A Joint Theory and Experimental Project in the Synthesis and Testing of Porous COFs/ZIFs for On-Board Vehicular Hydrogen Storage

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Project ID
ST022

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Overview

Timeline

Project start date: 9/1/2008 (funded from 4/1/2009)
Project end date: 1/31/2013
Percent complete: 35%

Barriers

Barriers addressed
- Improved gravimetric and volumetric density of hydrogen uptake
- Hydrogen capacity and fast kinetics at 77 K
- Improved hydrogen binding energy
- Synthetic scale up of COFs to cubic meters

Budget

- Total project funding
  - DOE share: $1.38 M
  - Contractor share: $0.41 M
- Funding received in FY10: $300 K
- Funding for FY11: $284 K

Collaborating Partner

- Fraser Stoddart (NW)
- Jaheon Kim (Soongsil University)
- BASF
Description of new materials

Covalent Organic and Zeolitic Imidazolate Frameworks (COFs and ZIFs)
- Control of structure, topology, and interpenetration
- Lightweight materials (COFs)
- Design of functionalities
- Suitable for light metal impregnation
- High-throughput material discovery is applicable
High-pressure $\text{H}_2$ isotherms of COFs at 77 K

$\text{H}_2$ uptake in 3D COFs is almost the same as that in MOF-177.
Objectives (FY10-11)

Accomplishments in last year:
- Predicted adsorption enthalpy of H₂ on various metal sites
- Began computation of H₂ uptake isotherms with developed Force Field
- Develop chemistry to realize stable frameworks
- Introduce potential metal binding sites through the COF synthesis

This year:
- Design new COFs with strong H₂ binding sites
- Predict H₂ uptake isotherm for designed frameworks with developed Force Field
- Prepare stable frameworks with potential metal binding sites
- Implement metalation experiments and evaluate the H₂ adsorption property
- Prepare mixed-metal ZIFs
Milestones (FY11)

1. Discover new COFs with potential metal binding sites and explore \( H_2 \) uptake properties of COFs.

2. Investigate pressure and temperature dependence of \( H_2 \) uptake in metalated COFs over the parameter range specified in DOE YR2015 guidelines (5.5 wt % and 40 g L\(^{-1}\) up to 100 bar, -40/85 \(^\circ\) C). Compare with predictions from theory.

3. Develop new force fields for modeling adsorption properties of COFs. Test models using reported adsorption data for a range of known COFs.

4. Design new architectures of promising materials for hydrogen storage that are favorable thermodynamically.
Strategy

- Improve the framework stability against impurity (e.g. water)
- Introduce metal binding sites through the COF formation

COF-5
COF-1
COF-202
COF-300

COF-41
COF-301
Postmodified MOF (JACS, 2009)
Hydrazone condensation

- Obtained hydrazone chemically stable in water and basic conditions.
- Polyacylhydrazones have been prepared showing monomer exchange under mild conditions.
- Potential metal binding sites

Last year, we prepared hydrazone COF (COF-41)
- Crystalline porous solid
- Stable in air
- BET surface area was 110 m²/g
Synthesis of COFs based on hydrazone linkages

COF-42

1. Reaction of components 1 and 2 in mesitylene/dioxane/acetic acid 6 M (aq) (15:5:2 v/v/v) at 120 °C for 72 h.

COF-43

2. Reaction of components 1 and 3 in mesitylene/dioxane/acetic acid 6 M (aq) (9:1:1 v/v/v) at 120 °C for 72 h.
PXRD patterns of COF-42 and 43

[Graph showing PXRD patterns for COF-42 and COF-43 with peaks labeled 100, 110, 200, 210, 220, 340, 003, and 001.]
Ar isotherms of COF-42 and COF-43

COF-42 shows 6.5 times higher BET area than COF-41.
**H₂ isotherms of COF-42 and COF-43**

<table>
<thead>
<tr>
<th></th>
<th>BET SA (m²/g)</th>
<th>H₂ uptake (wt%)</th>
<th>(Q_{st}) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COF-41*</td>
<td>110</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>COF-42</td>
<td>710</td>
<td>0.60</td>
<td>6.6</td>
</tr>
<tr>
<td>COF-43</td>
<td>620</td>
<td>0.51</td>
<td>6.6</td>
</tr>
</tbody>
</table>

*Reported last year*

Excess uptake

COF-42, 77 K
COF-43, 77 K
COF-42, 87 K
COF-43, 87 K
Calculated $\Delta G$ and $\Delta H$ of metalation reactions

From the calculation, each linker can hold atomic Pd except the hydrozone.

