

Aluminum Hydride Regeneration

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Project ID #
ST 034

Overview

Timeline

- Project start date: FY05
- Project end date: FY10
- 100 % complete

Budget

- Expected total project funding:
 - \$4.00M (DOE)
- Funding received in FY09
 - \$1.25M (DOE)
- Planned Funding for FY10
 - \$800K (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

MHCoE Partners and Collaborators

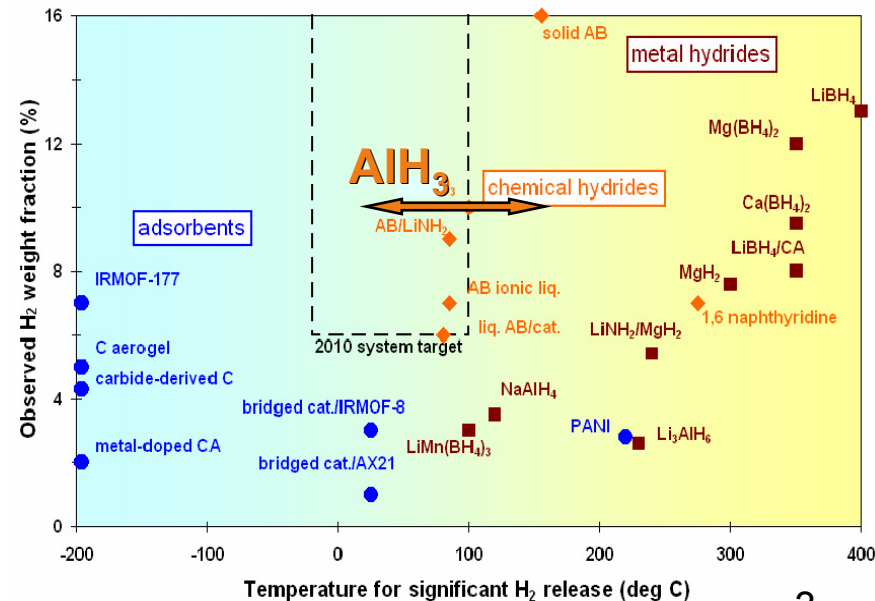
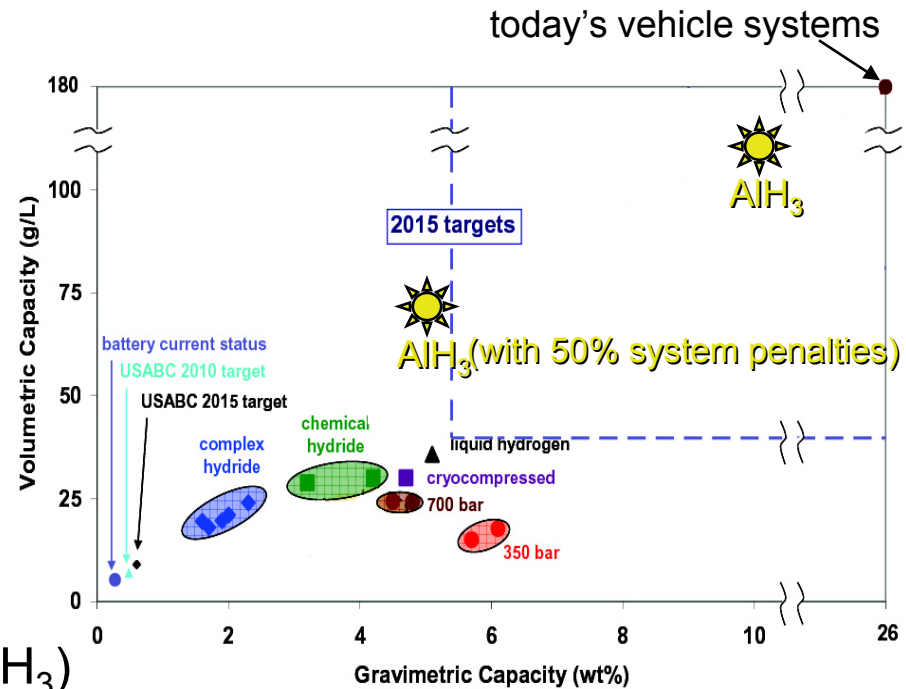
- Project D (aluminum hydride) Lead
 - UH-UNB, ORNL, SRNL, SNL
- Other collaborations: JPL, UIUC, ANL
- Chemical Hydride Center
- International Energy Agency (IEA)

