Project Title:

CO_2 Removal from Flue Gas Using Microporous Metal Organic Frameworks

Technology Area:	**Technology Maturity:**
Post-Combustion Sorbents	Laboratory-Scale, Simulated Flue Gas

Primary Project Goal:

To develop and design a carbon dioxide (CO_2) removal system that employs metal organic framework (MOF) sorbents.

Technical Goals:

- Use combinatorial chemistry to systematically synthesize and characterize a wide range of MOF and related materials.
- Screen materials for hydrothermal stability.
- Collect isotherm data for subsequent development and optimization.
- Determine the effects of water on CO_2 adsorption.
- Develop and validate material scale up and forming procedures.
- Select the best one or two materials for final optimization and scale up.
- Determine the effects of contaminants on the performance of scaled up materials.
- Understand detailed kinetic and equilibrium data for incorporation in a process design and an economic analysis.

Technical Content:

MOFs are extremely high surface area, crystalline, microporous, and thermally-stable materials that have shown exceptional storage capacity for CO_2, methane, hydrogen, and other gases. MOFs typically consist of transition metal vertices, or hubs, attached three-dimensionally to other metal vertices by organic 'linker' molecules. After removal of reaction solvent, the resulting porosity can be adjusted by simply changing the length or composition of the molecules used to link the metal vertices. Well-ordered openings, channels, and pockets in the structures are from a few angstroms to tens of angstroms. Figure 1 represents the building blocks used to create prototypical MOF-5, in which the green ball represents the metal-containing hub, and the yellow cylinder represents the organic linker.

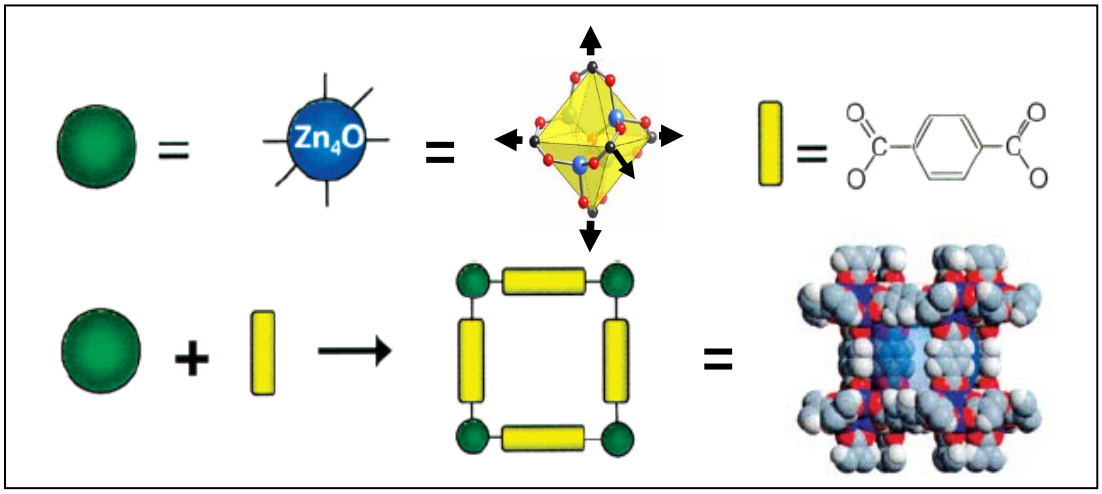

Figure 1: Building Blocks Used to Create Prototypical MOF-5

More than 50 MOFs for CO_2 adsorption were prepared from literature reports or designed by the experimenters. Table 1 displays the top MOFs for CO_2 capture.

Table 1: Top 10 MOFs for CO_2 Capture

Sample	Loading (mol/kg)	Loading (wt%)	Heat of adsorption (kJ /mol)
Mg\DOBDC (2)	4.73	20.9	60.1
Ni\DOBDC	3.40	15.0	27.2
Co\DOBDC	1.84	8.1	19.9
Mg\DOBDC (1)	1.28	5.6	21.3
HKUST-1 (CuBTC)	0.42	1.8	23.3
Zn\DOBDC	0.41	1.8	22.9
Al-MIL-110	0.24	1.1	21.7
Cr-MIL-101	0.18	0.8	13.3
Tb-MOF-76	0.18	0.8	21.7
Al-MIL-53	0.17	0.7	26
Zn-IRMOF-1	0.13	0.6	13.5

MOF-based adsorbents will be utilized in a vacuum pressure swing adsorption (VPSA) process for removal of CO_2 from flue gas. Figure 2 represents an example of MOF CO_2 adsorption capabilities as a function of pressure (for M/DOBDC, M represents the metal).

