Aluminum Hydride:

the organometallic approach

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BROOKHAVEN NATIONAL LABORATORY

Project ID #
ST 034

Overview

Timeline

- Project start date: FY10
- Project end date: Continuing

Barriers

MYPP Section 3.3.4.2.1 On-Board Storage Barriers:

- Weight & Volume
- Efficiency
- Durability/Operability
- Charge/Discharge Rates

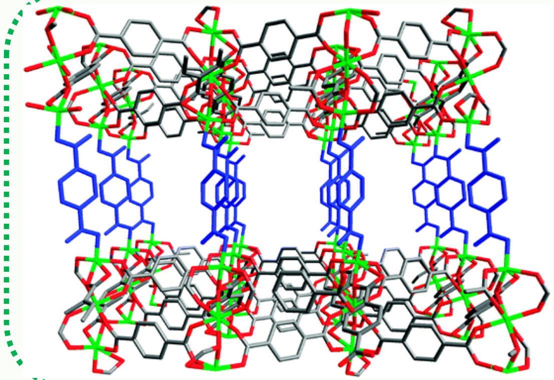
Budget

- Funding received in FY12
  – $250K (DOE)
- Planned Funding for FY13
  – TBD (DOE)

Target

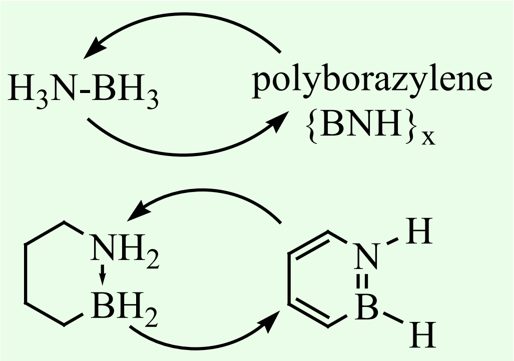
Material development for meeting the packaging, safety, **cost** and driving range (greater than 300 miles) DOE performance targets for the PEM hydrogen fuel vehicle.

Hydrogen storage materials:



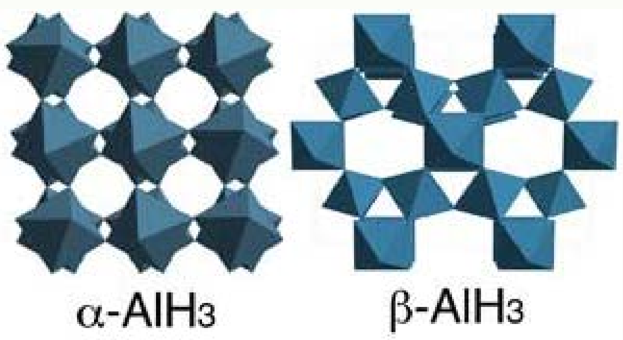
Metal-Organic Frameworks (MOF):

- physical adsorption/weak interaction;
- ***low*** H_2 weight percentage;
  (high mass of the MOF)
- low temperature (such as 77 K).



Amine-Borane Compounds:

- ***high*** H_2 percentage (19.6% vs. 14.2%);
- dehydrogenation well-studied (catalysis);
- rehydrogenation remains challenging.



Metal-Hydrides:

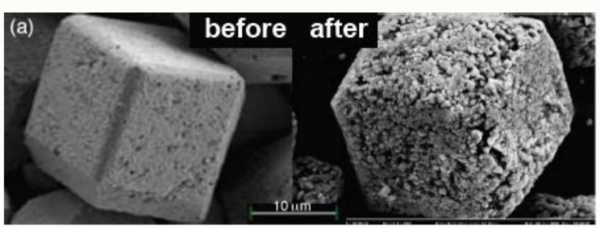
- LiH, MgH_2, **AlH_3**, $LiAlH_4$, and others;
- most of the hydrides are *quite stable*;
- rehydrogenation is challenging.

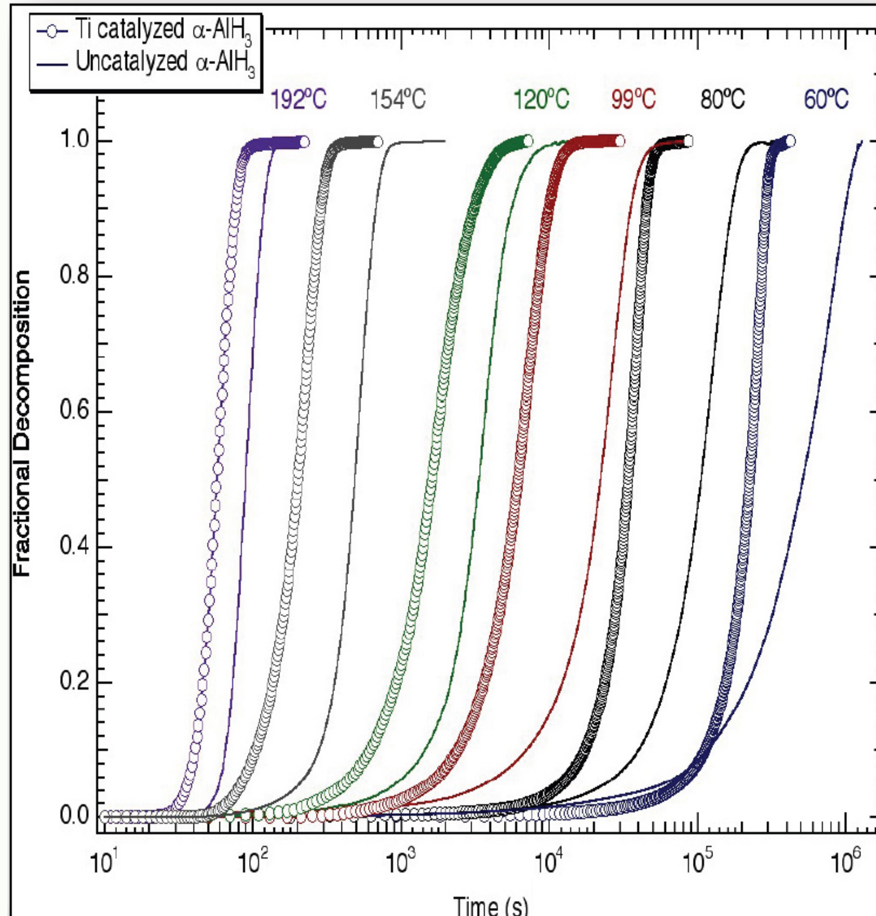
Chem. Soc. Rev. **2009,** *38,* 73; *Angew. Chem. Int. Ed.* **2012**, *51*, 6074.