Relevance: AlH_3

- High capacity: **10.1 wt%** and **149 g/L**
- Low decomposition enthalpy:
 $\Delta H \approx 7 \text{ kJ/mol H}_2 (\approx 1/5 \Delta H_{\text{NaAlH}_4})$
- Rapid H_2 evolution rates at low T
 Meets DOE target (0.02 gH_2/s) at 104°C
 (80 kW FC with 45% efficiency & 100 kg AlH_3)
- Decomposition rates can be tuned through particle size and coatings
- High purity H_2 - AlH_3 decomposes to Al and H_2 (no side reactions)

Challenge: AlH_3 not “on-board” reversible

Objective: Develop low energy pathway to regenerate AlH_3



Approach

Objective: Meet 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: These 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)

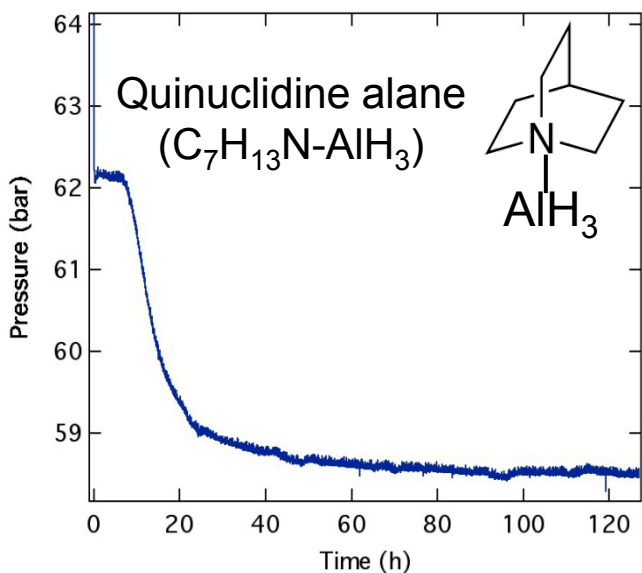
Step II: Remove stabilizing species and recover AlH_3

Accomplishments: Previous results

- Demonstrated a low-energy regeneration route for LiAlH_4 :

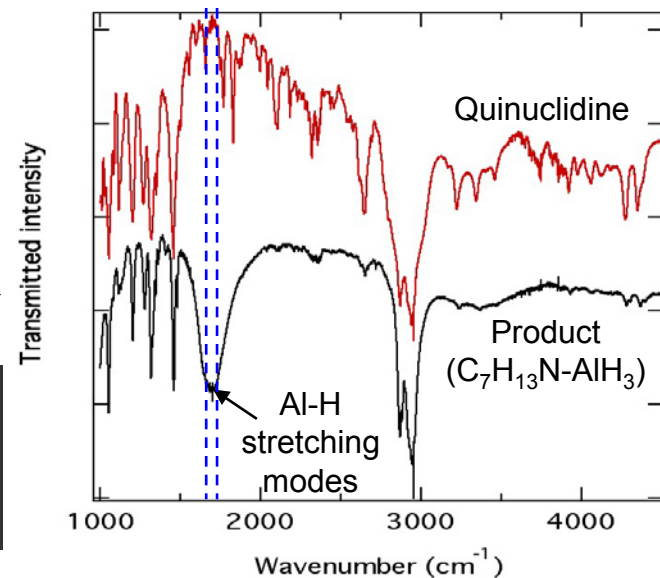


- Demonstrated the direct formation of AlH_3 from Al^* and H_2 under mild conditions using amines: $\text{C}_7\text{H}_{13}\text{N} + \text{Al}^* + 3/2\text{H}_2 \rightarrow \text{C}_7\text{H}_{13}\text{N-AlH}_3$



Pressure drop indicates hydrogenation of Al occurs at low pressures

Al-H stretch in FTIR confirms formation of AlH_3



- Preliminary results on H_2 evolution rates from AlH_3 in slurries

Accomplishments: New results

Revised regeneration procedure to incorporate transamination

Step 1: formation of $\text{NR}_3\text{-AlH}_3$ by direct hydrogenation

- Five alane adducts formed by direct hydrogenation under mild conditions (**complete** - no longer investigating new adducts)
- Alane adducts also formed by reacting amine directly with alane

Step 2: transamination exchange NR_3 for TEA

- Transamination demonstrated starting with DMEA and TMA (**complete** - may need follow up to decrease time, temp., ...)

