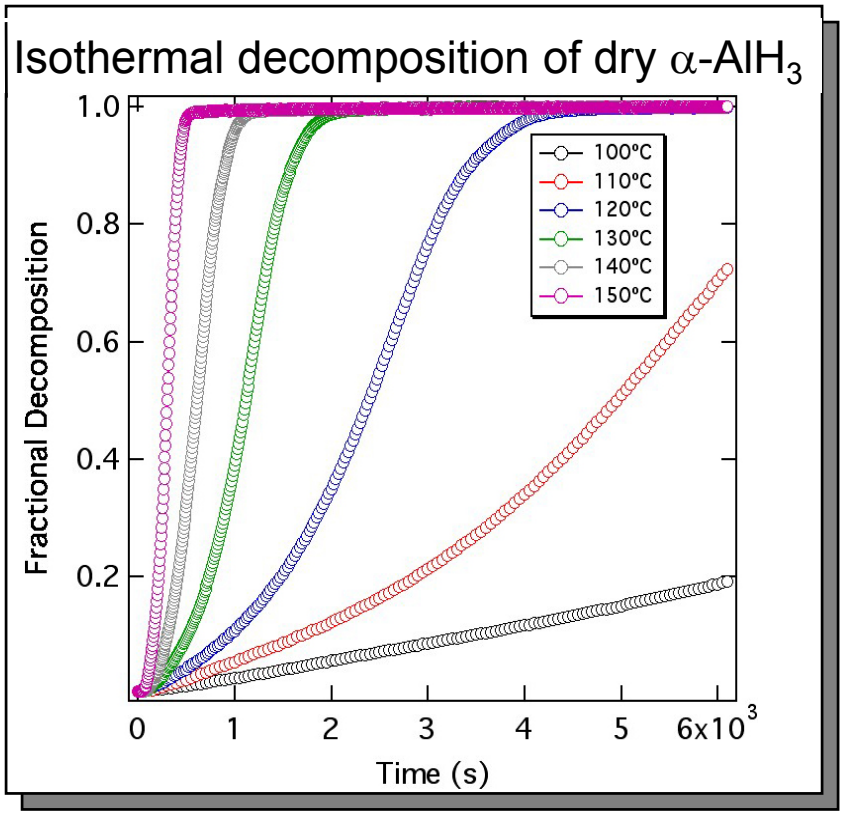
1. More quantitative transfer of hydrogen to the vehicle
2. Use of slurries speeds refueling of vehicle, removing spent AlH_3 from auto
3. May improve safety if slurry minimizes reactivity of AlH_3 to air

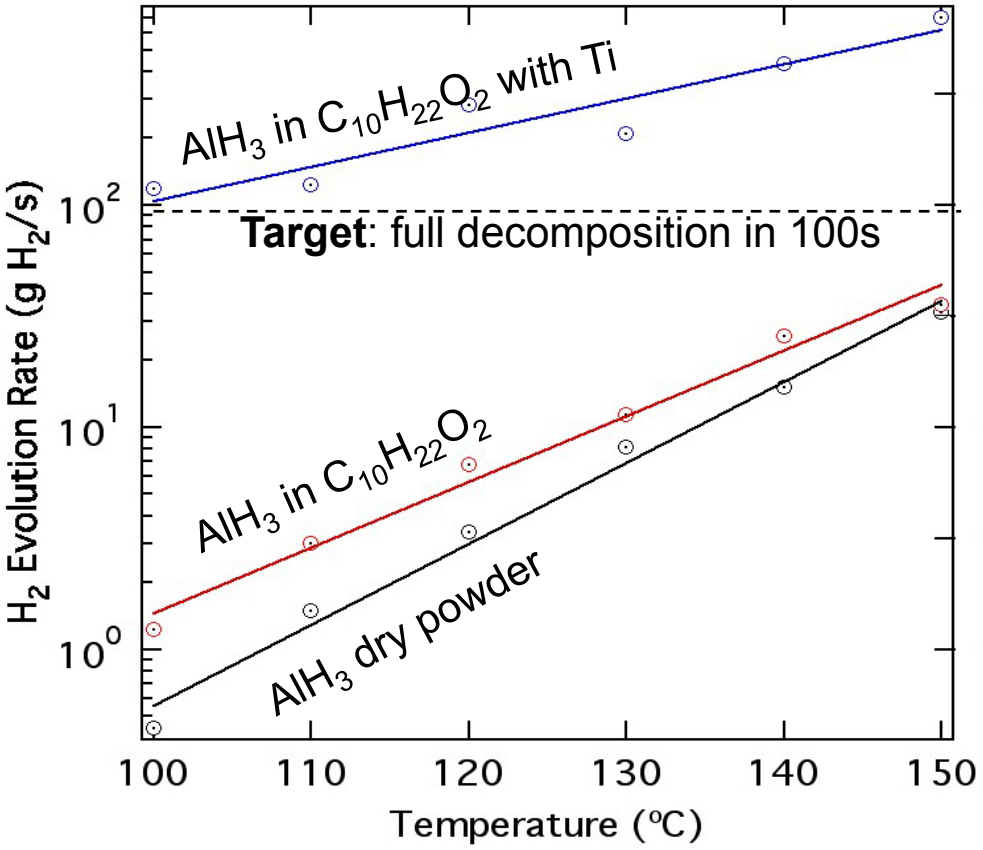
Challenges to Slurry Delivery:

1. Gravimetric Storage Density (less than 6% by wt.)
2. Engineering an onboard slurry fuel delivery system
3. Slurry pumped through external reactor will require full H_2 release in ~100s
4. Recovery from slurry for regeneration

Isothermal decomposition studies: (i) pure (dry) α-AlH_3
(ii) α-AlH_3 (20 wt%) in ethylene glycol dibutyl ether (Dibutoxyethane)
(iii) α-AlH_3 (20 wt%) in $C_{10}H_{22}O_2$ with 0.03 mol % Ti as $\{Ti(OB)_4\}$

Accomplishments: AlH_3 Slurries





- Dry α-AlH_3 requires T > 150° C to achieve full H_2 release in ~100s (target)
- α-AlH_3 in ethylene glycol dibutyl ether ($C_{10}H_{22}O_2$) showed faster H_2 rates
- Ti catalyzed α-AlH_3 in $C_{10}H_{22}O_2$ meets target (full decomp in 100s at 100°C)

Summary of Accomplishments

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

Major accomplishments (FY09):

(1) Four new pathways identified to form AlH_3 adducts from H_2 and Al

- Quinuclidine alane: $C_7H_{13}N + Al^* + 3/2H_2 \rightarrow C_7H_{13}N\text{-}\mathbf{AlH_3}$
- Dimethylethylamine alane: $C_4H_{11}N + Al^* + 3/2H_2 \rightarrow C_7H_{13}N\text{-}\mathbf{AlH_3}$
- Hexamine alane: $C_6H_{12}N_4 + Al^* + 3/2H_2 \rightarrow C_6H_{12}N_4\text{-}\mathbf{AlH_3}$
- Trimethylamine alane: $C_3H_9N + Al^* + 3/2H_2 \rightarrow C_3H_9N\text{-}\mathbf{AlH_3}$

(2) Improved adduct separation by introducing transamination step

(3) Two low energy pathways identified for complete regeneration of AlH_3 using TMA and DMEA (each step verified independently)

(4) Preliminary results on H_2 evolution rates from AlH_3 in slurries showed promising results for Ti catalyzed AlH_3 in $C_{10}H_{22}O_2$

Proposed Future Work

Remainder of FY09

(i) Improve and optimize regeneration pathways:

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

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

(ii) Demonstrate complete regeneration cycle and determine efficiency

(iii) Slurries: increase mass loading and investigate other liquid carriers

FY10 - completion

(i) Regenerate AlH_3 with *E* penalty ≤73 kJ/H_2 (30% of fuel energy)

(ii) Work with partners (ANL) to determine mass balance & energy cost

(iii) Continue investigation of alane slurries and liquid carriers

(iv) Work with partners on safety and engineering of alane system

Additional Slides

Methods and Materials

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

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

$$4AlH_3 \bullet Et_2O + 0.08Ti \xrightarrow[2\ hrs]{100\,^{\circ}C} 4Al + 0.08Ti$$

- 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

Theory Guides Choice of Adduct

1:1 Complexes	Al-N BDE* (kJ/mole)	1:2 Complexes	Al-N BDE* (kJ/mole)
AlH_3--NH_3	**142.7**	—	—
AlH_3--NMe_3	**147.6** ,**DFT: (108.1)**	AlH_3--$2NMe_3$	**217.9 (145.9)**
AlH_3--NEt_3	**118.6 (89.1)**	AlH_3--$2NEt_3$	**158.7 (90.9)**
AlH_3--TEDA	**156.3 (115.4)**	AlH_3--2TEDA	**233.8 (155.4)**
AlH_3--Quinuclidine	**159.9 (118.4)**	AlH_3--2Quinuclidine	**236.7 (156.0)**
AlH_3--pyridine	**135.2 (109.2)**	AlH_3--2pyridine	**193.3 (142.1)**
AlH_3--pyrazine	**125.3**	AlH_3--2pyrazine	—

- BDE = Energy to dissociate to AlH_3 + all ligands
- **Blue: BAC-MP2**; **Red: DFT/B3LYP** (McGrady et al., UNB)

Strongest Al-N Bond: AlH_3--quinuclidine; weakest Al-N Bond: AlH_3--$N(C_2H_5)_3$
1:2 complexes (e.g. (AlH_3)--2pyrazine): significantly less stable
1:2 complexes: Kinetics governed by Al-N in 1:1 (Al-N bond in 1:2 is weaker)
BAC absolute values differ from DFT predictions, but trends are similar