Aluminum hydride (alane, AlH_3):

$$AlH_3 \longrightarrow Al + \frac{3}{2} H_2$$

- High capacity: **10.1 wt%** and **1.48 g/L**;
- 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 (0.02 gH_2/s) at < 100ºC
- High purity H_2:
  no side reaction for the decomposition reaction
- Decomposition rates can be tuned by:
  particle sizes and ***coatings***





- Ti lowers the activation energy of the decomposition reaction;
- AlH_3 is completely unstable at Ti concentrations $\geq$ 0.1 mol%.

J. Alloys Compd. **2007**, *446*, 271.

Synthesis of AlH_3:

Conventional synthesis:

$$3\ LiAlH_4 + AlCl_3 \xrightarrow{Et_2O} 3\ LiCl + 4\ AlH_3(Et_2O)_n$$

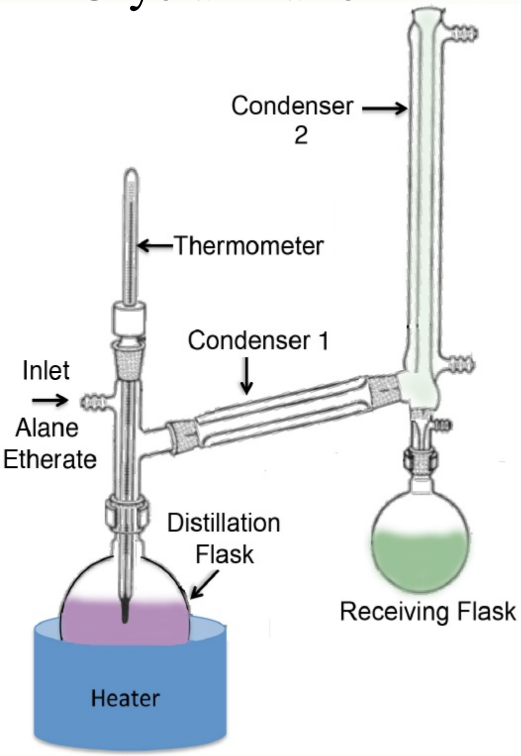
↓ filtration

$AlH_3(Et_2O)_n$

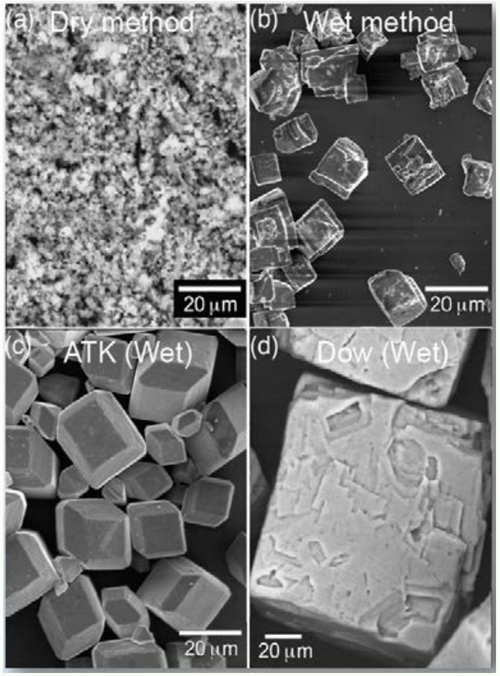
↓ desolvation/crystallization

AlH_3 polymorph

Crystallization



Morphology



Too expensive!

