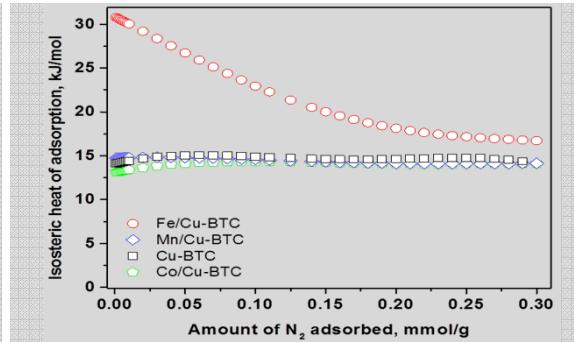
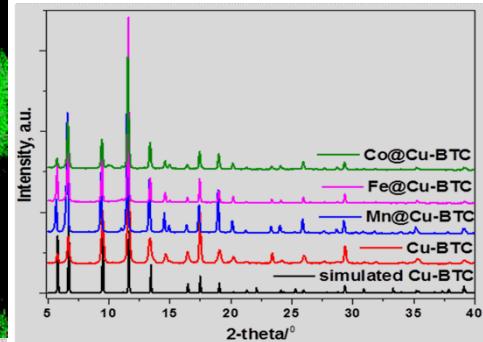
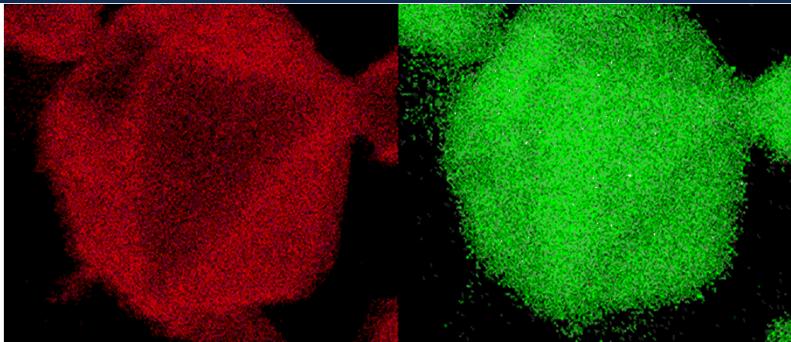


Exceptional service in the national interest



Efficient Light Gas Separations with MOFs via Predictive Modeling and Tuned Synthesis

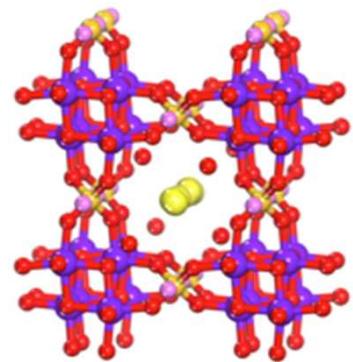
Tina M. Nenoff, Dorina F. Sava Gallis, Marie V. Parkes, Jeffery A. Greathouse, Mark A. Rodriguez, Scott M. Paap, and Christopher R. Shaddix
 Sandia National Laboratories, Albuquerque NM & Livermore CA

2015 ACS Fall Meeting, Boston MA
 August 16, 2015



This work is supported by the Laboratory Directed Research and Development Program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Novel SNL Separations and Waste Forms: Technologies for Environment and Energy Applications



