Core-Shell MOFs for Direct Air Capture

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Prof. Chris Wilmer (Pitt, co-PI)
Prof. Nathaniel Rosi (Pitt, co-PI)
Dr. Janice Steckel (NETL liaison)

UCFER Task 05-UPitt-S1-22
Annual Project Review Meeting
October 5, 2021
Who’s on our team?

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Project goal & objectives

**Project goal:** identify and characterize a core-shell MOF design that strongly binds CO$_2$ and has a high selectivity for CO$_2$ over N$_2$/O$_2$/H$_2$O

**Project objectives:**
1. Computationally identify optimal core-shell combinations for direct air capture.  
   Dr. Wilmer’s team
2. Synthesize and characterize optimal core-shell MOFs.  
   Dr. Rosi’s team
3. Determine the optimal core-shell MOF packing structure.  
   Dr. Hornbostel’s team
What are core-shell MOFs?

1. MOFs = Metal-Organic Frameworks
   1. organic-inorganic hybrid crystalline porous materials
   2. consist of a regular array of positively charged metal ions interconnected by organic 'linker' molecules

2. Core-Shell MOFs = Core MOF + Shell MOF
   1. Core MOF in center
   2. Different shell MOF grown around core MOF
Why core-shell MOFs for DAC?

1. MOFs are great for traditional carbon capture
   1. Can pack lots of gas into small volume (i.e., great for gas *storage*)
   2. Can have high affinity to CO₂ over other species (i.e., great for gas *separations*)
   3. Scalable to industrial applications

2. Core-shell MOFs allow us to optimize for two properties
   1. Core MOF has high affinity to CO₂
   2. Shell MOF rejects H₂O
Basic core-shell MOF design

Ideal shell MOF:
• Low H₂O diffusivity
• High CO₂ diffusivity

Ideal core MOF:
• High CO₂ working capacity
• Low N₂ working capacity

Size the thickness of the shell and the volume of the core so that by the time H₂O breaks through the shell into the core, the core is full of CO₂.
What is the process?

Stage 1: adsorption
- Air (with reduced CO₂)
- Concentrated CO₂
- Applied heat
- Partial vacuum

Stage 2: regeneration
- Packed Bed Reactor
- Air (at “outside” temp and pressure and humidity)
Objective 1: Computationally identify optimal core-shell combinations for direct air capture.

Dr. Chris Wilmer
### Screening Overview

#### Two MOFs

<table>
<thead>
<tr>
<th>MOF</th>
<th>Functional Groups</th>
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</thead>
<tbody>
<tr>
<td>UIO-66</td>
<td>F, N&lt;sub&gt;3&lt;/sub&gt;, alkane-OC&lt;sub&gt;3&lt;/sub&gt;, alkane-HNC&lt;sub&gt;3&lt;/sub&gt;, NC&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>UIO-67</td>
<td>OH, CF&lt;sub&gt;3&lt;/sub&gt;, alkane-OC&lt;sub&gt;4&lt;/sub&gt;, alkane-HNC&lt;sub&gt;4&lt;/sub&gt;, ring-HNC&lt;sub&gt;5&lt;/sub&gt;</td>
</tr>
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<td></td>
<td>NH&lt;sub&gt;2&lt;/sub&gt;, branched-HNC&lt;sub&gt;5&lt;/sub&gt;, alkane-OC&lt;sub&gt;5&lt;/sub&gt;, alkane-HNC&lt;sub&gt;5&lt;/sub&gt;, ring-HNC&lt;sub&gt;6&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

#### Three Gases: CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>

**Measure:**
- Diffusion in LAMMPS (all gases)
- Adsorption in RASPA at two process conditions:
  - STP (1 atm, 298K)
  - 15 mbar, 373K
MOFUN: Find / Replace Functionalized Linkers

Find / replace functionalized linkers into structure

Often results in unrealistic functional group overlap!