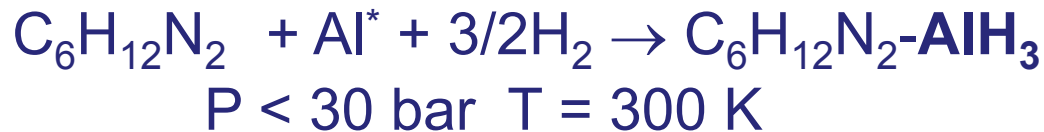
Step 3: separation of TEA-AlH_3

- Separation of TEA-AlH_3 successful with ~70% AlH_3 recovery (additional optimization is necessary to improve yields)

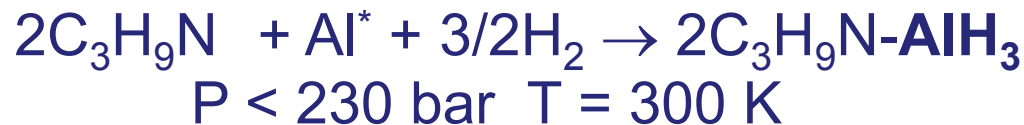
- Ongoing effort to combine steps 1-3 and optimize yield and efficiency
- Well-to-tank efficiency estimates of 40-55% using this route with TMA (WTT target is 70%)

Step 1: Low pressure AlH₃ formation

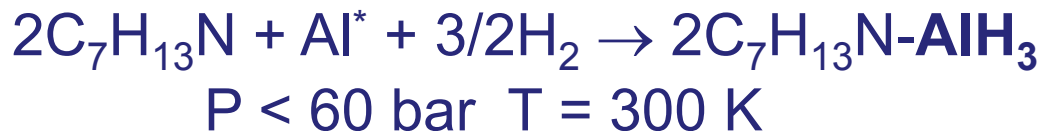
Triethylenediamine (TEDA) alane:



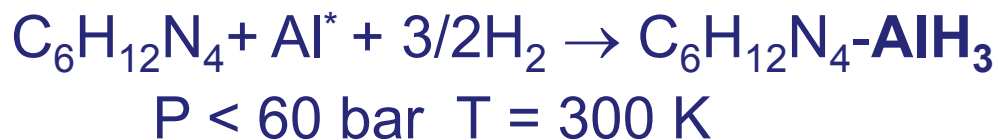
Trimethylamine (TMA) alane:



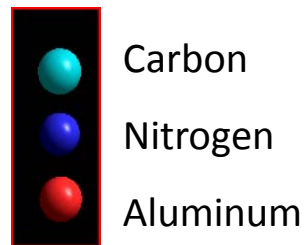
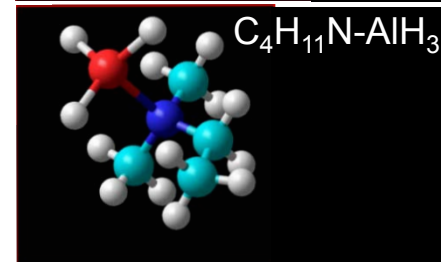
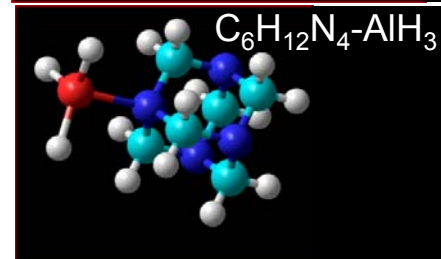
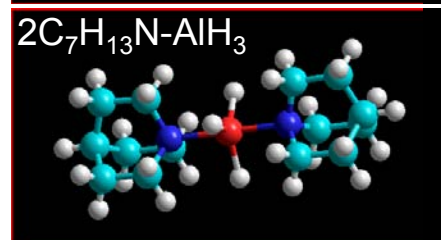
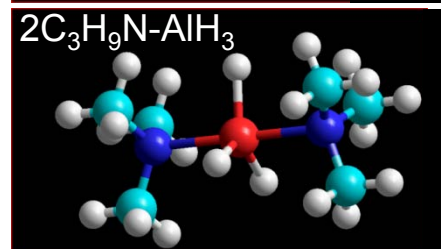
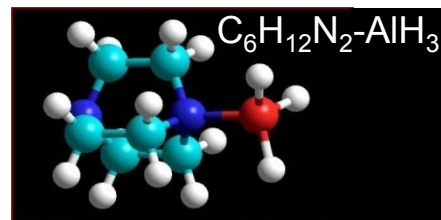
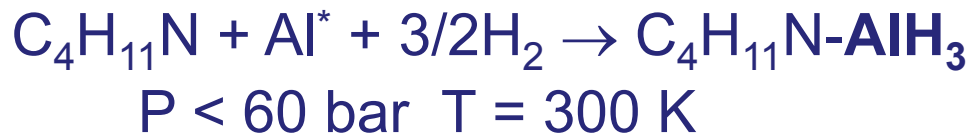
Quinuclidine alane:



Hexamine alane:



Dimethylethylamine (DMEA) alane:

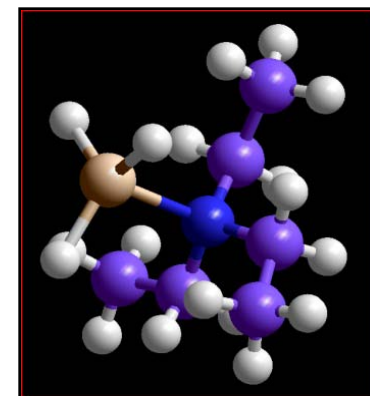


Step 1: Adduct Formation

- No success retrieving AlH_3 from any of the five alane amines synthesized by direct hydrogenation - adducts decompose upon heating
- Identified only one amine alane, triethylamine alane (TEA-AlH_3), that can be separated to recover pure $\alpha\text{-AlH}_3$



- TEA-AlH_3 cannot be formed by direct hydrogenation only by a direct reaction with AlH_3



...we found other adducts formed by same method:



TEA-alane and transamination

- No success separating any of the five alane amines synthesized by direct hydrogenation - adducts decompose upon heating
- Triethylamine alane (TEA-AlH₃) can be separated to recover AlH₃

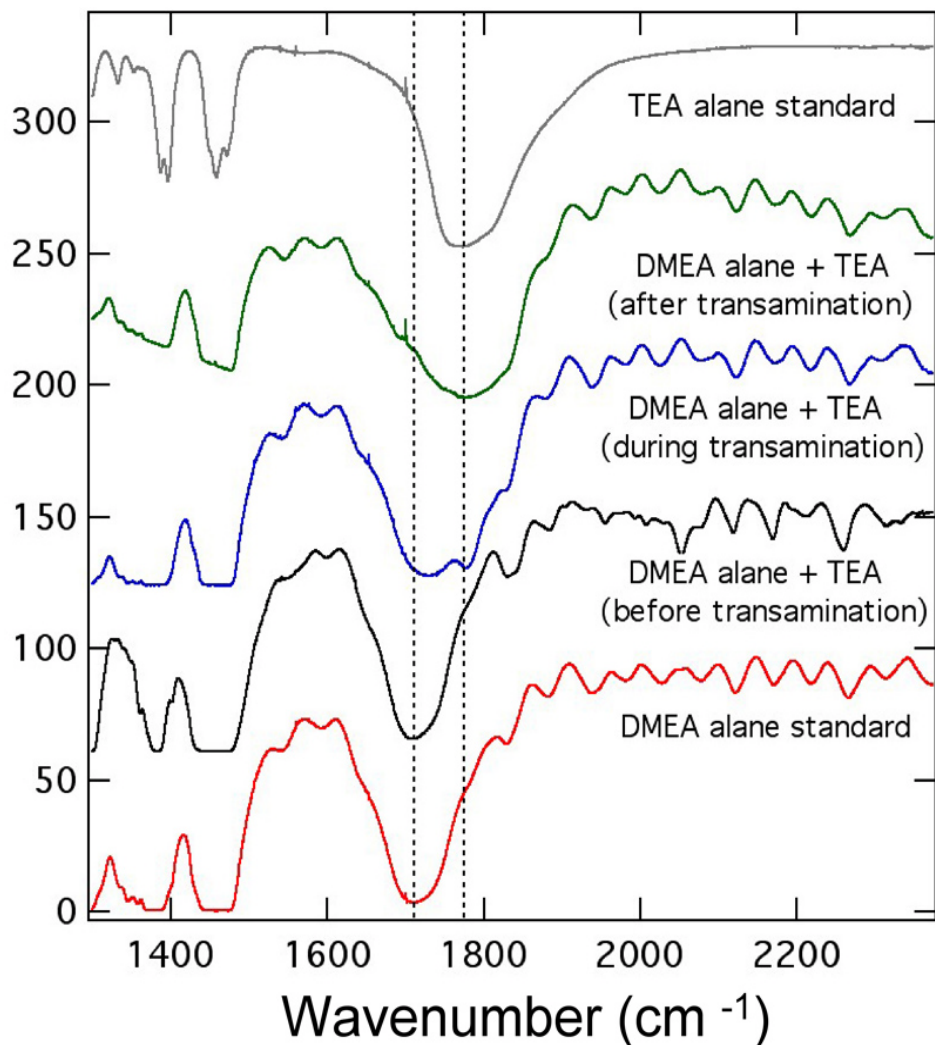


Since it is the only amine alane that is easily separated, TEA-AlH₃ is a critically important compound for the regeneration process...