Direct hydrogenation:

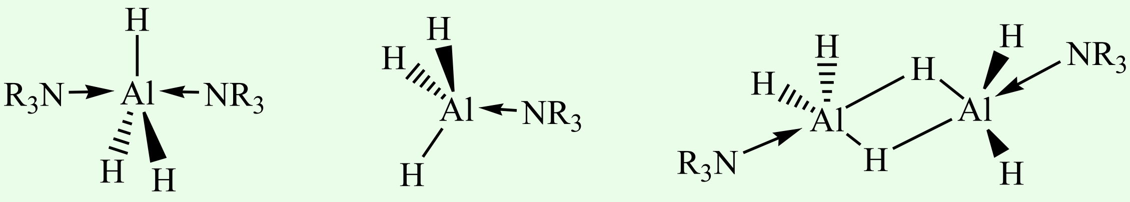
$$Al + \frac{3}{2} H_2 \xrightarrow{?} AlH_3$$

- ΔH_f = -9.9 ± 0.6 kJ/mol AlH_3; $\Delta G_{f\,(298K)}$ = 48.5 ± 0.6 kJ/mol AlH_3;
- **$P_{298K} \approx 10^5$ atm** (***too high*** for practical applications).
- AlH_3 only formed ***on the surface*** of Al metal;

J. Alloys Compd. **2007**, *446*, 271.

The organometallic approach:

➢ Common amine·alane structural types:



(I) (II) (III)

NR_3 is an amine.

➢ The 3-step regeneration process:

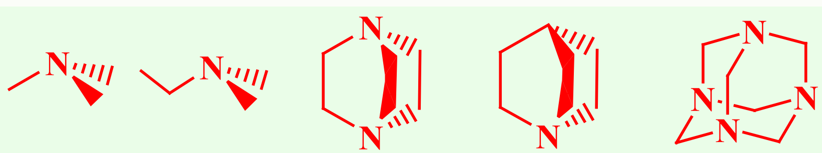
Hydrogenation: $\text{Al} + 2\,\textbf{amine}^1 + \frac{3}{2}\text{H}_2 \xrightarrow{\text{catalyst}} (\textbf{amine}^1)_2\cdot\text{AlH}_3$ (1)

Transamination: $(\textbf{amine}^1)_2\cdot\text{AlH}_3 + \textbf{amine}^2 \xrightarrow[\text{heat}]{\text{vacuum}} \textbf{amine}^2\cdot\text{AlH}_3 + 2\,\textbf{amine}^1\uparrow$ (2)

Decomposition: $\textbf{amine}^2\cdot\text{AlH}_3 \xrightarrow[\text{heat}]{\text{vacuum}} \textbf{AlH}_3 + \textbf{amine}^2\uparrow$ (3)

➢ The "Parodox" and challenges:

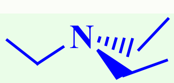
Amine^1:



TMA **DMEA** **TEDA** **quinuclidine** **hexamine**

- Strong amines, type I structure;
- Facilitate hydrogenation;
- Decomposition to Al metal directly.

Amine^2:



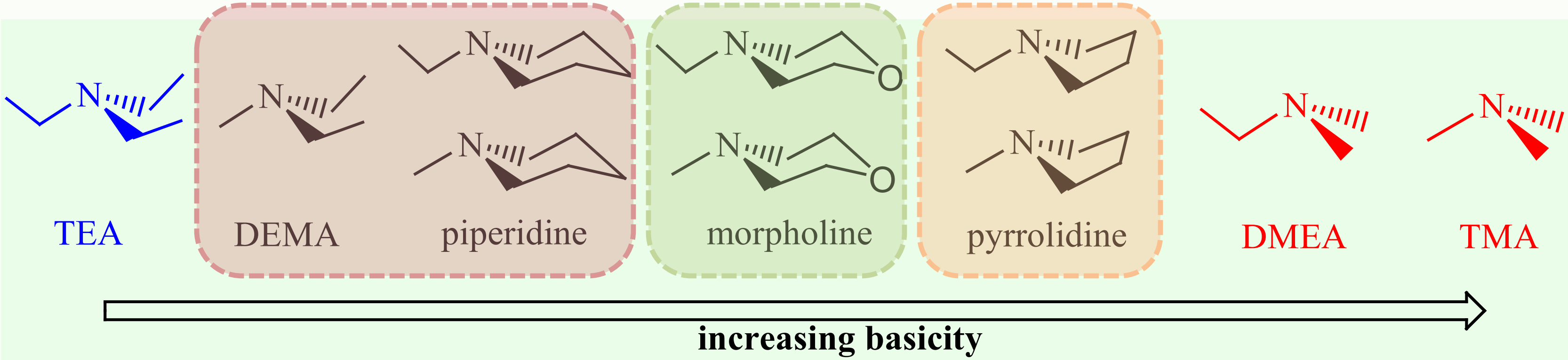
TEA

- Weak amines, type II or III structures;
- Decomposes to AlH_3 (with Al contamination;
- **Does not** facilitate hydrogenation.

Phys. Rev. B. **2006**, *74*, 214114;
Chem. Soc. Rev. **2009**, *38*, 73.

