Improving Porosity and H$_2$-Affinity of Porous Framework Materials

Trevor A. Makal
Representing Hong-Cai (Joe) Zhou
Texas A&M University
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Overview

**Timeline**
- Project start date: 7/1/2007
- Project end date: 6/30/2013
- Percent complete: 90%

**Barriers**
- $H_2$ uptake at room temperature is low despite high uptake at 77 K
- $\Delta H$ needs to be in the range of 15 to 30 kJ/mol to reach high storage capacity at ambient temperature
- Materials with high surface areas generally have low volumetric uptake

**Budget**
- Total project funding (DOE: $1,342,819; Contractor: $771,856)
- FY07 $100,000
- FY08 $0
- FY09 $742,260
- FY10 $300,000
- FY11 $0
- FY12 $200,559

**Partners**
*No formal partners, collaborators are*
- ANL (APS)
- ORNL, LLNL
- LBNL
- Dept. of Chem. Eng., TAMU
- KIT, Germany
- GM
- SWRI®
Enhance H$_2$ adsorption capacity

Dihydrogen affinity

- $15 \text{ kJ/mol} < Q_{st} < 30 \text{ kJ/mol}$ for ambient temperature application
- For most materials, $Q_{st} < 10 \text{ kJ/mol}$

Surface area

- High surface area is beneficial for gravimetric H$_2$ uptake
- Volumetric uptake and heat adsorption can be improved by metal incorporation

Increase surface areas

Develop new stabilization methods

Adopt multi-topic ligands

Stable
PPN-4(Si) has ultrahigh surface area ($S_{\text{BET}} = 6470 \text{ m}^2/\text{g}$) and is very stable. This surface area is one of the highest reported to date for any porous material. Yet, volumetric uptake is low due to extremely low framework density and lack of strong H$_2$-binding sites.

Isosteric heats of adsorption obtained from isotherms at 77 and 87 K. H$_2$ heat of adsorption has improved by 47% upon post-synthetic modification.
Dihydrogen affinity
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Surface area
- High surface area is beneficial for gravimetric H$_2$ uptake
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Enhance H$_2$ adsorption capacity
- Increase surface areas
- Adopt multi-topic ligands
- Introduce metal atoms or cations
- Introduce charge separation

Stable
<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Approach and Milestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nov-08</td>
<td>Milestone: Optimize the alignment of the coordinatively unsaturated metal centers of MOFs and construct a new MOF, PCN-12, which exhibits an exceptionally high $H_2$ uptake of 3.0 wt% (24.6 mg/cm$^3$) at 760 Torr and 77 K. The Hydrogen adsorption heat of PCN-12 can reach as high as 12.5 kJ/mol at low coverage. (Status – 100% complete)</td>
</tr>
<tr>
<td>Nov-09</td>
<td>Milestone: Construct the catenation isomer pairs of PCN-6 and PCN-6’. $H_2$ sorption measurements demonstrate that framework catenation can be favorable. The excess hydrogen uptake of PCN-6 is 6.7 wt % at 77 K/50 bar. Inelastic neutron scattering (INS) studies reveal that the interaction is substantially stronger in catenated PCN-6. The catenation leads to increase in volumetric $H_2$ uptake and the MOF-$H_2$ interaction. (Status – 100% complete)</td>
</tr>
<tr>
<td>Nov-10</td>
<td>Milestone: Construct MOFs containing mesocavities with microwindows may serve as a general approach towards stable MOFs with higher surface areas. Design and synthesize porous polymer networks (PPNs) for hydrogen storage with high surface area, tunable pore size, and flexibility. Determine $H_2$ adsorption of PPNs with metal incorporation. (Status – 100% complete)</td>
</tr>
<tr>
<td>Nov-11</td>
<td>Milestone: Construct PPNs with ultrahigh surface area. Explore the possibility of incorporation of charge and additional light metal ions such as Li$^+$, Na$^+$ or Mg$^{2+}$ into PPNs. The modified PPNs show improved hydrogen affinity and volumetric hydrogen uptake due to the increased density. (Status – 100% complete)</td>
</tr>
<tr>
<td>Jun-12</td>
<td>Milestone: Construct PPNs with high density of functional groups. Synthesize 10 porous materials with incorporated multivalent metal ions such as $V^{3+}$, $Fe^{3+}$ or $Ti^{3+}$. Approach $\Delta H_{ads}$ of 15 kJ mol$^{-1}$. Construct series of 10 stable and high-surface-area Zr-MOFs based on porphyrin ligand, study the effect on gas uptake by introducing different metals into their porphyrin linkers. (Status – underway)</td>
</tr>
</tbody>
</table>
Approach