R&D100 1996

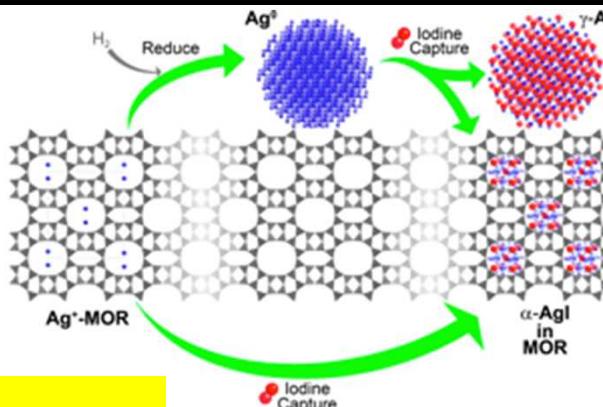
JACerS, 2009, 92(9), 2144

JACerS, 2011, 94(9), 3053

Solvent Extr. & Ion Exch, 2012, 30, 33

CST, Cs⁺ removal from water to Polycarbonate Waste Form

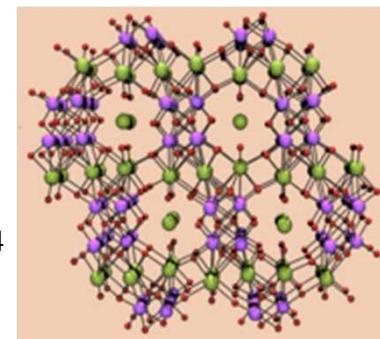
US Patents 6,479,427; 6,110,378



*Ag-MOR
I₂(g) capture & mechanisms*

JACS, 2010, 132(26), 8897

J Phys Chem Letters, 2011, 2, 2742



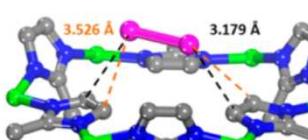
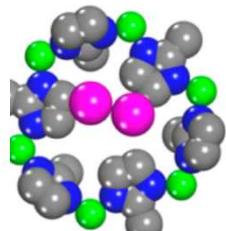
I₂/ZIF-8, Isolation to Waste Form

JACS, 2011, 133(32), 12398

US Patent filed 2012

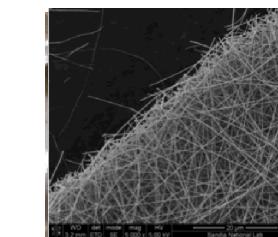
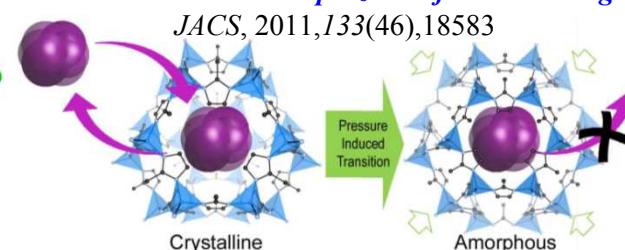
JACS 2013, 135, 16256

Fundamental Research to Applied to Commercial Products
Design the Separation Material To Develop the Waste Form

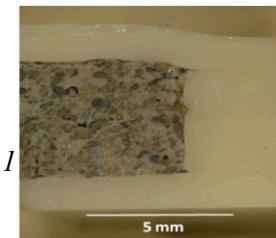


MOF Amorphization for Gas Storage

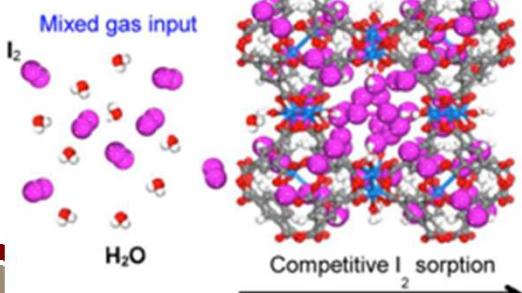
JACS, 2011, 133(46), 18583



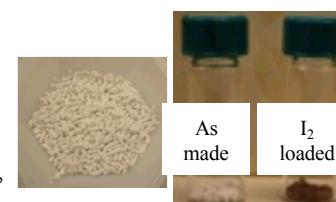
Nanoporous Nanofibers Volatile Gas Removal
US Patent Application, 2011



Universal Core-Shell Iodine Glass Waste Form & Getter
JACerS, 2011, 94(8), 2412
US Patent 8,262,950; 2012

