Hydrogen Storage by Novel CBN Heterocycle Materials

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in collaboration with the University of Alabama

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This presentation does not contain any confidential or otherwise restricted information
Overview

Timeline

start date: September 2008
end date: March 2012
percent complete: 95%

Barriers

A. system weight and volume
C. efficiency
E. charging/discharging rates
R. regeneration process

Budget

total project funding: $1,440,614
DOE share: $1,149,085
UO share: $291,529
FY 2011 funding: $300,000
Planned FY 2012 funding: $145,653

Project Collaborators

THE UNIVERSITY OF ALABAMA  Prof. David Dixon
Project Objectives - Relevance

Develop CBN heterocycles as novel hydrogen storage materials:

- liquid-phase
- gravimetric density (> 5.5 wt. %)
- volumetric density (> 40 g H₂/L system)
- thermodynamics (H₂ absorption and desorption)
- regeneration (reversibility)
- 2017 DOE targets for vehicular applications + near-term market applications

Specific Phase II Tasks

1) synthesize parent charged fuel of CBN heterocycle material (1); completed 1/22/2011
* 2) optimize CBN heterocycle materials synthesis; completed 10/20/2011
* 3) obtain experimental thermodynamic data for model CBN heterocycles; completed 7/21/2011
  4) formulate materials as liquids; completed 1/22/2011
* 5) develop/identify conditions to optimize H₂ desorption from CBN materials; 90% complete
* 6) develop/identify conditions for regeneration of the spent fuels; 90% complete
The CBN Heterocycle Approach

couple \textit{exothermic} \text{H}_2 desorption from \textit{BN} with \textit{endothermic} \text{H}_2 desorption from \textit{CC} in a \textit{cyclic} system to achieve optimal thermodynamics for the overall \text{H}_2 absorption/desorption process.

Overall thermodynamics is conducive to reversibility.
A Well-Defined Molecular Approach

- The materials remain well-defined molecular species throughout the lifecycle, from fully charged fuel to the spent fuel.
- Potential **advantages** of well-defined nature include:
  - no involvement of insoluble polymeric materials
  - better characterization of reaction products and reaction processes
  - facilitates computational and mechanistic studies
  - facilitates formulation as liquids
- Potential **disadvantages** of well-defined molecular approach include:
  - lower storage capacity
  - for single-component systems:
  - formation of polymers or larger networks $\rightarrow$ higher capacity (e.g., AB), solids

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**trade off between capacity, solid phase vs. liquid phase, well-defined species**
Previous Progress (Task 1, Completed)
Synthesis of Parent

Wei Luo

Synthesis of the parent molecule was successful.
### Previous Progress (Task 4, Completed)

**Formulate Materials as Liquids**

Potential capacities, assuming 3 equivalent H₂ release:

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<th>Neat Material</th>
<th>THF Solution</th>
<th>Et₂O Solution</th>
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<tbody>
<tr>
<td>t-Bu</td>
<td>mp: 96-98 °C</td>
<td>sol. (g/L): 284 ± 28</td>
<td>sol. (g/L): 84.4 ± 4</td>
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<td>vol. (g H₂/L): 3.47</td>
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<td></td>
<td>wt(%): 4.3</td>
<td>wt(%): 1.3</td>
<td>wt(%): 0.4</td>
</tr>
<tr>
<td>Me</td>
<td>mp: 72-73 °C</td>
<td>sol. (g/L): 292 ± 5</td>
<td>sol. (g/L): 106 ± 18</td>
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</tr>
<tr>
<td></td>
<td>wt(%): 6.1</td>
<td>wt(%): 2.0</td>
<td>wt(%): 0.73</td>
</tr>
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<td>sol. (g/L): 434 ± 20</td>
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<tr>
<td></td>
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<td>wt(%): 3.4</td>
<td>wt(%): 3.1</td>
</tr>
</tbody>
</table>
New Progress (Task 2, Completed)
Optimize Materials Synthesis

First generation (2009):
6 steps, 9% overall yield

Second generation + optimization (2011):
3 steps, 51% overall yield

First-fill synthesis was improved.
New Progress (Task 3, Completed)

Experimental Thermodynamic Analysis –

Discovery of suitable catalytic reaction conditions for calorimetry. Experimental thermodynamic data obtained and calibrated against theoretical values.

numbers in (): experimental values measured at 333K in kcal/mol
numbers in []: G3(MP2) values at 298K in kcal/mol

New Progress (Task 5)

H$_2$ Desorption from BN is Facile

H$_2$ desorption occurs thermally at ~150 °C, catalytically at < 80 °C for all three reactions.

Reviewer 3 is right! Trimerization occurs and needs to be considered.

