Engineering Accessible Adsorption Sites in Metal Organic Frameworks for CO$_2$ Capture

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Associate Professor of Chemistry

Co-principal Investigator: Dinadayalane Tandabany, Ph. D.
Associate Professor of Chemistry

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National Energy Technology Laboratory
Morgantown, WV

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Presentation Outline

- The project team
- Technical background/motivation for the project
- Potential significance of the results of the work
- Relevancy to fossil energy
- Statement of Project Objectives (SOPO)
- Project milestones, budget, and schedule as related to SOPO tasks
- Project management plan
- Project status and preliminary results
Project Team

Principal Investigator: Conrad W. Ingram, Ph. D.
Associate Professor of Chemistry
(Inorganic Chemistry, CAU)

Co-principal Investigator: Dinadanylane Tandabany, Ph. D.
Associate Professor of Chemistry
(Physical/computational chemistry, CAU)

Post Doc: Huayang Lee, Ph. D.

One graduate (Ph.D.) student

Students: Two project funded undergraduate students
Many leverage-funded undergraduate students
Department of Energy (DOE) is focused on improving the cost effectiveness of novel technologies for CO₂ capture so that fossil based systems with carbon capture are cost competitive.

Typically flue gas composition:
- CO₂: 3–15% (by vol.)
- O₂: 5%
- N₂: 81%

Adsorbents performance requirements for effective post combustion adsorption technology:
- chemically stable
- high CO₂ capacity and selectivity
- easily regenerated with minimal energy input
- easily synthesized with low capital cost

http://energy.gov/fe/science-innovation/carbon-capture-and-storage-research/carbon-capture-rd
Metal organic framework as CO$_2$ adsorbent

MOF = covalent linkage of metal ions as nodes + organic ligand as linker (also defined as 3D coordination polymer with permanent porosity)

Attributes
- Unprecedented high surface area – up to 5000 m$^2$/g
- Tunable surface chemistry and pore size
- Thermally stability (variability)
- Potential large concentration of adsorption sites

Drawbacks
- Limited accessible to sites
- Pore window less than 2 nm
- Thermally stability (variability)

Commonly used ligand: benzene dicarboxylate

http://yaghi.chem.ucla.edu/staticpages/research/01MOFs
A combination of amine functionality and unsaturated metal sites to increase adsorption capacity

Examples of MOFs with metal center as CO$_2$ adsorption sites

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>Common Name</th>
<th>BET (m$^2$/g)</th>
<th>Langmuir (m$^2$/g)</th>
<th>CO$_2$ (Wt. %)</th>
<th>Press. (bar)</th>
<th>Temp (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_2$(DOBDC)</td>
<td>Mg-MOF-74</td>
<td>1800</td>
<td>2060</td>
<td>35.2</td>
<td>1</td>
<td>298</td>
</tr>
<tr>
<td>Zn$_4$O(BBC)$_2$(H$_2$O)$_3$</td>
<td>MOF-200</td>
<td>4530</td>
<td>10400</td>
<td>70.9</td>
<td>50</td>
<td>298</td>
</tr>
</tbody>
</table>

DOBDC: 2,5-dioxido-1,4-benzenedicarboxylate
BBC: 4,4′,4″-(benzene-1,3,5-triyl-tris(benzene-4,1-iy1))tribenzoate

To synthesize metal organic framework (MOFs) with improved sites accessibility, thus enhanced CO$_2$ adsorption and selectivity properties.

Specific objectives:

• Synthesize MOFs with metal ions adsorption sites in more accessible locations

• Synthesize MOFs with nitrogen/amine containing-ligand linker as a possible improved alternative to amine-functionalized MOFs; and

• Understand the nature of the adsorption sites and mechanism(s) by computational studies relevant to the adsorption of CO$_2$ within the metal organic frameworks.
The proposed research supports the Department of Energy’s (DOE) Office of Fossil Energy and the National Energy Technology Laboratory (NETL) mission.

