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

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Timeline

Project start date: 9/1/2008
(funded from 4/1/2009)
Project end date: 1/31/2013
Percent complete: 20%

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
- Funding received in FY09: $400 K
- Funding for FY10: $400 K

Collaborating Partner

- BASF
Description of new materials

Covalent Organic Frameworks (COFs)
- Control of structure, topology, and interpenetration
- Lightweight materials
- Design of functionalities
- Suitable towards light metal impregnation
- High-throughput material discovery is applicable

G: bor

COF-108 \((d = 0.17 \text{ g cm}^{-3})\)

Science 2007
Covalent Organic Frameworks (COFs)
H$_2$ uptake in 3D COFs is almost the same as that in MOF-177.
Objectives (FY09-10)

Room temperature H₂ storage in COFs to meet DOE 2015 Targets

- Synergistic work between Yaghi (UCLA) and Goddard (Caltech)
- Build high-throughput preparation setups for COF synthesis (high temperature and pressure)
- Develop chemistry to realize stable frameworks
- Introduce potential metal binding sites through the COF synthesis
- Determine atomistic connectivity of COFs using an *ab initio* charge-flipping method using PXRD data
- Predict adsorption enthalpy of H₂ on various metal sites
Milestones (FY10)

1. Discover new COFs utilizing high-throughput methods and explore $H_2$ uptake properties of COFs in the same parameter range.

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 °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.
Strategy

Improve the framework stability against impurity (e.g. water)

Introduce metal binding sites through the COF formation

JACS, 2009
Imine-Linked 3-D Porous COF

N_2 and H_2 isotherms for COF-300

Permanent porosity was observed.

(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
Pore structure from low resolution PXRD data

*ab initio* charge-flipping method was applied to determine the pore structure with extracted intensities.
- Unit cell parameters are required.
- No information related to the connectivity and space group is necessary.
Imine-Linked porphyrin COF

Surface area
- BET: 990 m² g⁻¹
- Langmuir: 1270 m² g⁻¹

Type I isotherm implies a staggered stacking fashion.

![Chemical structures and diagrams](image-url)
Hydrazone condensation

- Contains imine and amide functionalities
- Obtained hydrazone chemically stable in water and basic conditions.
- Polyacylhydrazones have been prepared showing monomer exchange under mild conditions.
- Hydrazides are very easy to make.
- Potential metal binding sites
Building blocks

- terephthalohydrazide
- 2,5-dihydroxyterephthalohydrazide
- pyridine-2,5-dicarbohydrazide
- 1,3,5-tris(4-formyl-phenyl)-benzene
- terephthalaldehyde
- benzene-1,3,5-tricarbohydrazide
- benzene-1,3,5-tricarbaldehyde
Typical example: COF-41

- White-yellow product.
- Hot filtration & rinse with boiling dioxane & cold THF.
- Distance between $C_3$ centers: 26.2 Å.

**Expected pore size is large enough to hold metal complexes.**

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<th>$\nu$ (C=N) 1</th>
<th>$\nu$ (C=N) 2</th>
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<tbody>
<tr>
<td>COF-41</td>
<td>1558</td>
<td>1273</td>
</tr>
<tr>
<td>Model</td>
<td>1550</td>
<td>1288</td>
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</table>
Proposed structure of COF-41

COF-41
hexagonal P
\(a = 43.616(14) \text{ Å}\)
\(c = 3.6186(13) \text{ Å}\)

- **bnn**
  - \(P6/mmm\)
  - \(a = 45.322 \text{ Å}\)
  - \(c = 3.5177 \text{ Å}\)

- **gra**
  - \(P6_3/mmc\)
  - \(a = 45.341 \text{ Å}\)
  - \(c = 6.4553 \text{ Å}\)
N$_2$ isotherm for COF-41

- Presence of mesopore $\Rightarrow$ enough space for metal impregnation
- Activation procedure needs to be optimized
Future work: other building blocks (for 3D nets)

- 4,4',4'',4'''-methanetetrayltetrabenzaldehyde
- 1,3,5-tris(4-formyl-phenyl)-benzene
- terephthalaldehyde
- benzene-1,3,5-tricarbaldehyde
Four plausible model systems were tested.
- Calculated MO, $U_{\text{total}}$ and $H_{\text{total}}$ for each model.
- The DFT-MO6 functional was used to calculate the non covalent interactions with the basis set LACVP to calculate optimization.
- Adsorption enthalpy of these models is ranging from 3 to 4 kcal/mol (12-17 kJ/mol).
Theoretical prediction of binding energy #1

With metal

- MO6[&]/(SCFE)
- Utot (SCFE + ZPE + U)
- Htot (Utot + pV)

The binding energy is almost constant with the addition of H₂.

Without metal

H₂-H₂ interaction of the metal-complex is stable than that of the bipyridine system.
Theoretical prediction of binding energy #2

The most favorable interaction is observed over the bond of N-Pt, which is the same as N-Ni system (Model #1).

Predicted binding energy is smaller than Model #1 (ca. 1 kcal/mol).
Theoretical prediction of binding energy #3

Favorable interaction is observed when H₂ molecule locates over C atom of the five membered ring.

Model #3

Configuration of 1H₂---Complex
Theoretical prediction of binding energy #4

Adsorption sites of H\textsubscript{2} does not seem to be the metal itself.

The most favorable interaction is observed when H\textsubscript{2} locates over the N-Zn bond.
Approach 1: Proposed COF connectivity for metalation

Various connectivity is known
Approach 2: Intercalation of COFs with metals

Eclipse stacking fashion can be utilized for metal intercalation.

- Permanent porosity was confirmed
- BET SA = 410 m² g⁻¹
- Presence of micropore filling (eclipse stacking)
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:
- Build high-throughput preparation setups
- Develop structural determination technique using *ab initio* charge-flipping method
- Synthesis of new COFs through hydrazone condensation
- Began modeling study for optimal binding energy

Technology transfer/collaborations: Active relationship with collaboration partners and BASF.

Proposed future research:
- Employ metals to create strong binding sites.
- Material design based on theoretical prediction.