Low-Energy Carbon Capture Using Metal-Organic Frameworks

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U.S. DEPARTMENT OF ENERGY | Office of Science

CGS Center for Gas Separations
Relevant to Clean Energy Technologies

Center for Gas Separations Relevant to Clean Energy Separations

Jeffrey R. Long, Director
Berend Smit, Deputy Director

University of California, Berkeley
Lawrence Berkeley National Laboratory

Mission and Approach

The aim of the CGS is to develop new materials and membranes that enable energy-efficient separation of gas mixtures, as required in the clean use of fossil fuels and in reducing emissions from industry.

Particular emphasis is on:

(1) Separations that reduce CO_2 emissions from power plants

(2) Energy-intensive gas separations in industry and agriculture

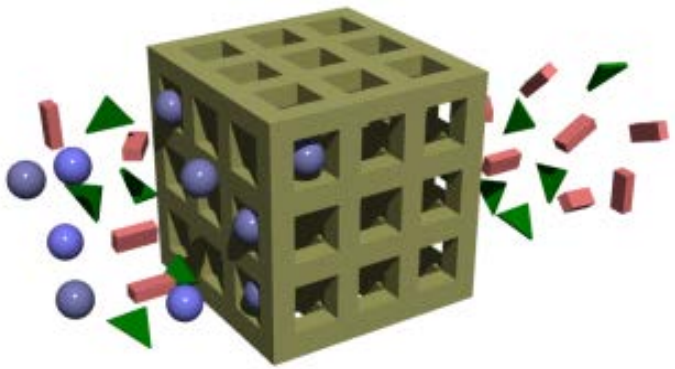
The research involves close cooperation between four teams:

Adsorbent Synthesis Team

Membrane Synthesis Team

Physical Characterization Team

Computational Team



CGS Principal Investigators

Adsorbent Synthesis Team

Jeffrey Long (UC Berkeley), Hong Cai (Joe) Zhou (Texas A&M University), Omar Yaghi (UC Berkeley)

Membrane Synthesis Team

Michael Tsapatsis (U Minnesota), Brett Helms (LBNL), David Hopkinson (NETL), Jeffrey Long (UC Berkeley), Ting Xu (UC Berkeley)

Physical Characterization Team

Jeffrey Reimer (UC Berkeley), Craig Brown* (NIST), Jeffrey Kortright (LBNL), Wendy Queen* (LBNL), Simon Teat (LBNL)

Computational Team

Berend Smit (UC Berkeley), Maciej Haranczyk* (LBNL), Laura Gagliardi* (U Minnesota), Jeffrey Neaton (UC Berkeley), David Prendergast (LBNL), Steve Whitelam (LBNL)

*Associated Investigator

CGS Science

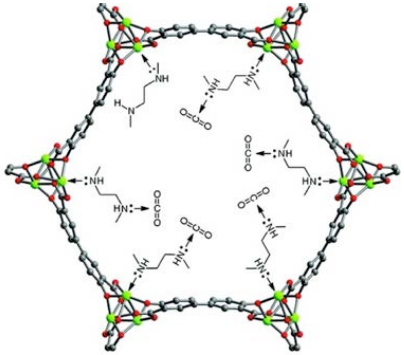
Novel Metal-Organic Frameworks and Porous Polymers

Phase-change adsorbents for CO_2 removal from: flue gas, natural gas, air

Redox-active adsorbents for the separation of O_2 from air

Back-bonding metals for the removal of N_2 from natural gas

Lock-and-key adsorbents for shape-selective hydrocarbon separations

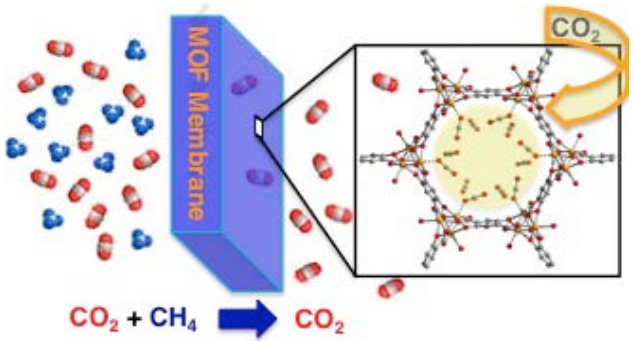


Novel Membranes

Supported metal-organic framework membranes

Mixed-matrix membranes

Metal-organic polyhedra-copolymer membranes

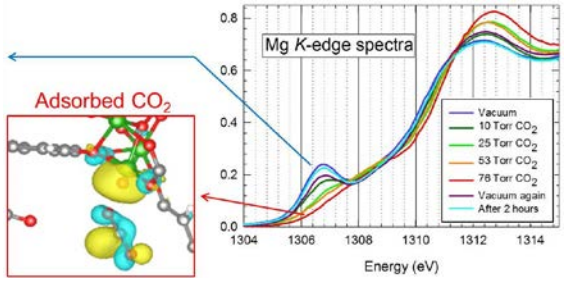


Cross-Cutting Research

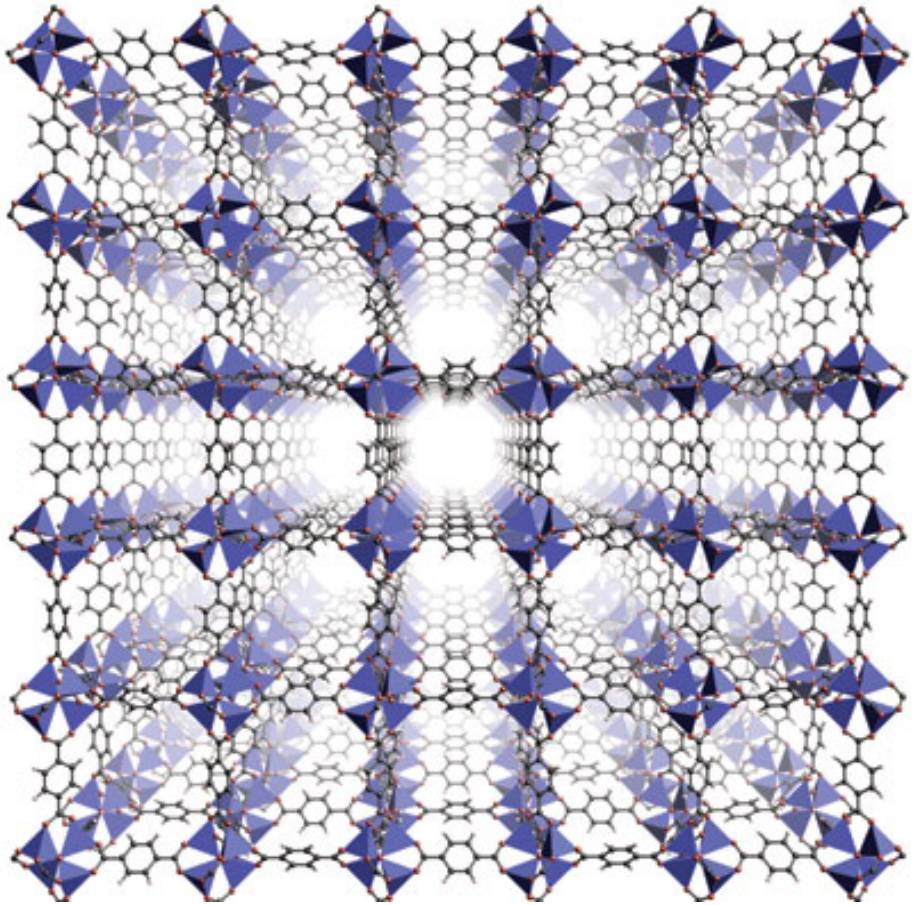
Mechanical properties of metal-organic frameworks

In-situ characterization of gas adsorption

Computational prediction of gas adsorption and transport



Metal-Organic Frameworks



$Zn_4O(1,4\text{-benzenedicarboxylate})_3$

MOF-5

- BET surface areas up to 7100 m^2/g
- Density as low as 0.13 g/cm^3
- Tunable pore sizes up to 10 nm
- Pores connected in 1-, 2-, or 3-D
- Internal surface can be functionalized

Can these materials be used for low-energy CO_2 capture?