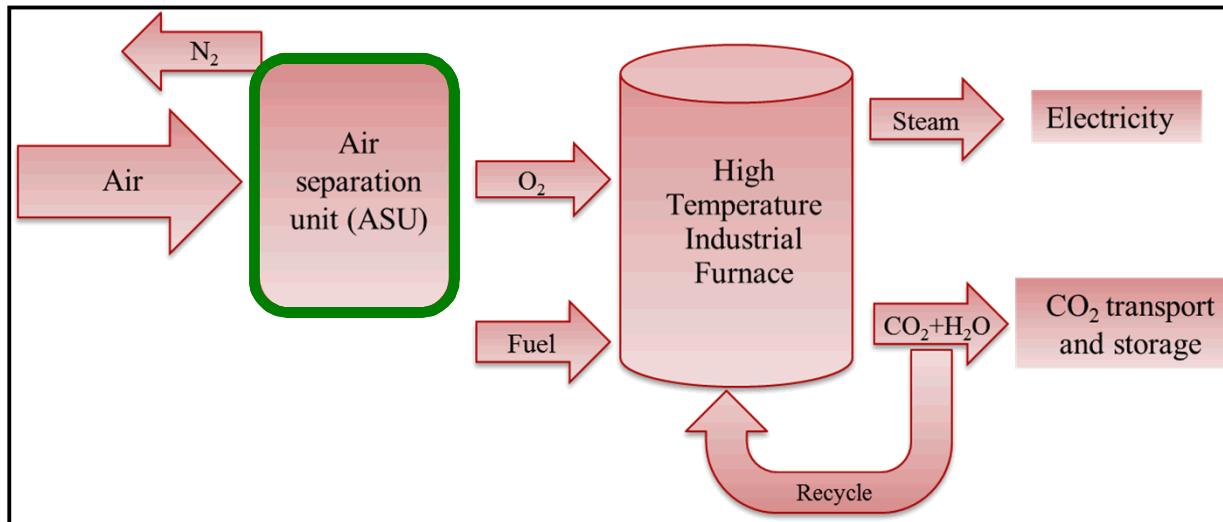


Cu-BTC: I₂ from Humid Gas Stream
Chem. Mater. 2013, 25(13), 2591



Binder Free MOF Pelletization
US Patent Pending 2014

O_2/N_2 air separations with MOFs to Increase the Efficiency of the *ASU*



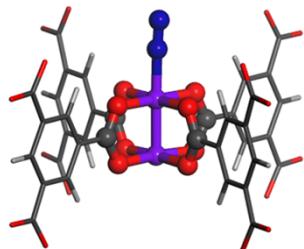
- Oxygen-enriched (oxy-fuel) combustion: burning the fossil fuel in an O_2 rich atmosphere results in a flue gas composed mainly of CO_2 and water (little or no SO_X and NO_X emissions)
- The limiting factor of this technology is the efficiency of the cryogenic ASU, a costly and energy intensive process (primarily compression)
- Our study is focused on new highly selective materials to increase the efficiency of this separation process

Goal: determine the O_2 and N_2 uptake dependency with temperature
in MOFs with coordinatively unsaturated metal sites

Integrated Research Plan: Modeling, Materials Development, Combustion Testing, & Systems Analysis

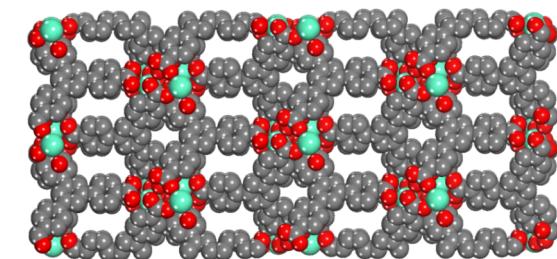
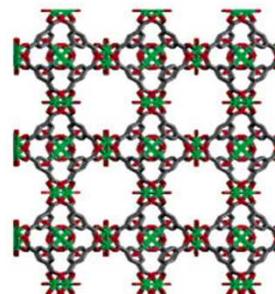
Predictive molecular modeling

Predictive molecular modeling designed to *measure the binding energy for O₂ and N₂* on coordinatively unsaturated metal sites in MOFs



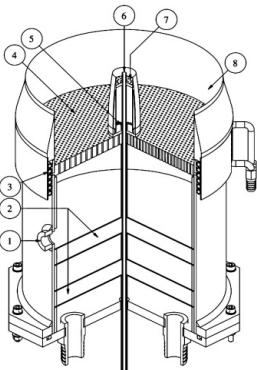
Materials development

Guided by the modeling results, experiments are directed at both the *synthesis of analogs of known/modified materials and of novel frameworks*.