Hydrogen Storage

Metal-Organic Frameworks (MOFs)

Porous Polymer Networks (PPNs)

Functionalization

Post-synthetic Treatment

Enhance H₂ uptake

- Framework functionalization
- Framework post-synthetic modification
- Introducing metal ions

New Achievements

- High-surface-area PCNs (PCN-82 and PCN-88) with potential anchors for metal incorporation
- Highly stable Zr-MOFs with porphyrin ligand (PCN-41) was synthesized and initial metal-insertion study was carried out, these materials exhibit high surface area and high heat of adsorption for H₂
- PPN enriched with phenol groups (PPN-43-OH) was synthesized, phenol group can be served as anchor for metal incorporation
- Design and synthesis of a series of biphenyl ring PPNs, these materials are relatively low cost, and exhibit high surface areas and high heats of adsorption for H₂
High-Surface-Area MOF with Anchors for Post-synthetic Modification

Strategy:
To expose phenol group and use it as anchor for binding metal ions

![Chemical structure and diagram of PCN-82](image)

- Phenol group exposure
- Cu(NO₃)₂ used as anchor
- Post-synthetic modification

**Cubic, Space Group Fm3m**
- \( a = 40.026(2) \) Å
- \( V = 64124 \) Å³

**BET Surface Area**
- 5200 m²/g

**77K H₂ uptake**
- Different temperatures: 77K, 87K

**Excess**
- Graph showing H₂ uptake vs Pressure

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ST018
High-Surface-Area MOF with Anchors for Post-synthetic Modification

**Strategy:**
To introduce metal-binding anchors by using pyrazine derivatives
Introduction of Functional Groups into MOFs by Using Mixed Ligands

The SO$_3$H group can be used as anchor for other metal incorporation.

The SO$_3$H group can be used as anchor for other metal incorporation.
Stable Zr-MOFs

Strategy:
To introduce multivalent metals through porphyrin ligand

\[ \text{ZrCl}_4 \rightarrow \text{PCN-41-Zr; PCN-41-Fe; PCN-41-Ni} \]

\[ \frac{120 \, ^\circ \text{C}}{} \]

\[ \text{S}_{\text{BET}}: 2600 \, \text{m}^2/\text{g} \, (\text{PCN-41-Ni}) \]
Strength of Zr-O coordination bonds prevents protonation of ligand under acidic conditions typically observed in MOFs.
Stable Zr-MOFs

Excess

- PCN-41-Zr at 77K
- PCN-41-Zr at 87K

Excess

- PCN-41-Fe at 77K
- PCN-41-Fe at 87K

Excess

- PCN-41-Ni at 77K
- PCN-41-Ni at 87K

Heat of Adsorption (kJ/mol)

- PCN-41-Zr
- PCN-41-Fe
- PCN-41-Ni
Porous Materials Stable in Air and Moisture for H₂ Storage

Stability is important for H₂ storage in application.

C, Si, Admantane, P⁺, B⁻, etc.
Introduction of Metal Ions into PPNs

The 2,2’-bipy group can be used as anchor for multivalent metals insertion
Phenolic PPN

The phenol group can be used as anchor for multivalent metals incorporation.

\[ \text{HCl, dioxane} \]
\[ 150 \, ^\circ C, \, 48 \, h \]

**Graphs:**
- **Nitrogen Uptake (77K):**
  - \( S_{BET} \): 1040 \( \text{m}^2/\text{g} \)
  - Plot showing uptake vs. relative pressure (P/Po).
- **Hydrogen Uptake:**
  - Excess PPN-43-OH at 77K and 87K.