Yaghi et al. *Nature* **2003**, *423*, 705
Kitagawa et al. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334
Férey *Chem. Soc. Rev.* **2008**, *37*, 191

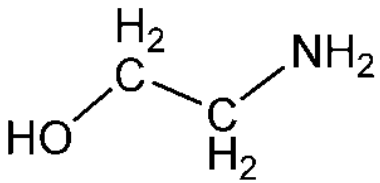
A Coal-Fired Power Plant Flue Gas

	vol %	diameter (Å)
N_2	73-77	3.64
CO_2	15	3.30
H_2O	5-7	2.65
O_2	3-4	3.46
SO_2	<0.08	
NO_x	0.05	
CO	0.002	3.76

Temperature = 40-50 ° C, total pressure = 1 bar

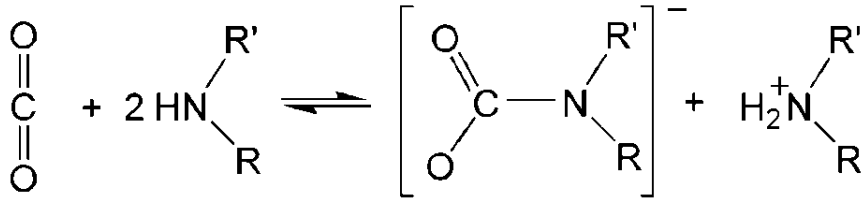
Aqueous Amine-Based CO_2 Capture

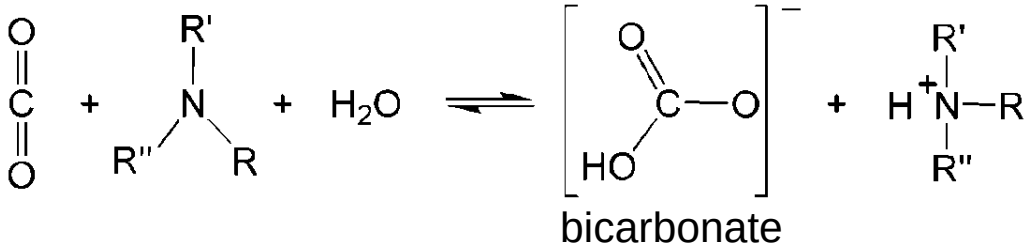
In water:



monoethanolamine

(**MEA**)



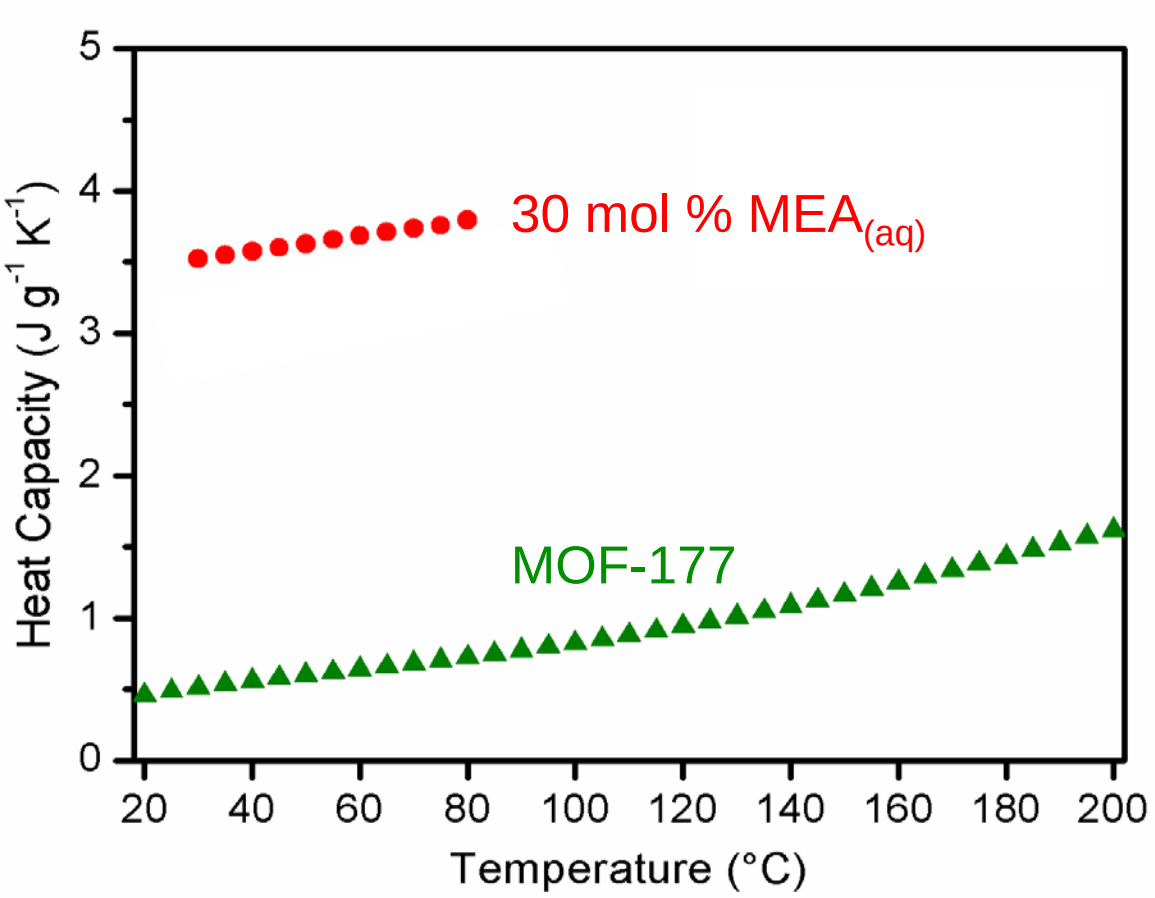


adsorption at 40 ° C and desorption at 120 ° C

Problems: Decomposition, low working capacity (~2 wt %), and high energy cost

(~30% energy penalty)