...but TEA-AlH₃ does not form by direct hydrogenation (from H₂)

- Can we use an exchange or **transamination** reaction to form AlH₃-TEA from another amine alane (NR₃-AlH₃) that forms more readily?
- Possibly, but exchange is thermodynamically uphill so we need to maintain a high concentration of TEA and preferentially remove NR₃ to drive reaction
- Fortunately, TEA-AlH₃ has a low vapor pressure so all we need is an amine (NR₃) with a high Vp that forms a stable NR₃-AlH₃ adduct: **TMA and DMEA**

Step 2: amine exchange (transamination)



Transamination reaction to form TEA- AlH₃ from DMEA-AlH₃



DMEA-AlH₃ + 4TEA
T = 50°C
Pi = 1 bar
Pf = 26 mbar
time = 4.5 hrs

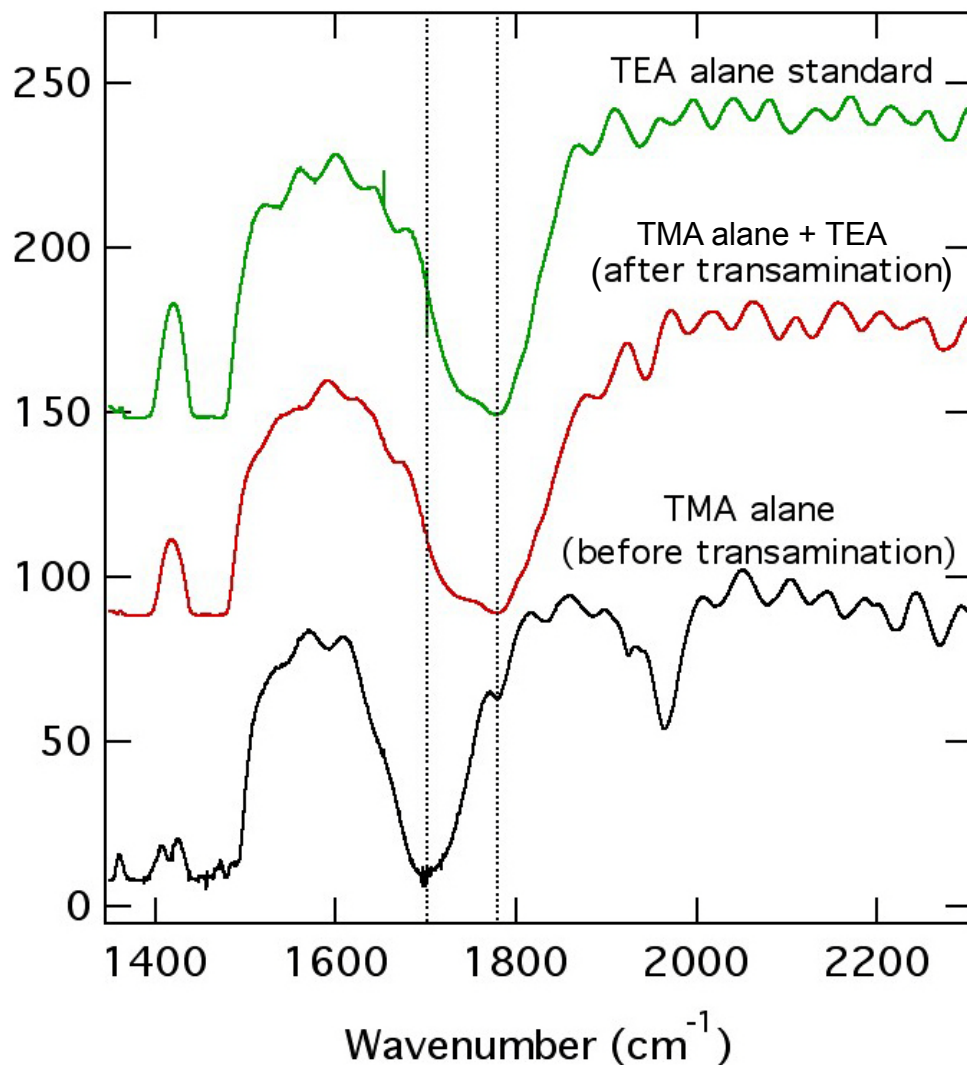
Al-H stretch in FTIR used to identify type of adduct:

DMEA-AlH₃: ~1710 cm⁻¹

TEA-AlH₃: ~1780 cm⁻¹

FTIR confirms final product after transamination is TEA-AlH₃

Step 2: amine exchange (transamination)