[Diagram showing chemical reactions and molecular structures]
Functionalized Biphenyl Ring PPNs

Strategy:
To “lock” the biphenyl ring by introducing functional groups at 2 & 2’ positions, therefore construct high surface area PPNs

PPN-10: \( S_{\text{BET}}: 1128 \text{ m}^2/\text{g} \)
PPN-11: \( S_{\text{BET}}: 1551 \text{ m}^2/\text{g} \)
PPN-12: \( S_{\text{BET}}: 3420 \text{ m}^2/\text{g} \)
PPN-13: \( S_{\text{BET}}: 1062 \text{ m}^2/\text{g} \)
PPN-14: \( S_{\text{BET}}: 1910 \text{ m}^2/\text{g} \)
Functionalized Biphenyl Ring PPNs

To-Do: Looking for efficient method to remove methyl group or using other phenol protecting group instead
Collaborations

Collaborators
- Dept. of Chem. Eng., TAMU, Theoretical Calculation
- KIT, Germany, Ligand Synthesis
- SWRI®, Gas adsorption measurements
- LLNL, Critical Point Activation
- ANL, APS, Crystal Structure Determination
- GM, High pressure Gas Adsorption Measurements

Technology Transfer
- Working with industrial partners closely
- Presented in Tech Team Meeting. Provided relevant parameters for the Engineering CoE on PPN-4
- Working with a start-up company
Accomplishments

Demonstrated through experiments that:

- Two PCNs (PCN-82 and PCN-88) with exceptionally high surface areas (5200 and 3300 m$^2$/g) have been designed and synthesized. They all have potential anchors for metal incorporation.

- A series of high-surface-area Zr-MOFs were synthesized by using porphyrin ligand, these MOFs are stable even in strong acidic conditions. Initial study shows that metal incorporation leads to high heat of adsorption for H$_2$.

- A phenolic PPN was synthesized, the phenol group can serve as anchor for multivalent metal incorporation.

- A series of biphenyl PPNs were designed and synthesized by using triple bond coupling reaction, the biphenyl ring is “locked” by introducing functional groups at 2 & 2’ positions, therefore leading to high surface area PPNs, and high heat of adsorption for H$_2$. 
**Future Work**

- To expose phenol group of PCN-82 and use it as anchor for metal incorporation to study its effect on heat of adsorption for $H_2$.
- Systematic study Zr-MOFs by incorporating different multivalent metals, such as $V^{3+}$, $Ti^{3+}$, etc.
- Optimize the procedure for phenolic PPN-43-OH for higher surface area, then incorporate multivalent metals, such as $V^{3+}$, $Fe^{3+}, Ti^{3+}$, etc.
- To expose the phenol group of PPN-14 by optimizing the demethylation procedure, and use it as anchor for metal incorporation.
- Measure $H_2$ storage capacity at high pressure for obtained high-surface-area materials, such as, PCN-82, 88, 41 and PPN-12.
## Summary Table

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Delta H_{ads}$ (kJ/mol)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCN-82</td>
<td>5.6</td>
<td>5200</td>
</tr>
<tr>
<td>PCN-88</td>
<td>6.0</td>
<td>3300</td>
</tr>
<tr>
<td>PCN-35, 35-SO$_3$H, 35-SO$_3$Na</td>
<td>5.6, 7.7, 8.9</td>
<td>-</td>
</tr>
<tr>
<td>PCN-41-Zr, 41-Fe, 41-Ni</td>
<td>8.7, 8.0, 8.5</td>
<td>2600 (Ni)</td>
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<tr>
<td>CPPN, CPPN-Pd</td>
<td>6.8, 8.3</td>
<td>-</td>
</tr>
<tr>
<td>PPN-43-OH</td>
<td>8.6</td>
<td>1040</td>
</tr>
<tr>
<td>PPN-10</td>
<td>8.4</td>
<td>1128</td>
</tr>
<tr>
<td>PPN-12</td>
<td>5.8</td>
<td>3420</td>
</tr>
<tr>
<td>PPN-13</td>
<td>8.2</td>
<td>1026</td>
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<tr>
<td>PPN-14, 15,16</td>
<td>7.1, 7.9, 8.7</td>
<td>1910, 873, 794</td>
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