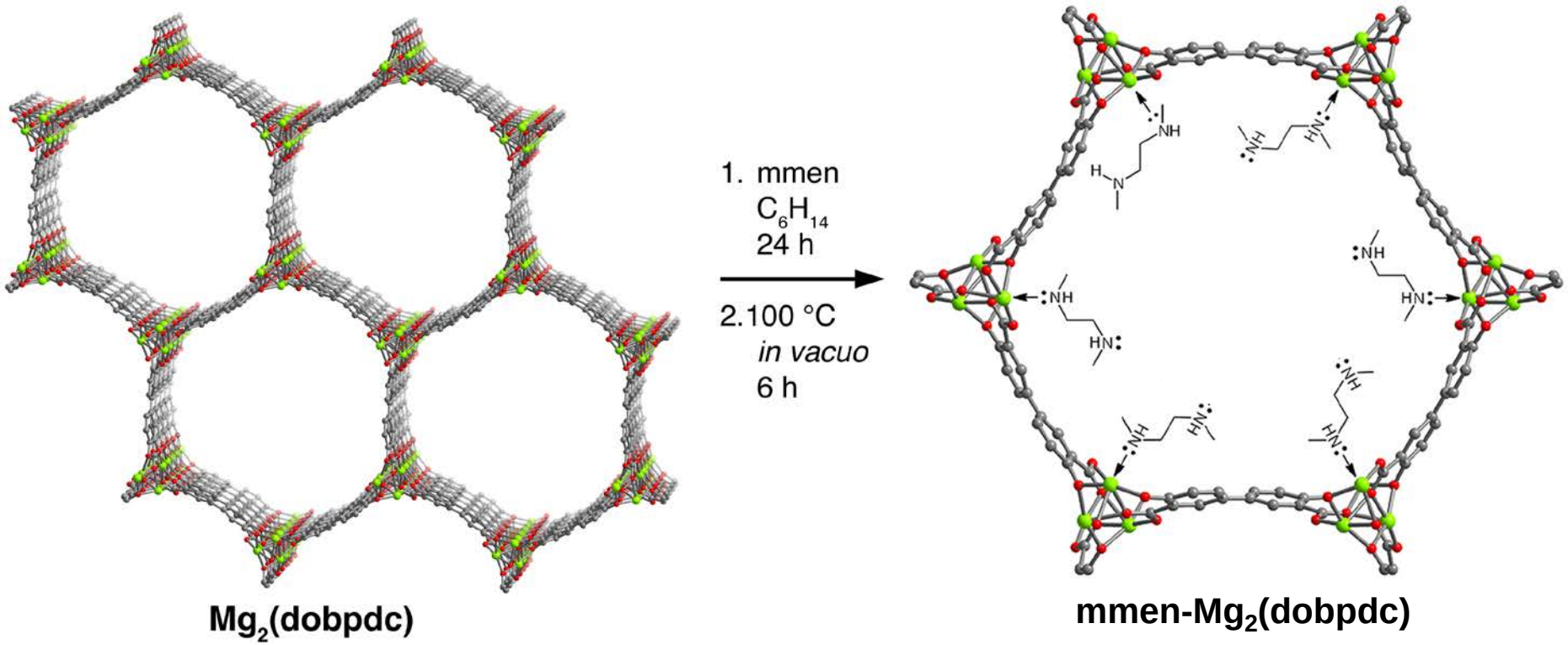
Heat Capacity of a Solid Adsorbent



- Concentration of MEA employed is limited by corrosivity issues

Mason, Sumida, Herm, Krishna, Long *Energy Env. Sci.* **2011**, *4*, 3030

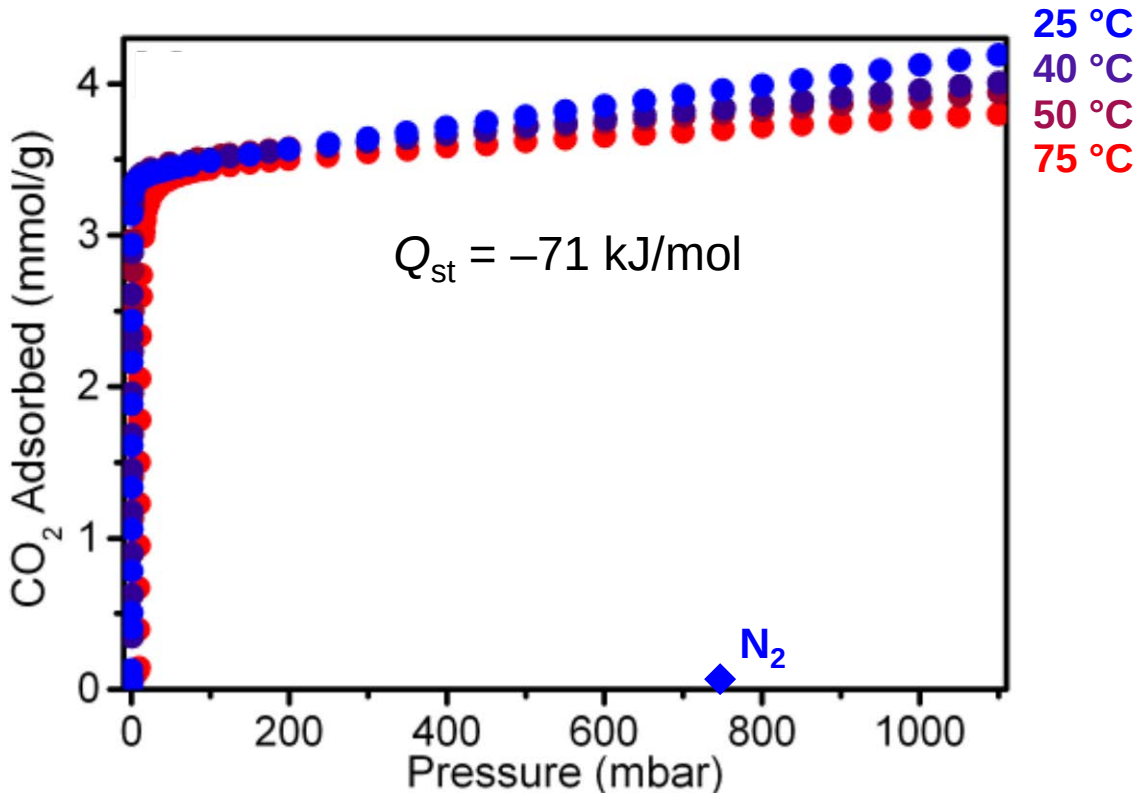
A Diamine-Appended MOF



- Dangling amines coat the periphery of the channels leaving space for rapid CO_2 diffusion

McDonald, Lee, Mason, Wiers, Hong, Long *J. Am. Chem. Soc.* **2012**, *134*, 7056

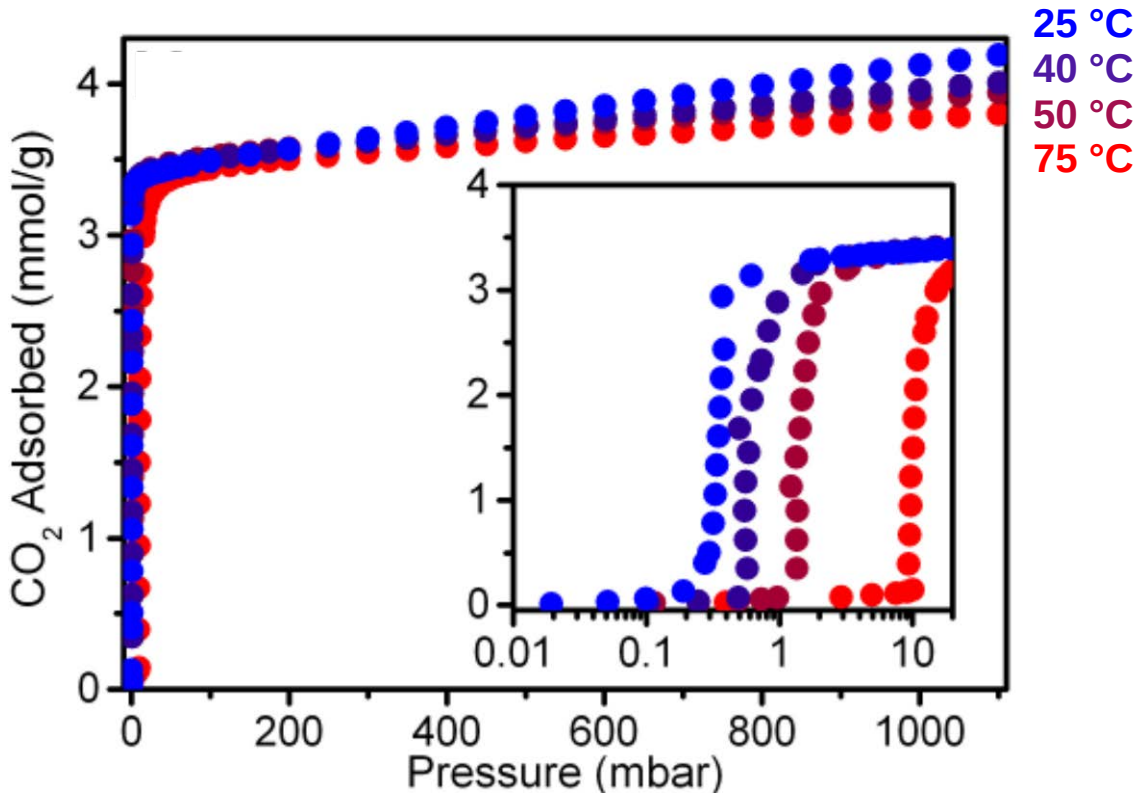
Strong, Selective CO_2 Adsorption



- Exposure to simulated dry flue gas leads to reversible uptake of 15 wt % CO_2
- Calorimetry data indicates regeneration energy of just 2.2 MJ/kg of CO_2