New burner design

New lab burner constructed to mimic practical oxy-fuel combustion in industrial applications: coupling burner design and oxy-fuel combustion to radiant heat transfer



Burner number	Description
1	Flashback over-pressure sensing port
2	Glass head filled cavities
3	Cooling water coil
4	Coolant preheated baseplate
5	Flame measurement slot
6	Central jet exit
7	Pilot perforated baseplate
8	Cowflow collar

Schematic diagram of the modified version of the Cabra Burner developed by Dunn et al. (Combust. Flame, 2007, 151, 46)- studying flame attachment in hot combustion products

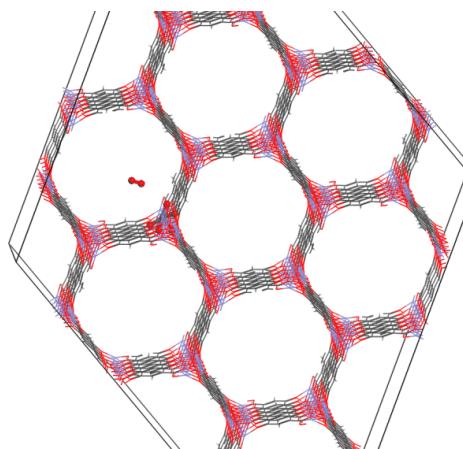
Systems Analysis

Data input to Systems Analysis for calculations of efficiency improvements of combined developed MOFs into Oxy-fuel Process Stream

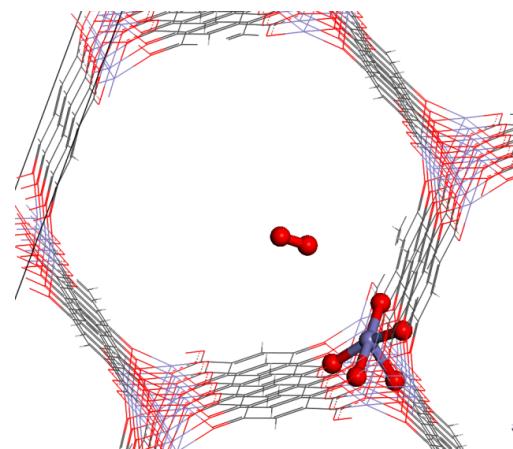
Input information/data from combustion to systems analysis for calculation of percent efficiency improvements

Metal-O₂ and Metal-N₂ Binding Energies and Geometries

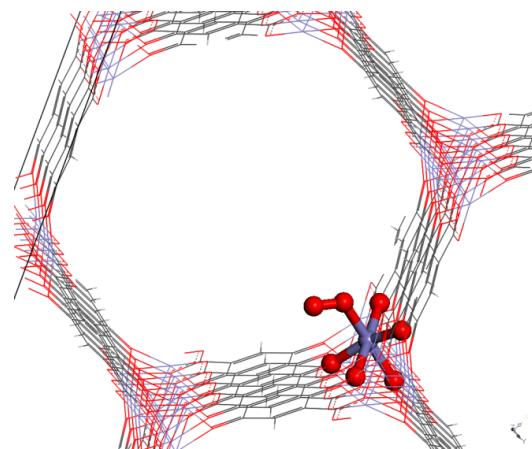
- MOFs with coordinatively unsaturated metal centers are promising materials for O₂/N₂ separations
- Two prototypical MOFs from this category, Cr₂(BTC)₃ (*J. Am. Chem. Soc.* **2010**, *132*, 7856–7857) and Fe₂(DOBDC) (*J. Am. Chem. Soc.* **2011**, *133*, 14814-14822) both show preferential adsorption of O₂ over N₂
- Plane wave DFT calculations were performed on periodic structures in the Vienna Ab initio Simulation Package (VASP)
- Binding geometries for side-on and bent O₂ and bent and linear geometries for N₂ were evaluated
- Static binding energies for O₂ and N₂ at 0 K