Transamination reaction to form TEA- AlH_3 from TMA- AlH_3



TMA- AlH_3 + 4TEA
T = 50°C
 N_2 flow (P = 1 bar)
time = 2 hrs

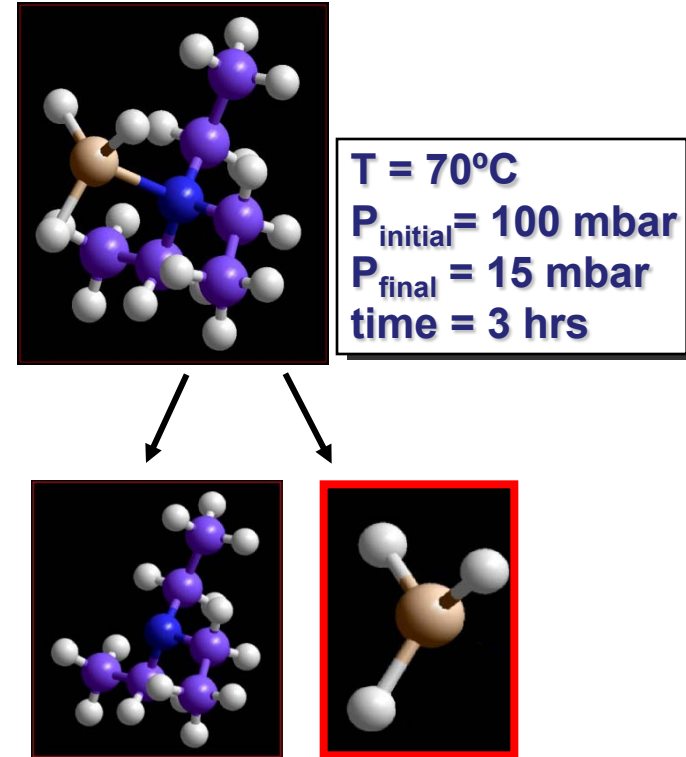
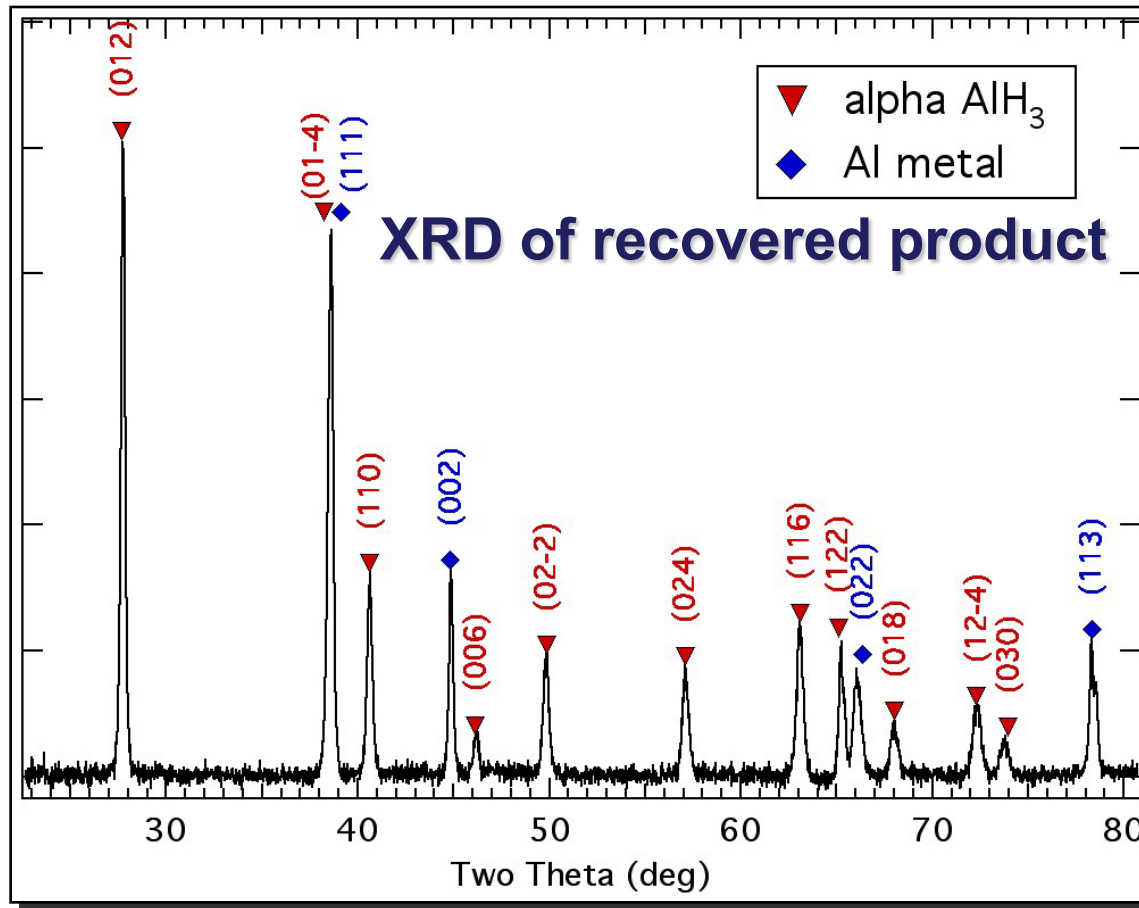
Al-H stretch in FTIR used to identify type of adduct:

TMA- AlH_3 : $\sim 1700 \text{ cm}^{-1}$

TEA- AlH_3 : $\sim 1780 \text{ cm}^{-1}$

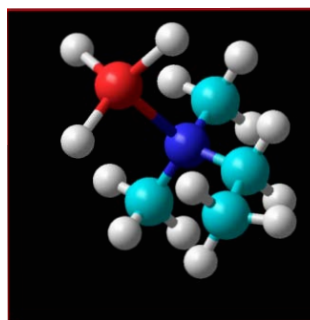
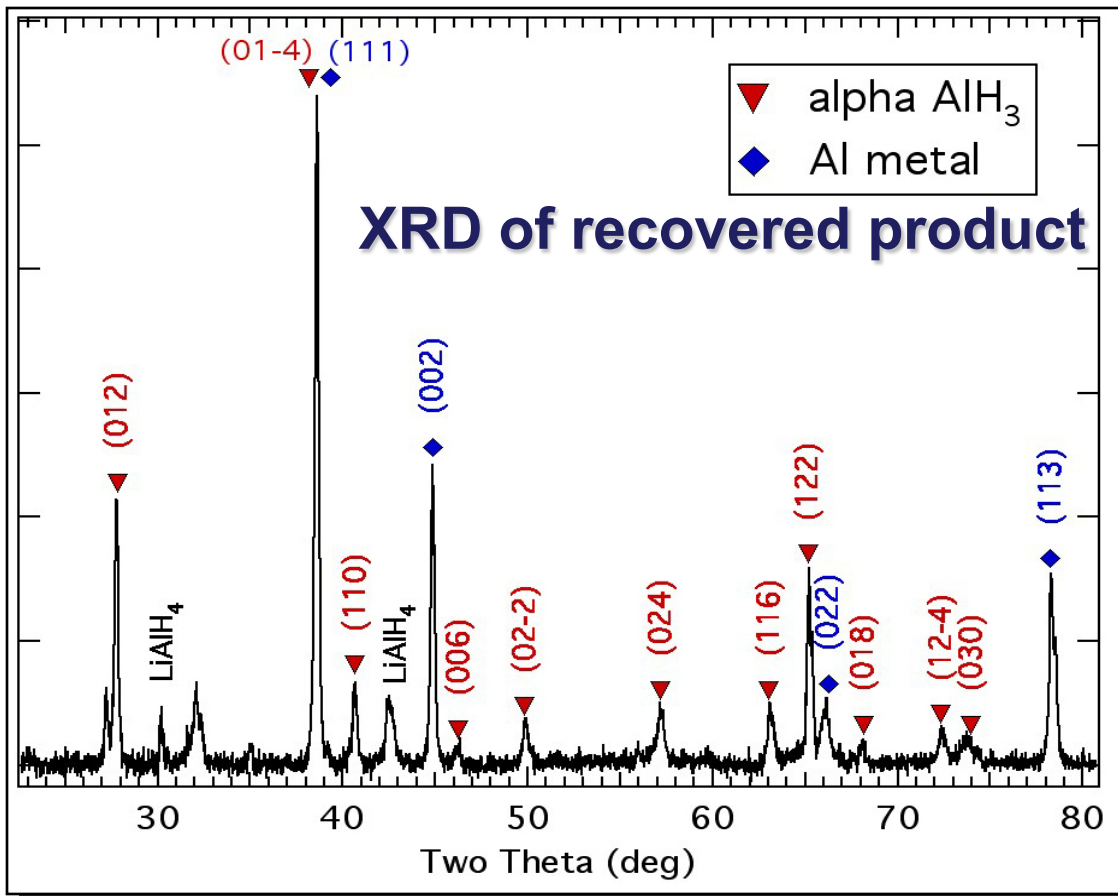
FTIR confirms final product after transamination is TEA- AlH_3

Step 3: Separation of TEA-AlH₃

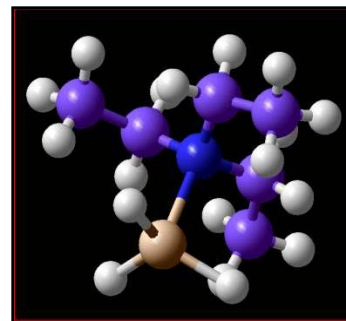


- TEA-AlH₃ successfully separated at 70°C under vacuum (<100 mbar)
- Analysis of recovered AlH₃ (XRD and decomposition) suggests ~70% AlH₃ with 30% Al