McDonald, Lee, Mason, Wiers, Hong, Long *J. Am. Chem. Soc.* **2012**, *134*, 7056

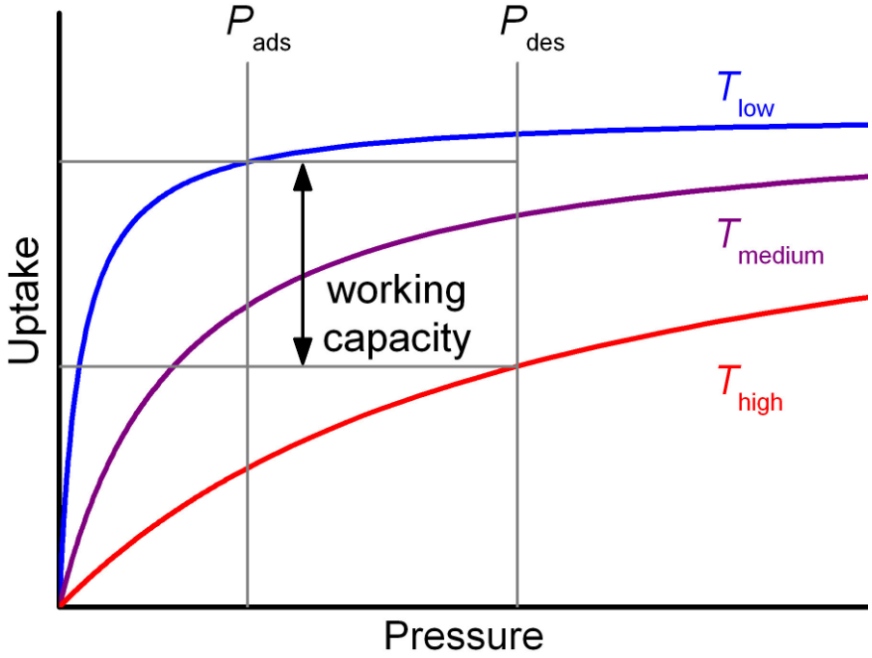
Stepped Isotherms Indicate Cooperativity

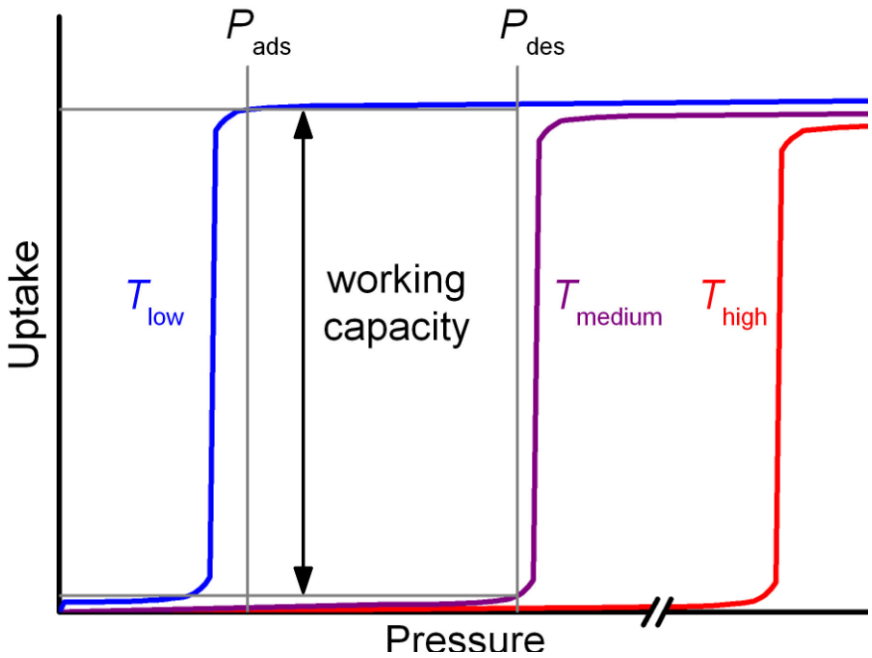


- Step position shifts rapidly to higher pressure upon increasing temperature
- Cooperativity is not due to framework flexibility, so what is the mechanism?

McDonald, Lee, Mason, Wiers, Hong, Long *J. Am. Chem. Soc.* **2012**, *134*, 7056