MOF with O₂ in pore

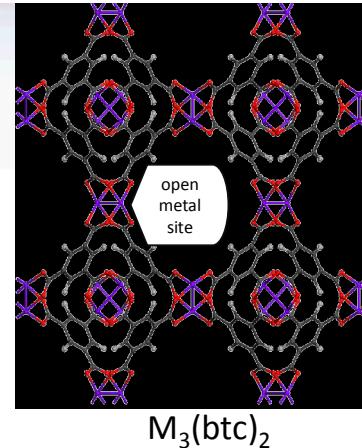
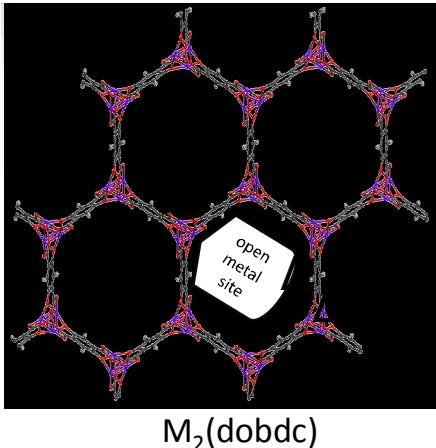


O₂ ready to bind to metal



O₂ bound to metal

DFT modeling of Oxygen Adsorption in Varied Metal-Centered MOFs



MOF metal sites = separate O_2/N_2 by differences in bonding & electronic properties

Plan wave density functional theory (DFT) calculations were performed on periodic structures of each MOF in the Vienna ab initio simulation package (VASP) with the Perdew-Burke-Ernzerhof (PBE) functional including dispersion corrections (DFT-D2). Geometries were optimized and static binding energies ($\Delta E_{\text{O}_2}, \Delta E_{\text{N}_2}$) were calculated by

$$\Delta E_{\text{O}_2} = E_{\text{MOF+O}_2} - E_{\text{MOF}} - E_{\text{O}_2}$$

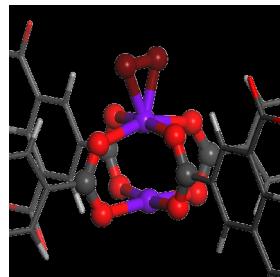
The differences in binding energies ($\Delta\Delta E$) for oxygen and nitrogen were calculated by