Approaches to the project:

- **Tune the Lewis Basicity of amines:**



- **Objectives:**

1. Search for an amine that facilitate both hydrogenation and decomposition:

$$\mathrm{Al} + 2\,\mathbf{amine^1} + \frac{3}{2}\mathrm{H_2} \xrightarrow{\text{catalyst}} (\mathbf{amine^1})_2\cdot\mathrm{AlH_3} \xrightarrow[\text{heat}]{\text{vacuum}} \mathbf{AlH_3} + 2\,\mathbf{amine^1}\uparrow$$

   - Reduce energy input and chemical costs
   - Increase the efficiency of the process

2. Optimize the transamination and thermal decomposition steps:

$$\mathbf{TEA}\cdot\mathrm{AlH_3} \xrightarrow[\text{heat}]{\text{vacuum}} \mathbf{AlH_3} + \mathbf{TEA}\uparrow$$

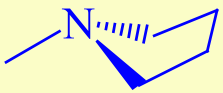
$$\mathbf{TEA}\cdot\mathrm{AlH_3} \xrightarrow[\text{heat}]{\text{vacuum}} \mathbf{Al + TEA + H_2}$$

$$\mathbf{TEA}\cdot\mathrm{AlH_3} \xrightarrow[\text{heat}]{\text{vacuum}} \mathbf{Evaporation}$$

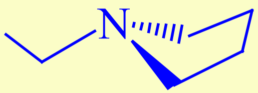
   - Suppress Al formation and alane evaporation
   - Increase the yield and purity of AlH_3

- *unpublished results*
- *ROI filed/manuscripts*
- *manuscript accepted*

Synthesis of alane adducts:

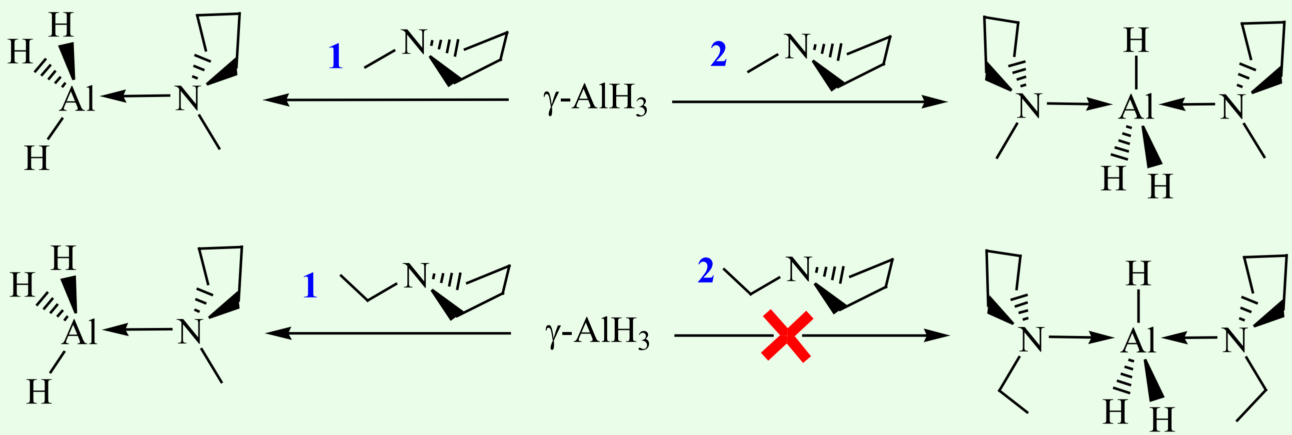


N-methylpyrrolidine
(NMPy)

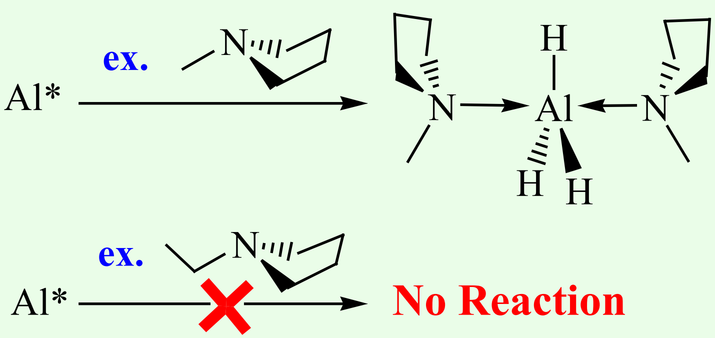


N-ethylpyrrolidine
(NEPy)

Direct synthesis:



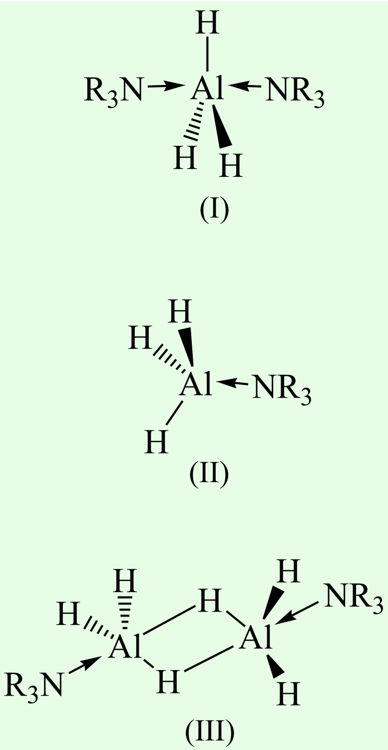
Hydrogenation:

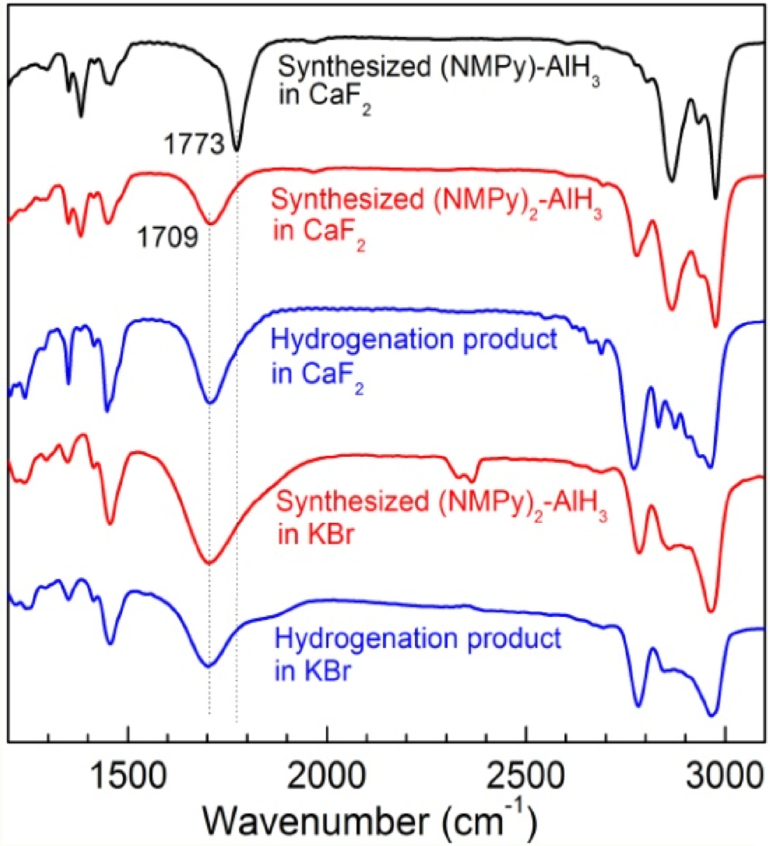


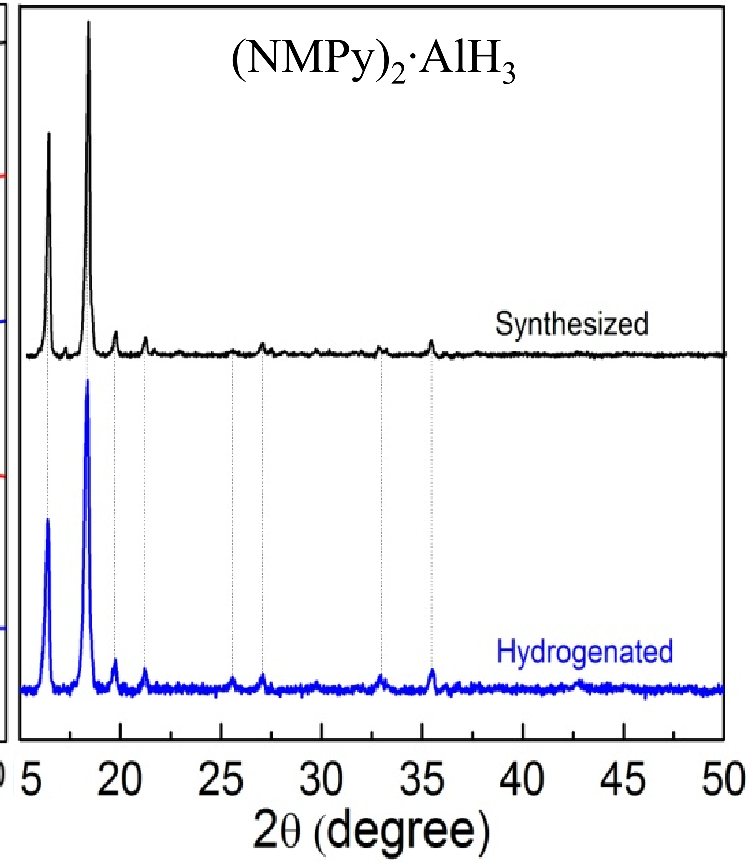
- Reactor set-up:
- H_2 pressure: ~ 1000 psi;
- Temperature: 0 ~ 25ÁC;
- Chemicals: Et_2O (80 mL) and amine (20 mL);
- Al*: Ti doped Al metal, ~ 2.0 g.

J. Phys. Chem. C. Just accepted;
DOI: 10.1021/jp310848u

Characterization (NMR, IR, and XRD):