Classical versus Phase-Change Adsorbents

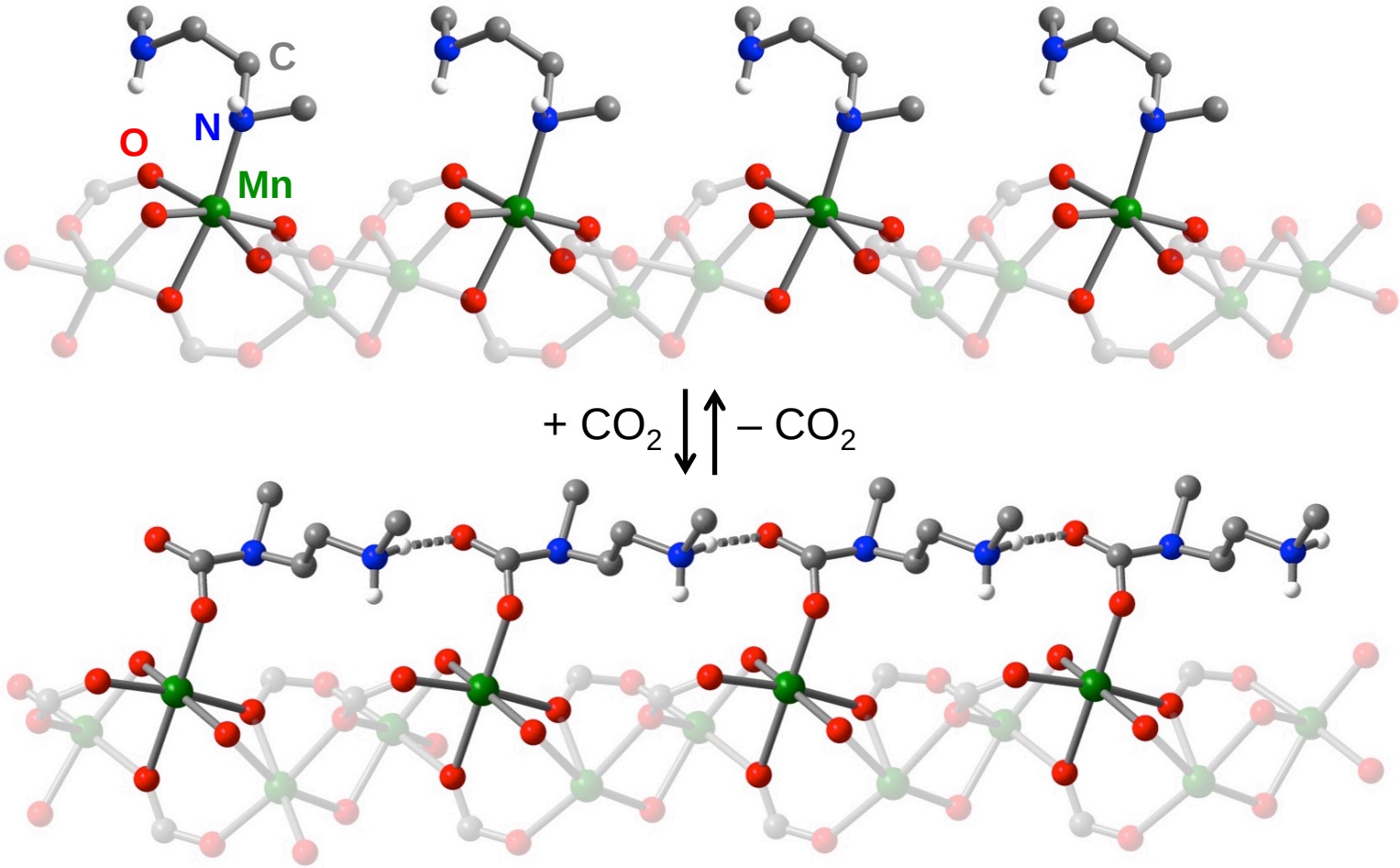




- For phase-change adsorbents, a small change in temperature gives a large separation working capacity

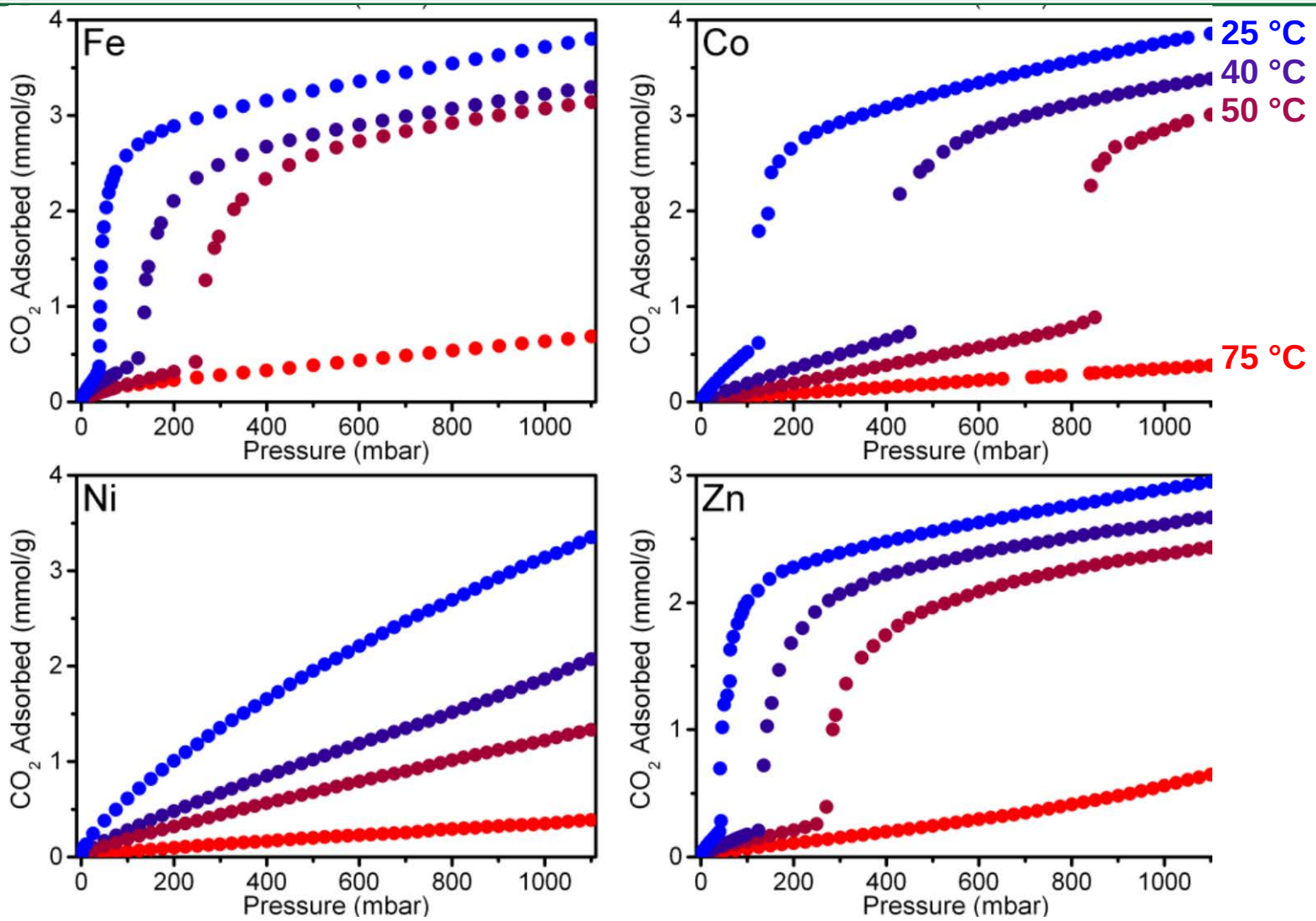
McDonald, Mason, Kong, Bloch, Gygi, Dani, Crocellà, Giordano, Odoh, Drisdell, Vlaisavljevich, Dzubak, Poloni, Schnell, Planas, Kyuho, Pascal, Prendergast, Neaton, Smit, Kortright, Gagliardi, Bordiga, Reimer, Long *Nature* **2015**, *519*, 303