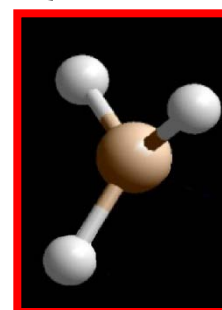
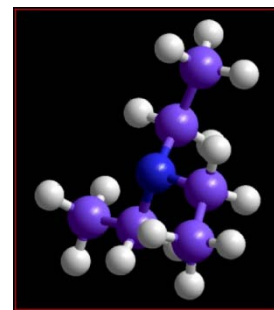
Combining step 2 + 3: Separation of DMEA-AIH₃



T = 50°C
P_{initial} = 270 mbar
P_{final} = 26 mbar
time = 2 hrs



T = 75°C
P_{initial} = 220 mbar
P_{final} = 5 mbar
time = 4.5 hrs



- DMEA-AIH₃ separated by combining steps 1 & 2
- Analysis of recovered AIH₃ (XRD) suggests ~35% AIH₃ with 65% Al when steps 1 & 2 are combined
- Improvements expected with optimization & washes to remove unwanted material

Energy consumption for AlH_3 regeneration (per kg H_2 in AlH_3)

Process (TMA route)	Operating Conditions			Q, MJ	E, kWh
	T, °C	P, bar	Reflux ratio		
Compress H_2 from SMR to 30 bar	70	30			0.3
Compress circulating H_2 to 30 bar	70	30			0.6
Distill trimethylamine	65	5	1.0	28.6	
Distill ether	25	0.3	0.3	22.9	1.1
Decompose triethylamine alane	50	0.2		20.2	1.4
Vacuum dry alane product	50	$10^{-4} - 10^{-1}$		0.2	0.2
Total				71.9	3.6

- Without using wasted heat, well-to-tank (WTT) efficiency is 40.5%
- Using wasted heat for thermal energy increases WTT to 55%
- **Target is 70%** - improvements possible by reducing excess H_2 , TMA and TEA, switching to gas flow (rather than vacuum) and using DMEA

Collaborations

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

<u>BNL (POC)</u>	<u>SRNL</u>	<u>U. Hawaii/UNB</u>	<u>ORNL</u>
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)

Industrial Partnerships

- We submitted a Navy STTR (N10A-T030) with Aspen Products to synthesize and characterize micron-sized AlH_3 particles for marine applications
- **A number of companies are interested in using AlH_3 in portable power systems and have contacted us requesting material or information**

Summary of Accomplishments

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

Major accomplishments:

Step 1: Five pathways identified to form AlH_3 adducts from H_2 and Al

.Triethylenediamine $\text{C}_6\text{H}_{12}\text{N}_2 + \text{Al}^* + 3/2\text{H}_2 \rightarrow \text{C}_6\text{H}_{12}\text{N}_2\text{-AlH}_3$

.Quinuclidine alane: $\text{C}_7\text{H}_{13}\text{N} + \text{Al}^* + 3/2\text{H}_2 \rightarrow \text{C}_7\text{H}_{13}\text{N-AlH}_3$

.Dimethylethylamine alane: $\text{C}_4\text{H}_{11}\text{N} + \text{Al}^* + 3/2\text{H}_2 \rightarrow \text{C}_4\text{H}_{11}\text{N-AlH}_3$

.Hexamine alane: $\text{C}_6\text{H}_{12}\text{N}_4 + \text{Al}^* + 3/2\text{H}_2 \rightarrow \text{C}_6\text{H}_{12}\text{N}_4\text{-AlH}_3$

.Trimethylamine alane: $2\text{C}_3\text{H}_9\text{N} + \text{Al}^* + 3/2\text{H}_2 \rightarrow 2\text{C}_3\text{H}_9\text{N-AlH}_3$

←
Most promising

Step 2: Transamination demonstrated with high yields for DMEA and TMA using dynamic vacuum and inert gas sweep methods

Step 3: TEA- AlH_3 separated with ~70% recovered AlH_3

• ANL analysis of WTT efficiency suggests 55% possible with TMA route using waste heat

Proposed Future Work

- Improve and optimize regeneration pathways:



- Regenerate AlH_3 with E penalty ≤ 73 kJ/ H_2 (70% Efficiency)
- Continue work with ANL to determine mass balance & energy cost for revised/improved regeneration method (TMA & DMEA)
- Continue investigation of alane slurries and liquid carriers - develop procedures to tune AlH_3 particle size during regeneration
- Work with partners on safety and engineering of alane system

Supplemental Slides

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