$\Rightarrow$ Design of imine-linked COFs
Design of imine-linked 3D porous COFs

**COF-300:**
- Permanently porous (BET SA = 1360 m$^2$/g, pore volume = 0.72 cm$^3$/g)
- 1.1 wt% H$_2$ uptake at 1 bar and 77 K
- However, no metal binding sites in the framework

Use terephthaldehyde derivatives to introduce metal binding sites
Synthesis of COF-301 and metalation

- Crystalline COF-301 was synthesized
- The formation of imine linkages in COF-301 was confirmed by FT-IR spectra
- Crystallinity remains after the metalation
**N₂ and H₂ uptake by COF-301 and metalated COFs**

<table>
<thead>
<tr>
<th></th>
<th>Metal salt</th>
<th>BET SA (m²/g)</th>
<th>H₂ uptake at 1 bar and 77 K (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COF-301</td>
<td>n/a</td>
<td>840</td>
<td>1.0</td>
</tr>
<tr>
<td>COF-301-Pd</td>
<td>PdCl₂</td>
<td>60</td>
<td>0.5</td>
</tr>
<tr>
<td>COF-301-Pt</td>
<td>PtCl₂</td>
<td>20</td>
<td>0.2</td>
</tr>
</tbody>
</table>
New COFs replete with metal binding sites

- All starting materials are in hand.
- Synthesis of these COFs has started.
Approach #1: Hexaazatriphenylene COFs

- Compound 3 was prepared.
- Studying COF synthesis condition of 3 with 2, 4, or 5.
Proposed target structure #1
TPymT-COF-PdCl

The calculation of the isotherm is underway.
Proposed target structure #2

HAT-COF-PdCl₂

The calculation of the isotherm is underway.
Proposed target structure #3
CpFe-COF

View 1
View 2
CpFe
CpFe-COF
Configuration 3
Configuration 5
CpFe-H₂

The calculation of the isotherm is underway.
Ideal $\Delta H$ for maximized delivery amount of $H_2$

- Langmuir model was used for the generalization.
- $\Delta H = 20$ kJ/mol is the optimal value to maximize the delivery amount between 5 and 100 bar.
Approach #2: Optimization of metal loading

- Simulated data indicate that delivery amount of $H_2$ (total, 298 K) can be maximized by either partial metalation or mixed metal impregnation.
- Implement calculations on other COFs (e.g. COF-301, COF-42) to optimize delivery amount of $H_2$.
- Study the effects of mixed metal impregnation to control the $Q_{st}$ profile.
- Based on the prediction, metalation experiments will be performed.
Summary

Relevance: For room temperature hydrogen storage, a systematic survey was started experimentally as well as theoretically.

Approach: Aim at increasing strong binding sites for maximum hydrogen uptake capacity without losing pore volume.

Technical accomplishments and progress:
- Synthesized new COFs through hydrazone and imine condensation
- Began metalation experiments of COFs
- Began synthesis of mixed-metal ZIFs for improved adsorption enthalpy
- Found linkers with optimal binding energy for H₂ storage (20 kJ/mol)
- Designed new architectures with these linkers and began simulation calculations of H₂ uptake

Technology transfer/collaborations: Active relationship with collaboration partners (organic synthesis and material design) and BASF (verification of the data).

Proposed future research:
- Prepare COFs with metal binding sites and optimize the activation condition
- Employ metals to create strong binding sites and experimentally evaluate the $Q_{st}$
- Predict H₂ isotherms for modeled compounds with metals
- Study plausible route to synthesize the modeled compounds based on the thermodynamics
- Calculate the diffusion coefficient to estimate the kinetic factor with new force field