Cooperative CO_2 Insertion to form Chains



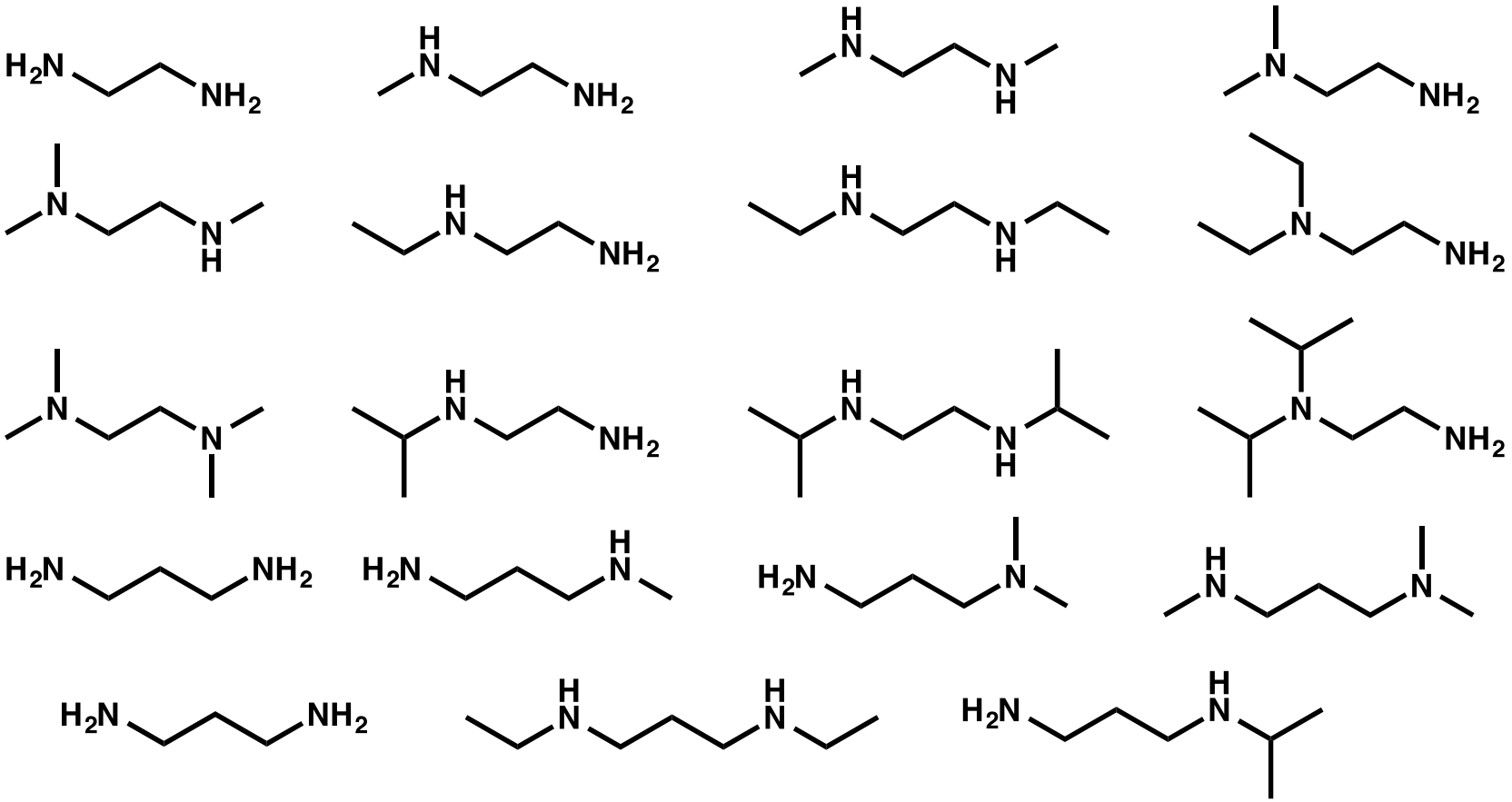
McDonald, Mason, Kong, Bloch, Gygi, Dani, Crocellà, Giordano, Odoh, Drisdell, Vlaisavljevich, Dzubak, Poloni, Schnell, Planas, Kyuho, Pascal, Prendergast, Neaton, Smit, Kortright, Gagliardi, Bordiga, Reimer, Long *Nature* **2015**, *519*, 303

Variation of Metal Shifts Step Position



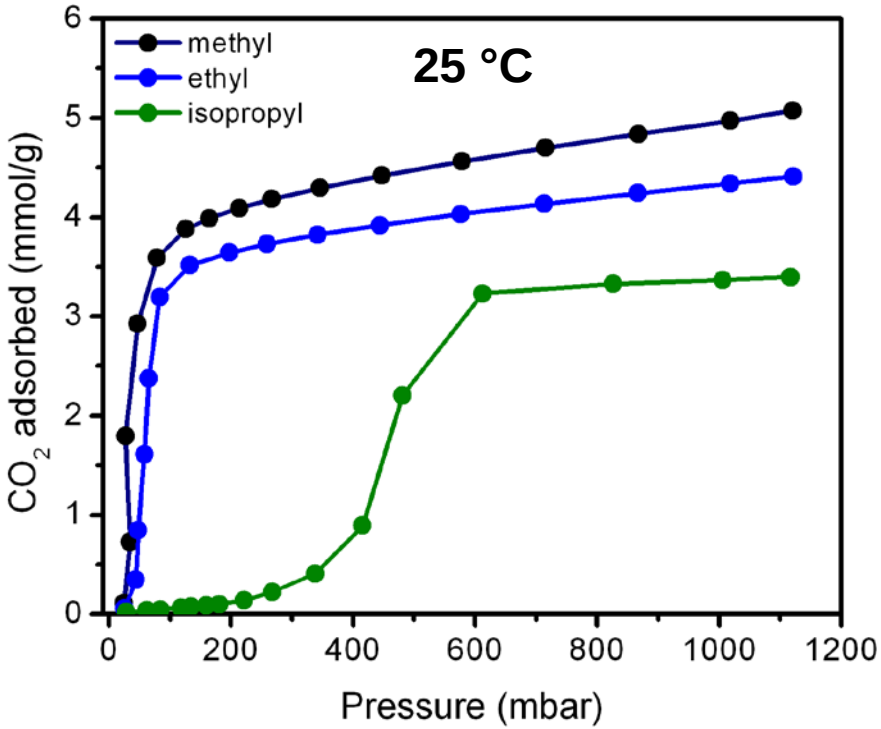
McDonald, Mason, Kong, Bloch, Gygi, Dani, Crocellà, Giordano, Odoh, Drisdell, Vlaisavljevich, Dzubak, Poloni, Schnell, Planas, Kyuho, Pascal, Prendergast, Neaton, Smit, Kortright, Gagliardi, Bordiga, Reimer, Long *Nature* **2015**, *519*, 303

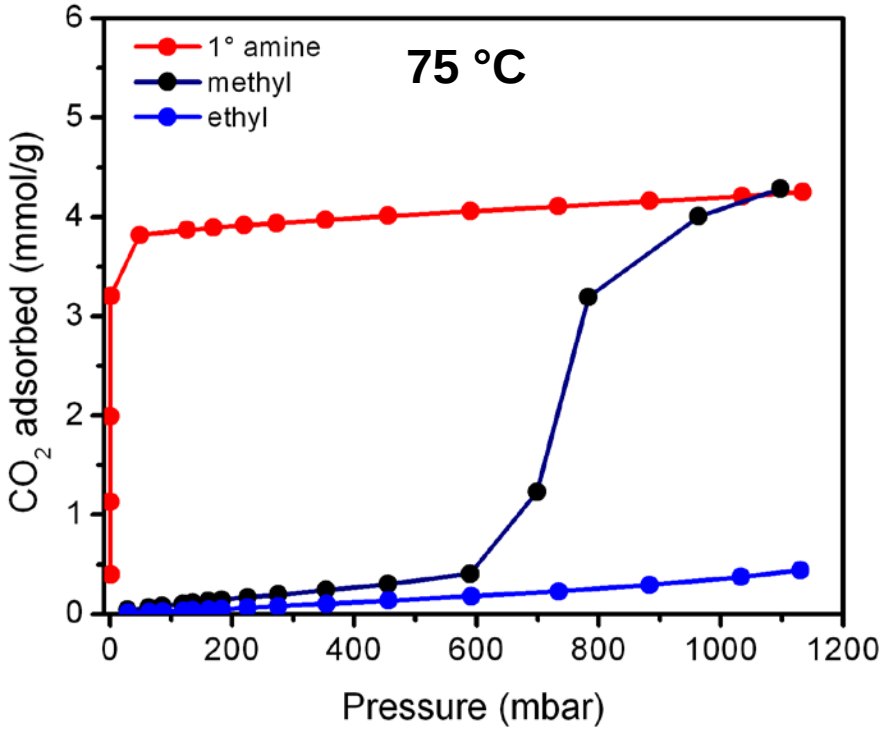
Variation of the Diamine Shifts Step Position



- >50 commercial diamines have now been tested in Mg_2(dobpdc)
- Step position at 40 °C varies from ~50 ppm to >1.2 bar

Variation of the Diamine Shifts Step Position





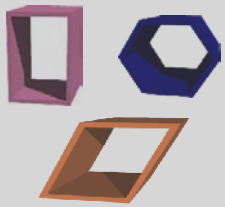
- Methyl and ethyl substituted amine materials can be regenerated at 75-80 °C
- Primary amine enables high-temperature CO_2 adsorption