- Advances in the science of coal/fossil fuel technologies, specifically carbon capture.
- The research will guide rational design/synthesis strategies towards producing advanced sorbents for CO$_2$ capture.
- Successful CO$_2$ adsorbent materials will have tremendous industrial and environmental (CO$_2$ mitigation) impact.
- Provide research opportunities for graduate and undergraduate students in the fields of chemistry, materials and science related to the use of fossil energy resources.
  - Develop the next generation of US scientists.
Approach

• Position metal in more accessible location.

• Increase thermal stability of resulting MOFs.

• Explore the effects of:
  
  ➢ chemical compositions of synthesis mixtures (such as, organic linkers/functionalities and metals)
  
  ➢ the synthesis conditions (such as temperature, and solvents)
Diaza crown ethers complexes as organic linkers
Five main activities:

1. Evaluate the CO$_2$ adsorption properties of diazo crown ether polycarboxylates based MOFs that were recently synthesized in our laboratory.

2. Synthesize new MOFs based on an expanded series of diazo crown ethers and judicious choice of metal ions, and, evaluate their CO$_2$ adsorption properties.

3. Evaluate the CO$_2$ adsorption properties of MOFs synthesized with the nitrogen-containing pyrazine linker, recently synthesized in our laboratory.
4. Investigate the nature of the sites and mechanism(s) of adsorption by conducting density functional theory (DFT) - based computational studies relevant to the adsorption of CO$_2$ within the metal organic frameworks:

- Density functional theory (DFT) level using double -z basis set with appropriate effective core potential (ECP) for metal ion will be employed for designing the materials and the capture of CO$_2$.

- A double-layered ONIOM (Our own N-layered Integrated Molecular Orbital and molecular Mechanics) approach will be employed in the benchmarking calculations.

- The DFT level will be used for the important region (adsorption site) of CO$_2$ adsorption and semi-empirical method will be used for rest of the region and larger molecular systems of the proposed MOFs.
Tasks

Task 1.0  Project management and planning

• Update the Project Management Plan

• Initiate project planning during kick-off meeting

Task 2.1  CO$_2$ adsorption studies on our recently synthesized diaza crown ether carboxylates MOFs

• Conduct CO$_2$ adsorption studies on the MOFs at temperatures between 273K and 298K and multiple dosing pressures between 0 and 1 atm.

• Generate single component adsorption-desorption isotherms and determine adsorption capacities from them.

• Determine selectivity factor from CO$_2$/N$_2$ ratios at the same temperature and pressure.
Task 2.2  Synthesis of MOFs with expanded diazo crown ether carboxylates

- Synthesis of diazo crown ethers polycarboxylates
- Synthesis of MOFs using expanded ligands of the ligands plus metals
- CO$_2$ adsorption properties and the CO$_2$/N$_2$ selectivity studies

- The metal ions will include at minimum s-block (Mg$^{2+}$ and Li$^+$), transition (including, Mg$^{2+}$, Mn$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Co$^{2+}$, Cu$^{2+}$ and Ni$^{2+}$)
Task 2.3  Synthesis of MOFs with diazo crown ether carboxylates containing side-arm substituents towards increasing stability

Use diazo crown ethers polycarboxylates, with side arm substituents to:
- Avoid interpenetrating structures, and to improve the thermal stability of the resulting MOFs, and used in MOFs preparation.
- Impart hydrophobic characteristics, thus aiding in the prevention of structural collapse following the thermal desorption of intercalated synthesis-solvent molecules.

Task 2.4  Evaluation of the CO$_2$ adsorption properties of MOFs synthesized with a nitrogen-donor pyrazine ligand

Task 3.0  Investigate the nature of the sites and mechanism(s) of adsorption by conducting density functional theory (DFT) - based computational studies relevant to the adsorption of CO$_2$ within the metal organic frameworks.
Characterization of the resulting framework structures