G3(MP2), 298K:

$\Delta H = -83.1; \Delta G = -107.3$ kcal/mol trimer

$\Delta H = -27.7; \Delta G = -35.8$ kcal/mol monomer

$\Delta H = -13.9; \Delta G = -17.9$ kcal/mol H$_2$
New Progress (Task 5)
Screening of Catalysts for Trimerization

- Neutral Rh(I) catalyst are most active (5 mol%, 15 min); entries 20 and 22.
- CoCl$_2$ is the most active (10 mol%, 30 min) among first-row transition metals that we screened in Table 1 (Entry 13).
- Most catalysts effect the trimerization.
- Without a catalyst, no reaction occurs after 3 hrs at 80 °C.

Table 1: Catalyst and condition screening for dehydrogenation of 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Loading (mol%)</th>
<th>Time(min)</th>
<th>% Yield Int</th>
<th>% Yield T</th>
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<tbody>
<tr>
<td>1</td>
<td>CoCl$_2$</td>
<td>10</td>
<td>60</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>(dppe)NiCl$_2$</td>
<td>10</td>
<td>60</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>Cr(MeCN)$_3$(CO)$_3$</td>
<td>10</td>
<td>60</td>
<td>N/R*</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>[Cl(cod)Ir]$_2$</td>
<td>10</td>
<td>60</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>[Cl(cod)Rh]$_2$</td>
<td>10</td>
<td>60</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>[(C$_2$H$_2$)$_2$ClRh]$_2$</td>
<td>10</td>
<td>60</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>7</td>
<td>Cp*RuCl$_2$</td>
<td>10</td>
<td>60</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>(cod)$_2$RhBF$_4$</td>
<td>10</td>
<td>60</td>
<td>N/R*</td>
<td>100</td>
</tr>
<tr>
<td>9</td>
<td>(PPh$_3$)$_2$NiCl$_2$</td>
<td>5</td>
<td>60</td>
<td>100</td>
<td>100</td>
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<tr>
<td>10</td>
<td>[(nbd)ClRh]$_2$</td>
<td>5</td>
<td>60</td>
<td>100</td>
<td>100</td>
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<tr>
<td>11</td>
<td>RuCl$_3$</td>
<td>10</td>
<td>60</td>
<td>N/R*</td>
<td>100</td>
</tr>
<tr>
<td>12</td>
<td>(dppe)NiCl$_2$</td>
<td>5</td>
<td>30</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>13</td>
<td>CoCl$_2$</td>
<td>10</td>
<td>30</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>14</td>
<td>[Cl(cod)Ir]$_2$</td>
<td>5</td>
<td>30</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>15</td>
<td>[Cl(cod)Rh]$_2$</td>
<td>5</td>
<td>30</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>16</td>
<td>Cp*RuCl$_2$</td>
<td>5</td>
<td>30</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>17</td>
<td>(PPh$_3$)$_2$NiCl$_2$</td>
<td>5</td>
<td>30</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>18</td>
<td>[(nbd)ClRh]$_2$</td>
<td>5</td>
<td>30</td>
<td>100</td>
<td>100</td>
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<tr>
<td>19</td>
<td>CoCl$_2$</td>
<td>10</td>
<td>15</td>
<td>50</td>
<td>50</td>
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<tr>
<td>20</td>
<td>[Cl(cod)Rh]$_2$</td>
<td>5</td>
<td>15</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>21</td>
<td>Cp*RuCl$_2$</td>
<td>5</td>
<td>15</td>
<td>60</td>
<td>40</td>
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<tr>
<td>22</td>
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* N/R means no reaction or mix of undesired products
New Progress (Task 5)

FeCl$_2$ Acts as Catalyst for Trimerization

- Conditions: 80 °C in toluene solution.
- Release of 2 equiv. H$_2$ corresponds to complete conversion.

- FeCl$_2$ is cheap ($0.30 / kg$)
- H$_2$ desorption behavior is catalyst dependent.
- Mechanistic details still under investigation.
New Progress (Task 5)
Progress toward Removing $\text{H}_2$ from CC

Overall potential:
9.4 wt.%; 94 g $\text{H}_2$/L

G3(MP2), 298K:
$\Delta H = +5.9$ kcal/mol monomer
$\Delta G = -19.3$ kcal/mol monomer
$\Delta H = +1.5$ kcal/mol $\text{H}_2$
$\Delta G = -4.8$ kcal/mol $\text{H}_2$
solid phase (single component)

Preliminary attempts using transition metal catalysts:

Keep in mind that this reaction is endothermic:
$\Delta H \sim 3 \times 30$ kcal/mol product.

by GC analysis:
- complete conversion of the starting material
- significant formation of the desired product

Jacob Ishibashi
New Progress (Task 6)  
Progress toward Regeneration

Conversion of the spent fuel trimer T back to the charged fuel 1 was accomplished.