ARPA-E IMPACCT PROJECT (2010-2015)

High-Throughput Synthesis

Highly-parallel, automated discovery of new MOFs

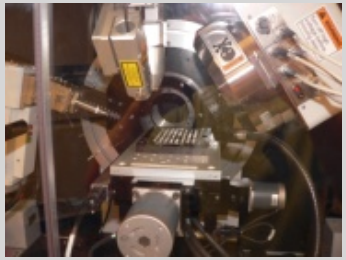
Automated Solid and Liquid Dosing



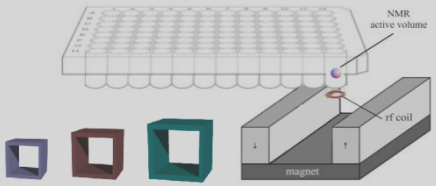
New Structure Types

High-Throughput Characterization

Rapid identification of new porous materials



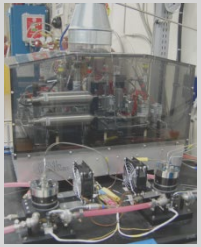
Powder X-ray Diffraction



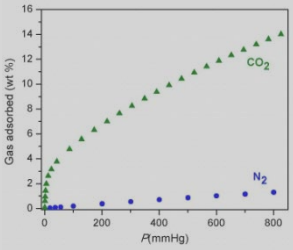
NMR Porosity Screening

CO_2 Adsorption Screening

Rapid screening of CO_2 capture performance



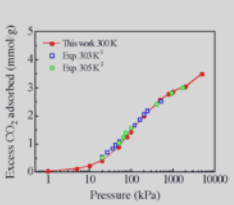
High-throughput Instrumentation

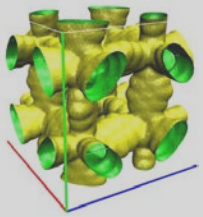


Adsorption Data

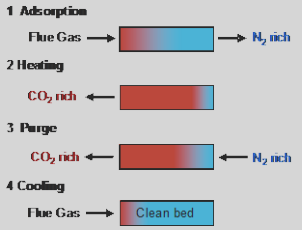
Computational Analysis

Data analysis, life cycle and sorbent performance analysis



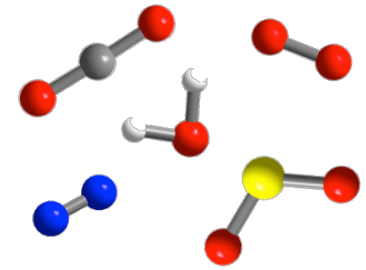


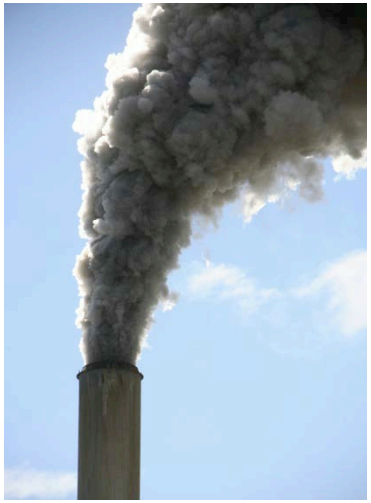
Simulations



Sorbent Performance

Wildcat Multicomponent Gas Adsorption Analyzer

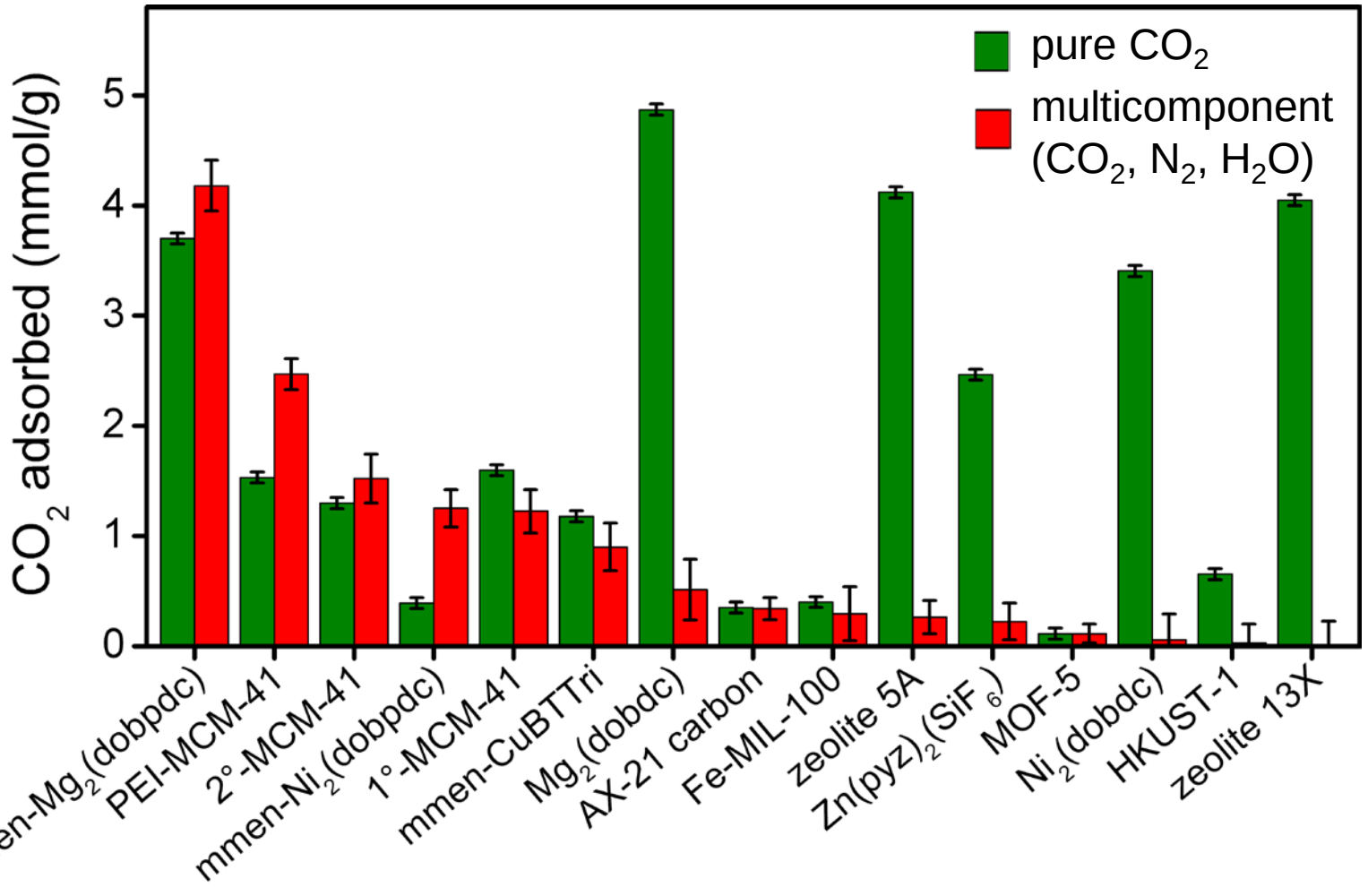




- Equilibrium adsorption measurements based upon mass spec analysis
- Can measure 28 samples in parallel for mixture including CO_2, N_2, H_2O, O_2, SO_2