$$\Delta\Delta E = -(\Delta E_{\text{O}_2} - \Delta E_{\text{N}_2})$$

Attention Paid to Bonding Geometries

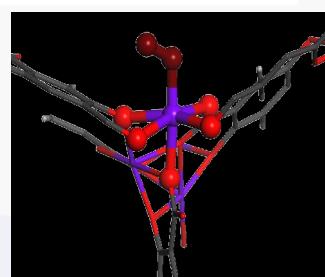
Side-on bonding

$$\Delta M\text{-X-X } 67^\circ - 71^\circ$$



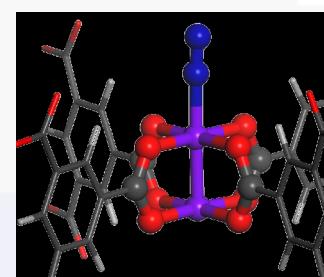
Bent bonding

$$\Delta M\text{-X-X } 116^\circ - 159^\circ$$

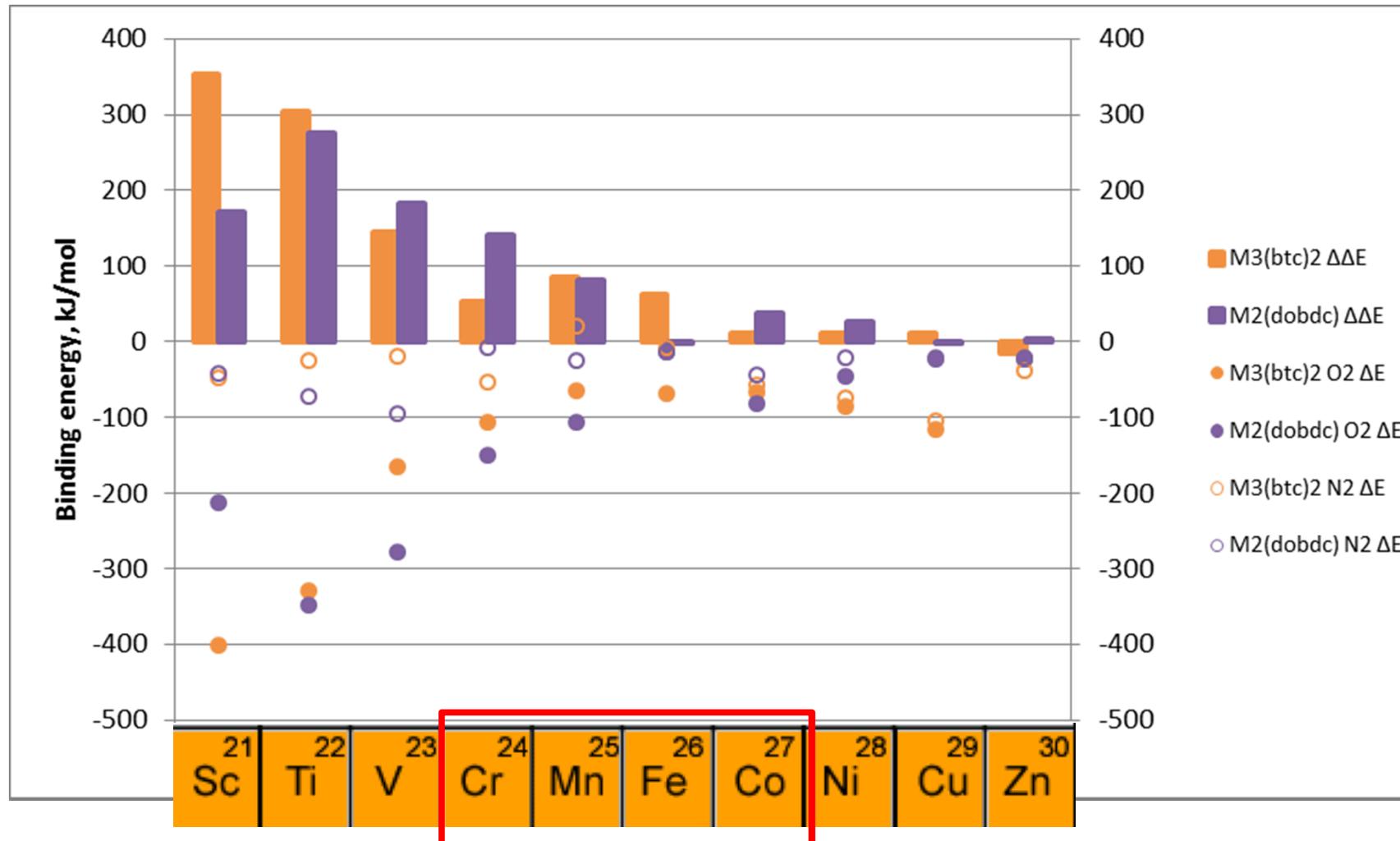


Linear bonding

$$\Delta M\text{-X-X } 165^\circ - 179^\circ$$

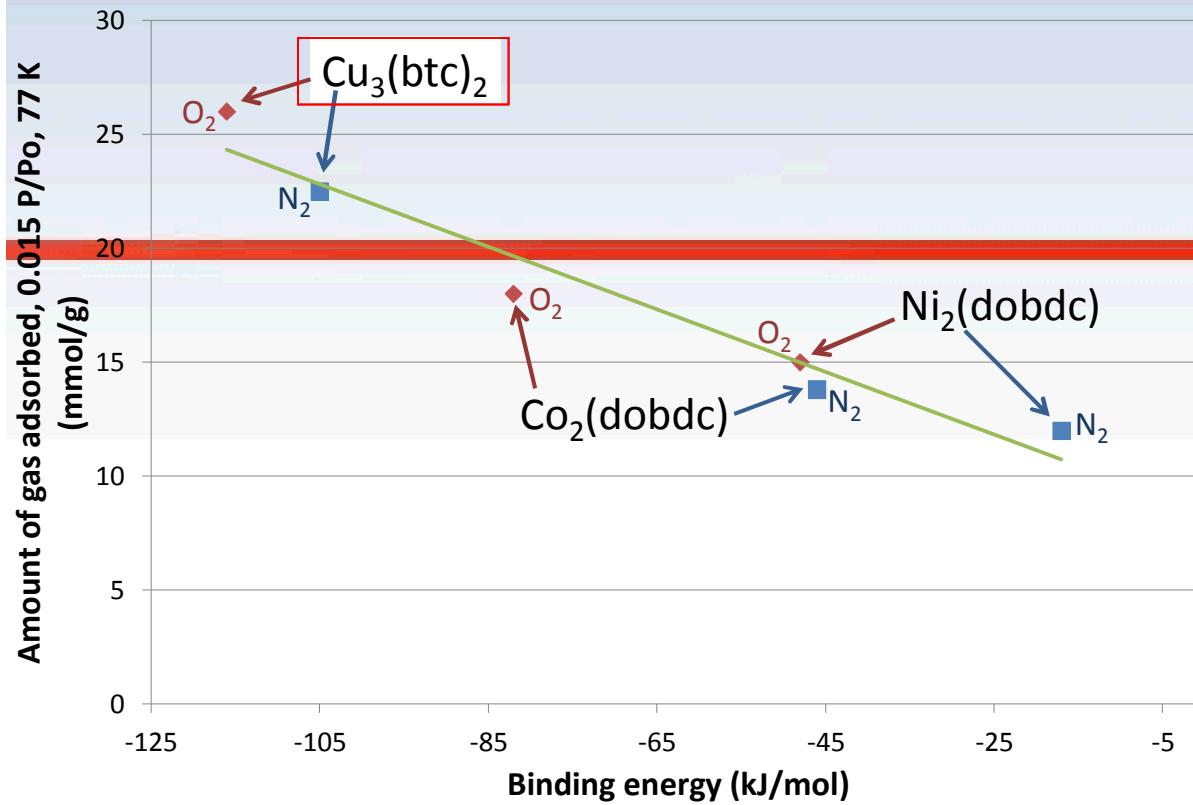