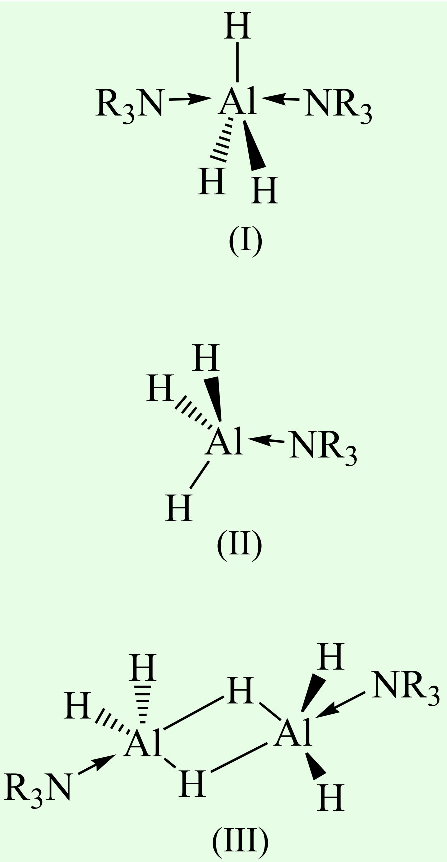


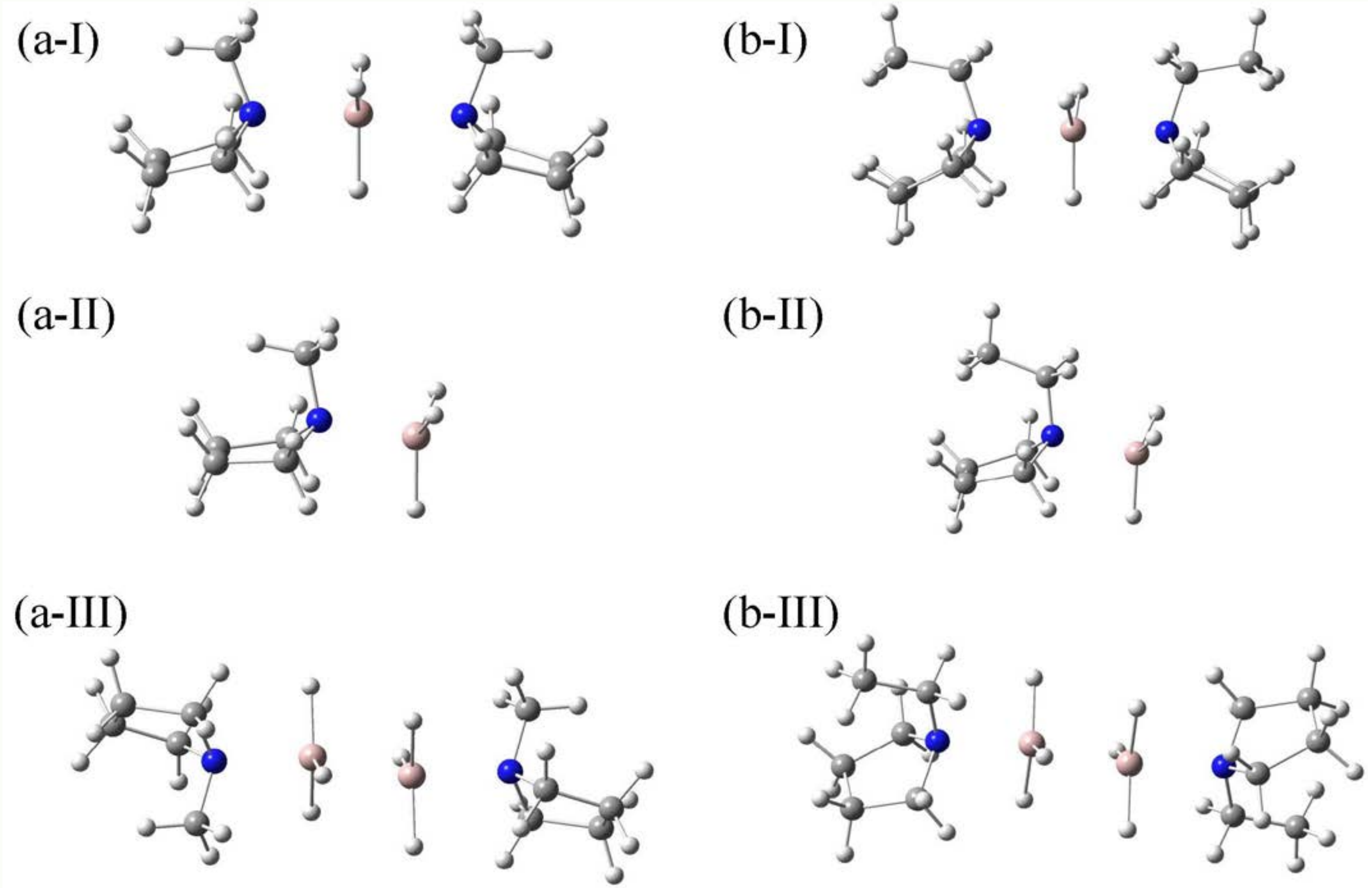


Al-H stretching frequencies (cm^{-1}):

alane adduct	Calculation			Experiment
	Type I	Type II	Type III	
NMPy	**1700**	**1789**	1598, 1793	**1709** (2:1), **1773** (1:1)
NEPy	1700	**1789**	1598, 1793	**1773** (1:1)

Theoretical calculations:

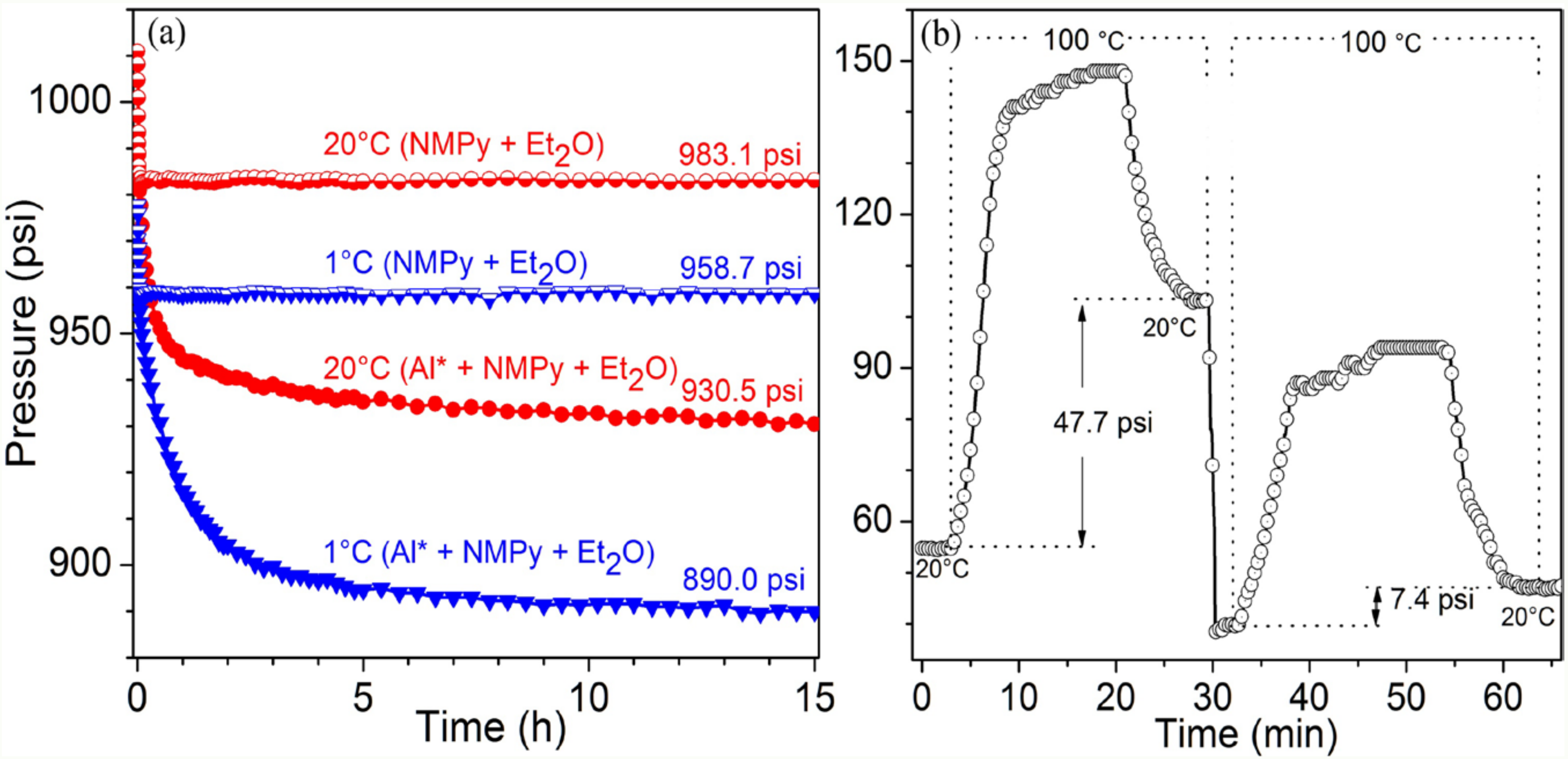




alane adduct	Binding Free Energy in Et_2O with BSSE Correction ($kcal \cdot mol^{-1}$)		
	Type I	**Type II**	Type III
NMPy	-19.91	**-22.11**	-18.57
NEPy	-14.72	**-19.49**	-15.94
Et_2O	-13.24	**-15.92**	-13.77

Reversible formation of $(NMPy)_2 \cdot AlH_3$:

$$2\,\mathrm{NMPy} + \mathrm{Al^*} + \frac{3}{2}\mathrm{H_2} \underset{\text{heat}}{\overset{\mathrm{Et_2O}}{\rightleftharpoons}} (\mathrm{NMPy})_2\cdot\mathrm{AlH_3}$$