Preliminary investigation using hydrazine did not lead to regeneration.
Formic acid:
- produced ~700,000 tons / year (commodity chemical)
- relatively cheap at $0.8-1.2 / kg
- potential for use as near-term solution for regeneration

Formic acid serves as a digestion agent and proton source to break up the trimer.

NMR indicates clean reaction. Loss in yield may be due to isolation procedures.
Summary of Accomplishments: Material Synthesis and Properties

1. Synthesized family of novel CBN-heterocyclic materials, including parent:

   \[
   \begin{align*}
   & \text{H}_2 \text{N-} \text{t-} \text{Bu} \quad \text{BH}_2 & \quad \text{H} \quad \text{Me} \quad \text{BH}_2 & \quad \text{H} \quad \text{NH}_2 \quad \text{BH}_2 \\
   & \text{4.3 wt\% H}_2 & \quad \text{6.1 wt\% H}_2 & \quad \text{7.1 wt\% H}_2 \quad \text{3 equiv. release} \\
   & \text{9.5 wt\% H}_2 & \quad \text{4 equiv. release}
   \end{align*}
   \]

1. Improved material synthesis: all 3 steps, > 50% overall yield from commercially available starting materials

2. Completed experimental thermodynamic measurements to corroborate computational results (in kcal/mol):

   \[
   \begin{align*}
   & \text{H}_2 \text{N-} \text{t-} \text{Bu} \quad \text{BH}_2 \quad \xrightarrow{\text{—3 H}_2} \quad \text{H} \quad \text{N-} \text{t-} \text{Bu} \quad \text{BH} \\
   & \Delta H = 25.2 \text{ G3(MP2)} \\
   & \Delta H = 28.6 \text{ experimental}
   \end{align*}
   \]

3. Formulated materials as liquids, determined H\(_2\) capacity in solution
Summary of Accomplishments: H₂ Release and Regeneration

5. Hydrogen release (materials are thermally stable beyond their melting points):
   a. Loss of H₂ from B–N is facile, numerous hetero- and homogeneous catalysts promote loss of H₂ at ≤ 80 °C
   b. Trimerization of parent molecule occurs, releasing 2 equiv. H₂ per monomer
   c. Proof-of-concept success for H₂ desorption from C–C

6. Regeneration of spent fuel material has been demonstrated:
Toward a Liquid Fuel

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It appears the smaller the molecule the lower the melting point.
A Single-Component Liquid H₂ Storage Material

Synthesis of a liquid material without phase change was accomplished.

Synthesis:

\[
\text{Me} \sim \sim \text{N(TMS)}_2 \xrightarrow{\text{BH}_3 \cdot \text{Et}_3\text{N}} \xrightarrow{160 \, ^\circ \text{C, } 48 \text{h}} \left[ \begin{array}{c} \text{Me} \sim \sim \text{B} \sim \sim \text{NH}_2 \\
\text{Me} \sim \sim \text{BH}_2 \end{array} \right] \xrightarrow{1) \text{KH, THF}} \xrightarrow{2) \text{HF} \cdot \text{pyr}} \text{Me} \sim \sim \text{NH}_2 \sim \sim \text{BH}_2
\]

Highlighted in:


Fe-Catalyzed H₂ Release (Neat Liquid)

Catalyst particles (black) are on the surface of a magnetic stir bar.

Dehydrogenation is feasible at larger scales as a neat liquid.

Collaborations

Project Collaborators

computational studies of H$_2$ desorption pathways of cyclic CBN materials, evaluation of thermodynamics and energetics

experimental mechanistic studies of H$_2$ absorption/desorption to/from cyclic CBN materials, thermodynamic measurements using reaction calorimetry, H$_2$ charge/discharge characteristics
Project Summary

Relevance: development of novel hydrogen storage materials with desirable storage capacity and thermodynamics for potential reversible H₂ absorption and desorption

Approach: coupling of exothermic H₂ desorption from BN with endothermic H₂ desorption from CC in a cyclic system to achieve optimal thermodynamics for H₂ absorption/desorption; distinct from amine-borane and cyclic organic materials

Progress: • completed synthetic optimizations (Task 2)
• completed experimental thermodynamic analysis (Task 3)
• discovered FeCl₂ as effective catalyst for H₂ desorption from BN (Task 5)
• preliminary discovery of dehydrogenation from CC (Task 5)
• completed regeneration of trimer spent fuel (Task 6)
• discovered formic acid as a digestion agent (Task 6)
• discovered a single-component liquid-phase storage material

Collaborations: active partnership with UA and PNNL
Technical Backup Slides
PNNL M-H Regeneration Route


Use acid-base chemistry to drive an uphill process