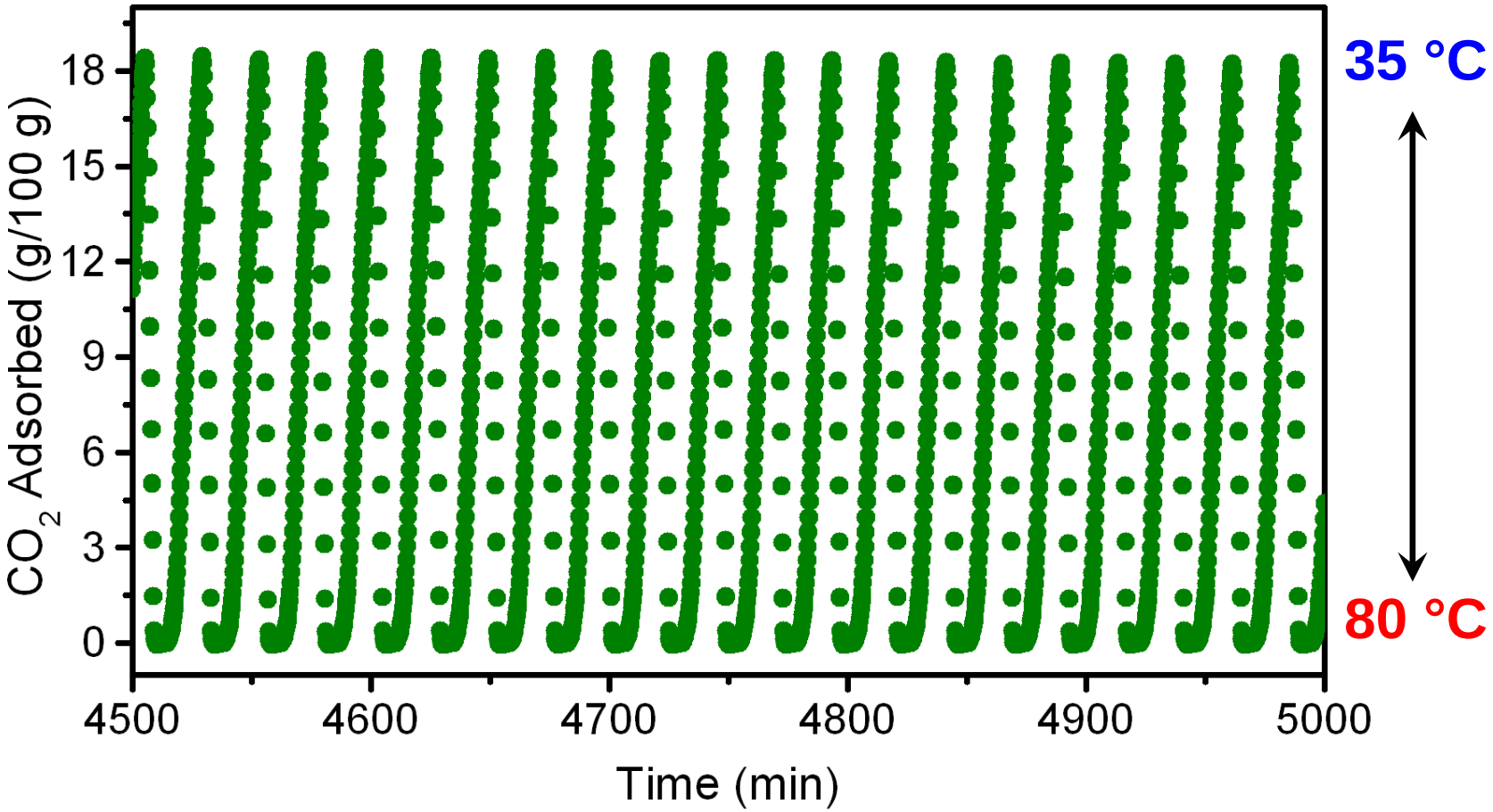
Mason, McDonald, Bae, Bachman, Sumida, Dutton, Kaye, Long, *J. Am Chem. Soc.* **2015**, *137*, 4787

CO_2 Adsorption in the Presence of Water at 40 °C



Mason, McDonald, Bae, Bachman, Sumida, Dutton, Kaye, Long, *J. Am Chem. Soc.* **2015**, *137*, 4787

Low Temperature Cycling for CO_2 Capture



- >15 wt % CO_2 adsorbed from stream of 15% CO_2, 4% O_2, 1% H_2O, 80% N_2
- Over 1000 cycles, capacity loss is just 0.0017% per cycle

Mosaic Materials, Inc.

Founders

Dr. Steven Kaye, LBNL

- Chief Science Officer, Wildcat Discovery Technologies
- 7 years of technology venture and business development experience
- 29 patents on new materials/equipment
- B.S. MIT, Ph.D. UC Berkeley (Long Group)

TR50
MIT TECHNOLOGY REVIEW
Top 50 Most Innovative Companies

Prof. Jeffrey Long, UC Berkeley and LBNL

- Director, DoE Energy Frontier Research Center for Gas Separations
- Director, Berkeley Hydrogen Storage Program
- >220 publications, >10 patents on MOFs

THE UNIVERSITY OF CALIFORNIA 1868

BERKELEY LAB

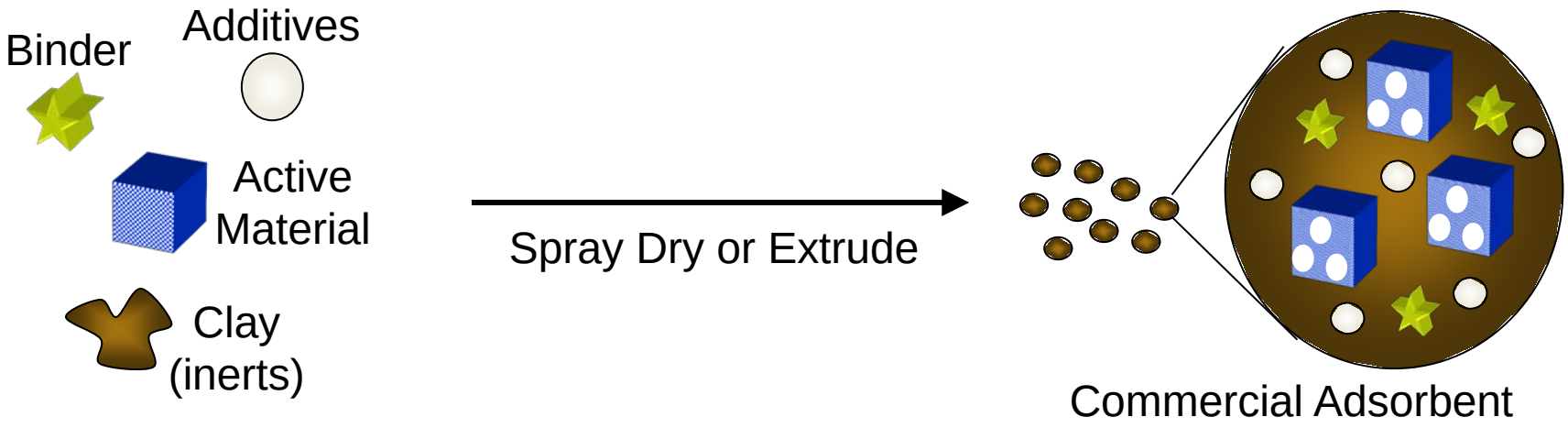
Funding

Cyclotron Road, LBNL

- New division founded by Dr. Ilan Gur (ARPA-E)
- Incubator for new energy technologies
- Provides seed funding, facilities, and equipment

cyclotronroad

Pelletization, Scale-Up, Process Design



Scale:


grams


kgs


~100 kg


tons

- Inexpensive synthesis developed for key MOFs suggests a production cost < $10/kg