- **X-Ray crystallography:** MOFs framework structure and composition
- **Powdered X-ray diffraction:** Phase crystallinity and phase purity
- **Porosimetry:** Surface area and pore size, pore volume
- **Thermogravimetric analysis:** Thermal behavior
- **Infrared spectroscopy:** Chemical functionalities
- **Porosimetry/Surface area analyzer:** Adsorption studies of CO$_2$ and nitrogen
- **Inductively coupled plasma/mass spectrometry:** Metal content
<table>
<thead>
<tr>
<th>Tasks Schedule</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q1</td>
<td>Q2</td>
<td>Q3</td>
</tr>
<tr>
<td>1.0 Project planning</td>
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<tr>
<td>(select personnel, literature review, experiments design, procure chemicals)</td>
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<tr>
<td>2.1 Adsorption of CO₂ on three crown ether polycarboxylate MOFs already synthesized in our lab</td>
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<td>2.2 Synthesis of new s &amp; d block metal, expanded and side arm crown ether polycarboxylate</td>
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<tr>
<td>2.3 Adsorption of CO₂ on new s &amp; d block, metal expanded and side arm crown ether polycarboxylate MOFs</td>
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<td>Tasks and Schedule</td>
<td>Year 1</td>
<td>Year 2</td>
<td>Year 3</td>
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<tr>
<td></td>
<td>Q1</td>
<td>Q2</td>
<td>Q3</td>
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<tr>
<td>2.4 Adsorption studies of CO₂ on new pyrazine based MOFs</td>
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<td>3.0 Theoretical and computational studies of MOFs adsorption of CO₂ on MOFs</td>
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<td>4.0 Periodic reports to DOE</td>
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<tr>
<td>CATEGORY</td>
<td>Year 1 Costs</td>
<td>Year 2 Costs</td>
<td>Year 3 Costs</td>
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<tr>
<td>----------------------------------</td>
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<td>a. Personnel (include students)</td>
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<td>c. Travel</td>
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<td>e. Supplies</td>
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<td>i. Indirect Charges</td>
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<tr>
<td>Total Project Costs</td>
<td>$83,759.6</td>
<td>$85,108</td>
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Clark Atlanta University

- A private, historically black institution (HBCU)
- Formed in 1988 with the consolidation of Clark College (founded in 1869) and Atlanta University (founded in 1865).

CAU Thomas W. Cole, Jr. Research Center for Science and Technology

- Approximately 240,000 sq. ft. of state-of-the-art laboratories
Facilities and Equipment
• Project commencement October 1, 2014

• One Post Doc selection in process through leveraging from CAU CREST

• One current undergraduate selected: Ms. Kimberli Hill

• 2nd undergraduate student will be selected in November, 2014

• Graduate student to be selected in November 2014

• Background/literature review has commenced

• Laboratory training and familiarity with MOF synthesis and characterization procedures by student(s) have commenced
Diazo crown carboxylate ligands synthesis

\[
\text{2} + \text{3} \xrightarrow{\text{a}} \text{4}
\]

\[
\text{4} \xrightarrow{\text{b}} \text{1}
\]

a). Na₂CO₃, CH₃CN, reflux, 1 d; b). HCl (aq. 6 N), 90 °C 5 h.

Scheme 1
1. New 1D chain-like Zn- diazo crown ether carboxylate coordination polymer

\[
\text{Zn}^{2+} \\
\text{or} \\
\text{Co}^{2+} \\
= \text{1D MOF}
\]

2. New 2D cobalt-diazo crown ether carboxylate MOF

Ingram et al. 2013, Crystal Growth and Design.
4. $\text{H}_2\text{C-} \quad \text{N} \quad \text{N} \quad \text{O} \quad \text{C}_2\text{H}_4 \quad \text{CO}_2\text{H}$ $+ \quad \text{M}^{2+}$
5. New 3D cobalt- diazo crown ether carboxylate MOF

\[ \text{Ingram et al. 2013, Crystal Growth and Design.} \]

\[ \text{Ingram et al. 2013, Crystal Growth and Design.} \]
B. Paramagnetic 3D-MOF

\[ \text{6. } \begin{array}{c}
\text{O} \\
\text{C} \\
\text{O} \\
\text{C} \\
\text{O} \\
\end{array} + \text{Gd}^{2+} \]

Ingram et al. 2012, Inorganica Chimica Acta., 2012
Thank You!