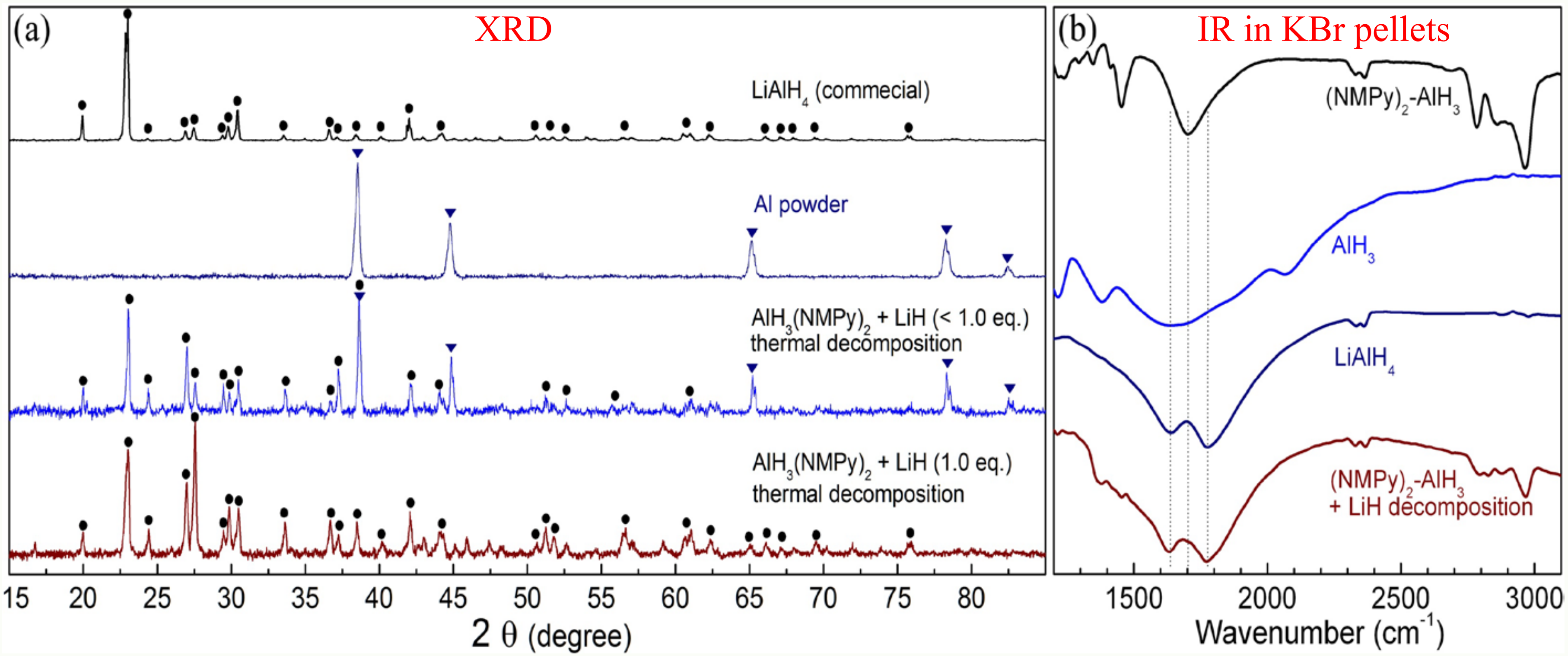
Hydrogenation **Decomposition**

- Reversible formation of $(NMPy)_2 \cdot AlH_3$ in the reactor (~ 60% yield);
- Low temperature enhances the reaction rate, but not the final yields;

Thermal decomposition Studies:

$$2\,NMPy\uparrow + AlH_3 \xleftarrow{\times} (NMPy)_2\cdot AlH_3$$

- **Role of LiH:** $(NMPy)_2\cdot AlH_3 + \mathbf{LiH} \xrightarrow{\text{decomposition}} ?$

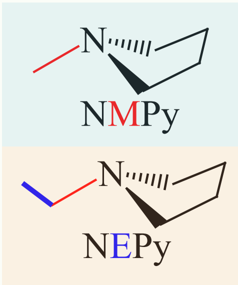


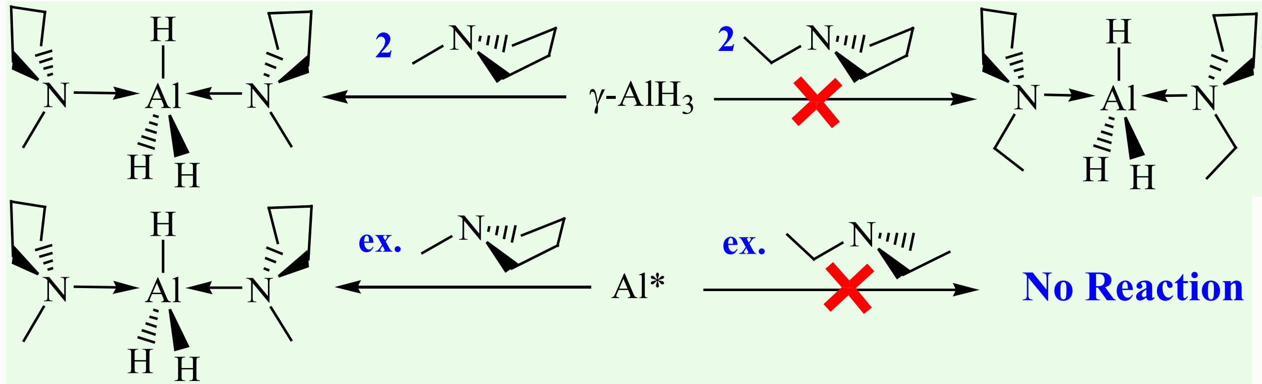
- **Hydrogenation coupled with decomposition with LiH:**

$$Al^* + 2\,NMPy \xrightarrow[Et_2O]{1000\text{ psi }H_2} (NMPy)_2\cdot AlH_3 \xrightarrow[\text{vacuum, }50^\circ C]{\mathbf{1.0\ eq\ LiH}} \mathbf{LiAlH_4} + 2\,NMPy\uparrow$$

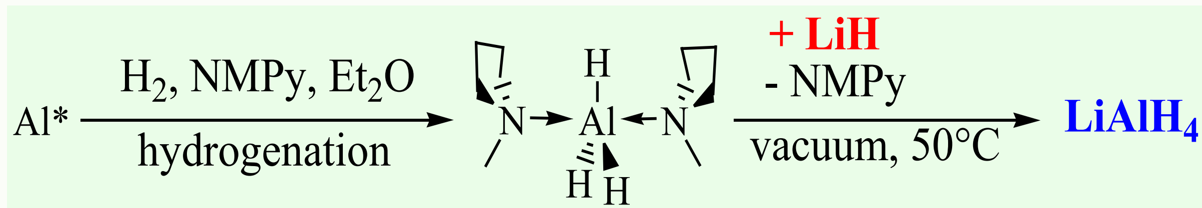
Summary:

- Steric effects:





- LiAlH$_4$ regeneration:



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