Aluminum Hydride: the organometallic approach

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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.

Aluminum hydride (alane, AlH₃):

AlH₃ → Al + \frac{3}{2} H₂

- High capacity: 10.1 wt% and 1.48 g/L;
- Low decomposition enthalpy:
  \[ \Delta H \approx 7 \text{ kJ/mol H}_2 \approx 1/5 \Delta H_{\text{NaAlH}_4} \]
- Rapid H₂ evolution rates at low T:
  meets DOE target (0.02 gH₂/s) at < 100°C
- High purity H₂:
  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;
- AlH₃ is completely unstable at Ti concentrations ≥ 0.1 mol%.

Synthesis of AlH$_3$:

**Conventional synthesis:**

\[ 3 \text{ LiAlH}_4 + \text{ AlCl}_3 \rightarrow \text{ Et}_2\text{O} \]
\[ 3 \text{ LiCl} + 4 \text{ AlH}_3(\text{Et}_2\text{O})_n \]

- filtration
- \( \text{AlH}_3(\text{Et}_2\text{O})_n \)
- desolvation/crystallization

\( \text{AlH}_3 \) polymorph

**Direct hydrogenation:**

\[ \text{Al} + \frac{3}{2} \text{H}_2 \rightarrow \text{AlH}_3 \]

- \( \Delta H_f = -9.9 \pm 0.6 \text{ kJ/mol AlH}_3 \);
- \( \Delta G_f (298K) = 48.5 \pm 0.6 \text{ kJ/mol AlH}_3 \);
- \( P_{298K} \approx 10^5 \text{ atm} \) (too high for practical applications).
- \( \text{AlH}_3 \) only formed on the surface of Al metal.

**Morphology**

Too expensive!

The organometallic approach:

- **Common amine-alane structural types:**

  ![Structural types](image)

  - (I) \( \text{R}_3\text{N} \rightarrow \text{Al} \rightarrow \text{NH}_3 \)
  - (II) \( \text{H} \rightarrow \text{Al} \rightarrow \text{NH}_3 \)
  - (III) \( \text{R}_3\text{N} \rightarrow \text{Al} \rightarrow \text{Al} \rightarrow \text{NH}_3 \)

  \( \text{NR}_3 \) is an amine.

- **The 3-step regeneration process:**

  1. **Hydrogenation:** \( \text{Al} + 2 \text{amine}^1 + \frac{3}{2} \text{H}_2 \xrightarrow{\text{catalyst}} (\text{amine}^1)_2 \cdot \text{AlH}_3 \) (1)
  2. **Transamination:** \((\text{amine}^1)_2 \cdot \text{AlH}_3 + \text{amine}^2 \xrightarrow{\text{vacuum heat}} \text{amine}^2 \cdot \text{AlH}_3 + 2 \text{amine}^1 \) (2)
  3. **Decomposition:** \( \text{amine}^2 \cdot \text{AlH}_3 \xrightarrow{\text{vacuum heat}} \text{AlH}_3 + \text{amine}^2 \) (3)

- **The “Paradox” 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 \( \text{AlH}_3 \) (with Al contamination;
    - **Does not** facilitate hydrogenation.

Approaches to the project:

➢ Tune the Lewis Basicity of amines:

- TEA
- DEMA
- piperidine
- morpholine
- pyrrolidine
- DMEA
- TMA

Increasing basicity

➢ Objectives:

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

\[
\text{Al} + 2 \text{amine}^1 + \frac{3}{2} \text{H}_2 \xrightarrow{\text{catalyst}} (\text{amine}^1)_2 \cdot \text{AlH}_3 \xrightarrow{\text{vacuum heat}} \text{AlH}_3 + 2 \text{amine}^1
\]

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

2. Optimize the transamination and thermal decomposition steps:

- 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:

Direct synthesis:

- N-methylpyrrolidine (NMPy)
- N-ethylpyrrolidine (NEPy)

Hydrogenation:

- Reactor set-up:
  - H₂ pressure: ~ 1000 psi;
  - Temperature: 0 ~ 25°C;
  - Chemicals: Et₂O (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):

<table>
<thead>
<tr>
<th>alane adduct</th>
<th>Calculation</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMPy</td>
<td>1700</td>
<td>1709 (2:1), 1773 (1:1)</td>
</tr>
<tr>
<td>NEPy</td>
<td>1700</td>
<td>1773 (1:1)</td>
</tr>
</tbody>
</table>

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

(NMPy)$_2$·AlH$_3$
Theoretical calculations:

<table>
<thead>
<tr>
<th>alane adduct</th>
<th>Binding Free Energy in Et$_2$O with BSSE Correction (kcal·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Type I</td>
</tr>
<tr>
<td>NMPy</td>
<td>-19.91</td>
</tr>
<tr>
<td>NEPy</td>
<td>-14.72</td>
</tr>
<tr>
<td>Et$_2$O</td>
<td>-13.24</td>
</tr>
</tbody>
</table>

(a-I)  
(b-I)  
(a-II)  
(b-II)  
(a-III)  
(b-III)
Reversible formation of (NMPy)$_2$·AlH$_3$:  

\[ 2 \text{NMPy} + \text{Al}^* + \frac{3}{2} \text{H}_2 \xrightleftharpoons{\text{heat}} \xrightarrow{\text{Et}_2\text{O}} (\text{NMPy})_2\cdot\text{AlH}_3 \]

- Reversible formation of (NMPy)$_2$·AlH$_3$ in the reactor (~ 60% yield);
- Low temperature enhances the reaction rate, but not the final yields;
Thermal decomposition Studies:

- Hydrogenation coupled with decomposition with LiH:
  \[ \text{Al}^* + 2 \text{NMPy} \xrightarrow{1000 \text{ psi H}_2} \text{(NMPy)}_2 \cdot \text{AlH}_3 \xrightarrow{1.0 \text{ eq LiH}} \text{LiAlH}_4 + 2 \text{NMPy} \]

- Role of LiH:
  \[ \text{(NMPy)}_2 \cdot \text{AlH}_3 + \text{LiH} \xrightarrow{\text{decomposition}} \]

- XRD Matched with IR in KBr pellets:
  - \text{LiAlH}_4 (commercial)
  - \text{Al powder}
  - \text{AlH}_3(\text{NMPy})_2 + \text{LiH} (< 1.0 \text{ eq.})
  - \text{thermal decomposition}
  - \text{AlH}_3(\text{NMPy})_2 + \text{LiH} (1.0 \text{ eq.})
  - \text{thermal decomposition}

- IR in KBr pellets:
  - \text{(NMPy)}_2 \cdot \text{AlH}_3
  - \text{AlH}_3
  - \text{LiAlH}_4
  - \text{(NMPy)}_2 \cdot \text{AlH}_3 + \text{LiH} \text{ décomposition}
Summary:

- **Steric effects:**

  ![Steric effects diagram]

- **LiAlH₄ regeneration:**

  ![LiAlH₄ regeneration diagram]

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