CO$_2$ Binding in Metal-Organic Frameworks

By: Tim Dougherty

Road Map: Where we’re headed

• Background

• Applications

• Current work at NIST

• Future work after SURF
Today’s CO₂ Problem

Global Fossil Carbon Emissions

- Total
- Petroleum
- Coal
- Natural Gas
- Cement Production

Million Metric Tons of Carbon / Year

1800  1850  1900  1950  2000

http://commons.wikimedia.org
Today’s CO₂ Problem

http://www.epa.gov/climatechange/ghgemissions/gases/co2.html
Current Industrial Capture of CO₂ – Monoethanolamine (MEA) absorption

\[ \text{C}_2\text{H}_4\text{OHNH}_2 + \text{H}_2\text{O} + \text{CO}_2 \overset{\leftrightarrow}{\rightarrow} \text{C}_2\text{H}_4\text{OHNH}_3^+ + \text{HCO}_3^- \]

Commercial CO₂ Applications:
- Dry ice production
- Carbonation of beverages
- Urea production

- High cost in energy and capital
  - MEA reduces efficiency by 30%
- MEA is also toxic
- More efficient, less costly process are being developed
  - MOFs?

What exactly is a metal organic framework?

- MOFs are metal cations or clusters connected through organic ligands to form rigid 3-D, often porous, structures.

- Structure allows for much diversity among MOFs (synthetic precursors not constrained to those illustrated here).

- Synthetic make-up gives rise to diverse pore dimensionality, incredibly large surface areas, among other unique properties.

What exactly is a metal organic framework?

Applications of MOFs

- Catalysis
- H$_2$ storage
- Gas separations
  - Reversible CO$_2$ capture

Research at the NCNR

Synthesis and CO$_2$ adsorption study of the MOF family M$_3$(BTC)$_2$

Determination of CO$_2$ binding sites
3-Dimensional Structure of $M_3(BTC)_2$

- As synthesized structure contains solvent molecules
- Solvent is easily removed upon heating
- Structural features attractive for gas adsorption:
  - 1 open metal site
  - 2 large channels or pores
  - 1 small pore

Oxygen – Red
Carbon – Gray
Metal – Blue
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Coordinatively-unsaturated metal site
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Synthesis

- \( \text{Cu}_3(\text{BTC})_2 \)
- \( \text{Cr}_3(\text{BTC})_2 \) – air sensitive
- \( \text{Mo}_3(\text{BTC})_2 \) – air sensitive (ongoing)

\[
\text{Cu(NO}_3\text{)}_2 \cdot 2.5\text{H}_2\text{O} + \text{Benzene-1,3,5-carboxylic acid (BTC)} \xrightarrow{85^\circ\text{C}} \text{Cu}_3(\text{BTC})_2
\]

\[
\text{DMF:H}_2\text{O:EtOH}
\]

\[
\text{Chromium/Molybdenum hexacarbonyl} + \text{Benzene-1,3,5-carboxylic acid (BTC)} \xrightarrow{155^\circ\text{C}} \text{Cr}_3(\text{BTC})_2 \quad \text{Mo}_3(\text{BTC})_2
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Copper Nitrate Hemipentahydrate

Copper Nitrate

Hemipentahydrate

Benzene-1,3,5-carboxylic acid (BTC)

Chromium/Molybdenum hexacarbonyl

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Benzene-1,3,5-carboxylic acid (BTC)

DMF:H$_2$O:EtOH

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Cu(NO$_3$)$_2$·2.5H$_2$O + Benzene-1,3,5-carboxylic acid (BTC) $\rightarrow$ Cu$_3$(BTC)$_2$

DMF

155$^\circ$C

Chromium/Molybdenum hexacarbonyl + Benzene-1,3,5-carboxylic acid (BTC) $\rightarrow$ Cr$_3$(BTC)$_2$

Mo$_3$(BTC)$_2$


Neutron Powder Diffraction

Bragg’s Law:
\[ 2d \sin \theta = n\lambda \]

- \(d\) – lattice spacing
- \(\theta\) – scattering angle
- \(\lambda\) – incoming wavelength
- \(n\) – integer value

Lattice of sample

http://www.ncnr.nist.gov/instruments/bt1/
Neutron Powder Diffraction

1.03 g Cr$_3$(BTC)$_2$ dosed at 6.12 bar CO$_2$ (1.5 CO$_2$ per Cr)
3.40 g Cu$_3$(BTC)$_2$ dosed at 30.98 bar CO$_2$ (2.5 CO$_2$ per Cu)

Benefits over X-ray Powder Diffraction:
• Gives accurate information about atomic positions due to availability of high scattering angles
• Allows easier **quantitative** analysis for gas dosing studies than XRPD
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Neutron Powder Diffraction (cont.)

Cr$_3$(BTC)$_2$ Bare
Cr$_3$(BTC)$_2$ dosed with 1.5 CO$_2$ per Cr
Rietveld Refinement for $\text{Cr}_3(\text{BTC})_2$ – dose of 1.5 $\text{CO}_2$ per Cr

Chromium
Oxygen
Carbon
Hydrogen
Rietveld Refinement for $\text{Cr}_3(\text{BTC})_2$ – dose of 1.5 CO$_2$ per Cr

- Fourier map gives areas of missing density
- Manually input locations of CO$_2$
- Refinement cycles to obtain best fit of site occupancy and location
Rietveld Refinement
for Cr$_3$(BTC)$_2$ – dose of 1.5 CO$_2$ per Cr
Rietveld Refinement for $\text{Cr}_3(\text{BTC})_2$ – dose of 1.5 $\text{CO}_2$ per Cr

- $\text{CO}_2$ modeled at Cr site disordered over 4 orientations
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Slight inward pucker of paddlewheel for Cr compared to Cu
Comparison of Cr$_3$(BTC)$_2$ and Cu$_3$(BTC)$_2$

<table>
<thead>
<tr>
<th>CO$_2$</th>
<th>Cr$_3$(BTC)$_2$</th>
<th>Cu$_3$(BTC)$_2$</th>
<th>Cr$_3$(BTC)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>93 % metal sites occupied</td>
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<td>68 % pocket occupied</td>
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<td>23 % large pore site #1 occupied</td>
<td>14 % large pore site #2 occupied</td>
<td></td>
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</tbody>
</table>

Conclusions

- Primary CO$_2$ adsorption sites for both Cr$_3$(BTC)$_2$ and Cu$_3$(BTC)$_2$ found at:
  - unsaturated-metal center
  - inside tetrahedral pocket
- CO$_2$ displays slight preference towards metal site for both Cr and Cu, but both sites fill simultaneously
- Shorter interaction distance between CO$_2$ and unsaturated metal site for Cu$_3$(BTC)$_2$ over Cr$_3$(BTC)$_2$ due to pucker of Cr paddlewheel
Future Work

- More gas studies on Cr$_3$(BTC)$_2$
- Finish synthesis of Mo$_3$(BTC)$_2$
- Perform Neutron Diffraction Studies on Mo$_3$(BTC)$_2$
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