Run NVT to relax functional group into more reasonable configuration.
Diffusion Selectivities

Functional Group - Diffusivity x 1e4 [Å² / fs ]
Adsorption Selectivities
### Screening Results

#### MOFs

<table>
<thead>
<tr>
<th>MOFs</th>
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</thead>
<tbody>
<tr>
<td>UIO-66</td>
<td><img src="image" alt="UIO-66 MOF" /></td>
</tr>
<tr>
<td>UIO-67</td>
<td><img src="image" alt="UIO-67 MOF" /></td>
</tr>
</tbody>
</table>

#### Functional Groups

- **F**
- **N₃**
- **alkane-OC₃**
- **alkane-HNC₃**
- **NC₄**
- **OH**
- **CF₃**
- **alkane-OC₄**
- **alkane-HNC₄**
- **ring-HNC₅**
- **NH₂**
- **branched-HNC₅**
- **alkane-OC₅**
- **alkane-HNC₅**
- **ring-HNC₆**

Best shell MOF candidates (UIO-67): F, OH, NH₂, alkane-OC₄

Best core MOF candidates (UIO-67): longest hydrocarbons

Best core MOF candidate: UIO66-NC₄
Objective 2: Synthesize & characterize optimal core-shell MOFs.

Dr. Nathaniel Rosi
Core-Shell MOFs for Molecular Separations

Li, Rosi, et al. JACS 2013

UiO-Based Core-Shell MOFs

Luo, Rosi, et al. JACS 2019
Ligand Design

Core ligand design strategy:
Lewis basic groups: \( \text{NH}_2^-, \text{OH}^-, \text{N}_3^- \)

Forming Lewis acid-base pair with \( \text{CO}_2 \)

Shell ligand design strategy:
Hydrophobic groups: alkylamino, alkylhydroxyl, F-

Preventing water from entering core MOF
Synthesis of UiO-67 MOFs

H₂-BPDC (UiO-67)
H₂-Me-BPDC (Me-UiO-67)
H₂-NH₂-BPDC (NH₂-UiO-67)
H₂-2NH₂-BPDC (2NH₂-UiO-67)

2 Theta/Degree

UiO-67
NH₂-UiO-67
Me-UiO-67
2NH₂-UiO-67
UiO-67 simulated
Characterizations of UiO-67 MOFs

N₂ adsorption isotherms at 77K

CO₂ adsorption isotherms at 298K

N₂ adsorption isotherms at 298K
Comparison of Experimental Results vs. Simulation Results

Adsorption @ STP:

CO$_2$ loading $a$ cc/g at 4.2x10$^{-4}$ bar, 298 K
N$_2$ loading $b$ cc/g at 0.79 bar, 298 K

Adsorption selectivity = $\frac{a}{4.2 \times 10^{-4}} \div \frac{b}{0.79}$

<table>
<thead>
<tr>
<th></th>
<th>UiO-67</th>
<th>NH$_2$-UiO-67</th>
<th>2NH$_2$-UiO-67</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation Results</td>
<td>7.11</td>
<td>7.45</td>
<td>8.33</td>
</tr>
<tr>
<td>Experimental Results</td>
<td>7.20</td>
<td>28.9</td>
<td>133</td>
</tr>
</tbody>
</table>

Simulation results have lower selectivity but similar trend
Selection of Core-shell MOF Pair

Core:

- Highest CO$_2$ over N$_2$ adsorption selectivity: 31
- High CO$_2$ capacity: 0.0104 cm$^3$/g (STP, 42.18 Pa, 298K)

Shell:

- High CO$_2$/H$_2$O diffusion selectivity: 307
- High CO$_2$ diffusivity: 4.98 Å$^2$/fs
**(CyNH)**$_2$–**UiO-67** (Core MOF) synthesis

**ZrCl$_4$** + **[(CyNH)$_2$]**$ightarrow$**CH$_3$COOH, DMF**$ightarrow$120 °C

**(CyNH)$_2$-****UiO-67**

**Average diameter**: 422 ± 22 nm
NH$_2$-UiO-67 (Shell MOF) Synthesis

Zr(O$^n$Pr)$_4$ +

\[
\text{CH}_3\text{COOH, DMF}
\]