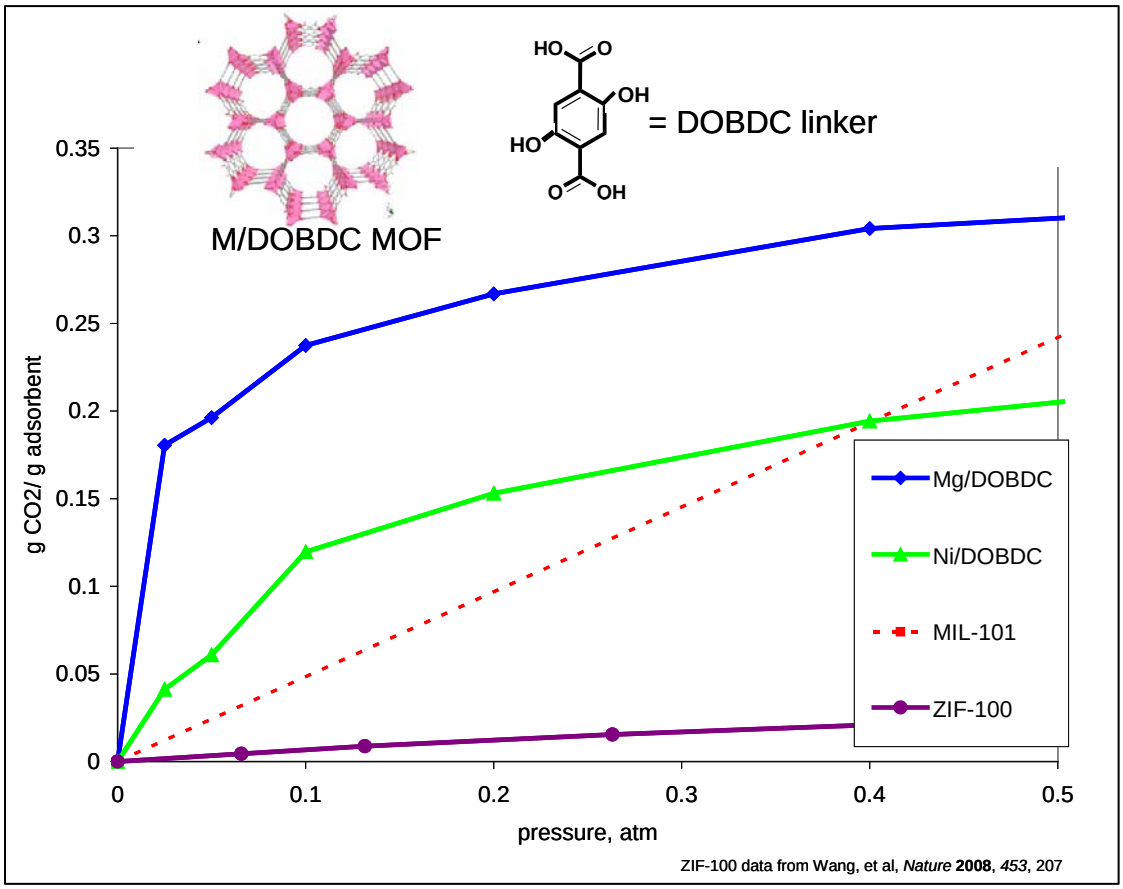

Figure 2: Example of MOF CO_2 Adsorption Capabilities as a Function of Pressure

Table 2: Process Parameters for MOF Sorbents

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	MOF	
	Heat of adsorption (kJ/mole CO_2)	40 – 60	
	CO_2 loading/working capacity, wt.%	10 – 20	
	Surface area, m^2/g	500 – 2000	
	Particle density, g/cm^3		
	Packing density, g/cm^3	0.3 – 0.7	
	Particle size (mm)	0.5 – 2.0	
	Heat capacity (kJ/K/kg)		
	Thermal stability, °C	250 – 400	
	Hydrothermal stability, °C	100 – 200	
Process Configuration	Attrition rate (fluidized bed), %/year		
	Cycle time (fixed bed), minutes	4 – 16	
	Pressure drop (fixed bed), psia	1 – 2	
Operating Conditions	Adsorption temperature, °C	25 – 45	
	Adsorption pressure, atm.	0.1 – 0.15	
	CO_2 capture efficiency, %	90 – 95	
	Regeneration method	VPSA	
	Regeneration temperature, °C		
	Regeneration pressure, atm.	0.01 – 0.05	
Heat Integration	Required regeneration steam temperature, °C		
Miscellaneous	Sorbent make-up rate, $kg/kgCO_2$		
Product Quality	CO_2 purity, %	90 – 98	
	N_2 concentration, %	Balance	
	Other contaminants, %		
Process Performance	Electricity requirement, $kJ/kgCO_2$		
	Heat requirement, $kJ/kgCO_2$		
	Total energy (electricity equivalent), $kJ/kgCO_2$		

Technology Advantages:

- High CO_2 adsorption capacity.
- Good adsorption/desorption rates.
- Good hydrothermal stability.
- Environmentally friendly.

R&D Challenges:

- Effects of sulfur oxides (SO_X), and nitrogen oxides (NO_X) on the MOF material.
- The necessity for separating nitrogen (N_2) from CO_2 before further compression and transport.
- Need for large vacuum pumps to compress the CO_2 from the outlet of the VPSA.
- Pressure drop across the VPSA beds.

Results To Date/Accomplishments:

From the more than 50 MOF materials evaluated, two were selected for further development and testing. The CO_2 capacity for these MOFs was evaluated in the presence of water and other contaminants and measured at several temperatures. Hydrothermal stability testing at accelerated conditions was also carried out for these MOFs.

Next Steps: • Collect more CO_2 adsorption data in moisture- and contaminant-containing streams. • Explore new synthesis space by creating new MOFs.	
Available Reports/Technical Papers/Presentations: UOP MOF Sorbent – March 2009 Presentation, Existing Plants R&D Meeting, Pittsburgh, Pennsylvania.	
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