65 °C

NH$_2$-UiO-67

Average diameter: 363±22 nm

Size distributions (based on 300 counts)
Core-Shell MOF Synthesis

$\text{(CyNH)}_2\text{-UiO-67 seeds} + \text{Zr(OnPr)}_4 + \text{NH}_2\text{-BPDC} \xrightarrow{\text{CH}_3\text{COOH, DMF}} 65 \degree \text{C} \xrightarrow{} \text{(CyNH)}_2\text{-UiO-67⊂NH}_2\text{-UiO-67}$

Average diameter:
- $\text{(CyNH)}_2\text{-UiO-67 seeds: 546±61 nm}$
- $\text{(CyNH)}_2\text{-UiO-67⊂NH}_2\text{-UiO-67: 746±78 nm}$
Objective 3: Determine the optimal core-shell MOF packing structure.

Dr. Katherine Hornbostel
Goal: Optimize the particle and reactor designs for core-shell MOFs.

1. Optimize pellet/particle design

2. Optimize reactor design

Benchmark: Separate MOF reactors

https://commons.wikimedia.org/wiki/File:Fluidized_Bed_Reactor_Graphic.JPG
Q1: Developed COMSOL Multiphysics model of packed bed reactor filled with MOF pellets.
Q2: Developed COMSOL Multiphysics model of individual MOF pellet exposed to air flow.
Q3: Langmuir constants were extrapolated from experimental data and incorporated into the single pellet model.
Q3: Initial modeling results using the predicted isotherm values show physical accuracy.
Q4: Investigated different options for 3D-printed MOF monoliths available at Pitt.

- **Filament Printer**
- **Filament Extruder**
- **Food Printer**
- **Current Industry Method**
- **Binder Jet Printer**
- **Laser Sintering Process**

**Printing Method**

**Shortcomings**
## Project Schedule

<table>
<thead>
<tr>
<th>Obj.</th>
<th>Task</th>
<th>Year 1</th>
<th>Year 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.1 Simulate CO$_2$/N$_2$/H$_2$O adsorption in all CoRE database MOFs.</td>
<td>Q1 Q2</td>
<td>Q4 Q1</td>
</tr>
<tr>
<td></td>
<td>1.2 Simulate CO$_2$/N$_2$/H$_2$O diffusivity in all CoRE database MOFs.</td>
<td>Q4 Q1</td>
<td>Q4 Q1</td>
</tr>
<tr>
<td></td>
<td>1.3 Identify optimal core-shell MOF pairs.</td>
<td>Q3 Q3</td>
<td>Q3 Q4</td>
</tr>
<tr>
<td></td>
<td>1.4 Model water stability in 5 highest ranked core-shell MOF candidates.</td>
<td>Q3 Q3</td>
<td>Q4 Q4</td>
</tr>
<tr>
<td></td>
<td>Year 1</td>
<td>Year 2</td>
<td></td>
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<tr>
<td>2.1 Prepare and characterize adsorption properties of target MOFs for core and shell domains.</td>
<td>Q1</td>
<td>Q2</td>
<td>Q3</td>
</tr>
<tr>
<td>2.2 Develop synthetic protocols for preparing core-shell MOFs with selected core and shell domains with optimal properties.</td>
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<tr>
<td>2.3 Characterize CO₂ capture performance of core-shell MOFs in dry and humid air.</td>
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<tr>
<td>3.1 Create 3D-printed monolith with core MOF.</td>
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<td>3.2 Coat monolith in shell MOF and test core-shell monolith.</td>
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<tr>
<td>3.3 Perform experiments on core-shell MOF powder.</td>
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Next steps

1. **Wilmer team:**
   1. Score and rank core-shell MOF combinations based on combined adsorption/diffusion properties
   2. Screen smaller subset of candidate core-shell MOFs with higher fidelity simulations

2. **Rosi team:**
   1. Adsorption characterization of core-shell system
   2. Examination of properties as function of core and shell thickness

3. **Hornbostel team:**
   1. Finish developing single pellet core-shell model and perform parametric studies
   2. 3D-print first core-shell MOF monolith

4. **Everyone:** start drafting first journal paper(s) based on this work
Thank you! Questions?

Shell MOFs + Core MOFs → Core-Shell MOF Combinations