O_2 and N_2 binding energies trends across the first row transition metal series



Transition to Quantum Calculations to Estimate Metal-Oxygen Binding Energy

Low-temperature, low-pressure O₂ and N₂ adsorption measurements were done for three MOFs: Cu₃(btc)₂, Co₂(dobdc), and Ni₂(dobdc).

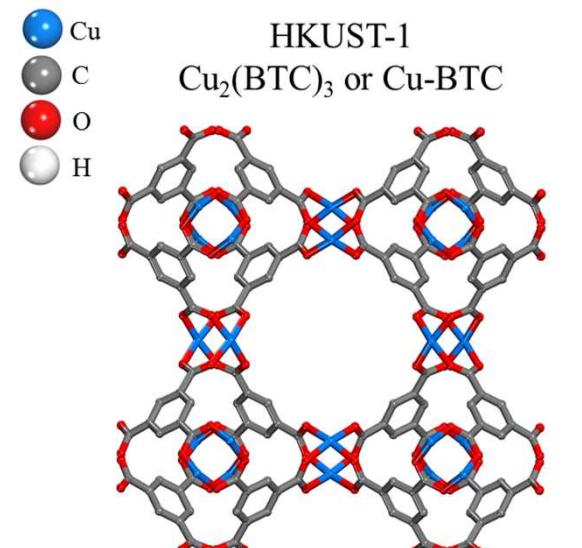


Excellent correlation between simulated binding energies and low-temperature, low-pressure experimental gas uptake.

Targeted Synthesis of Porous Mn-, Fe- and Co- Analogues of Cu-BTC

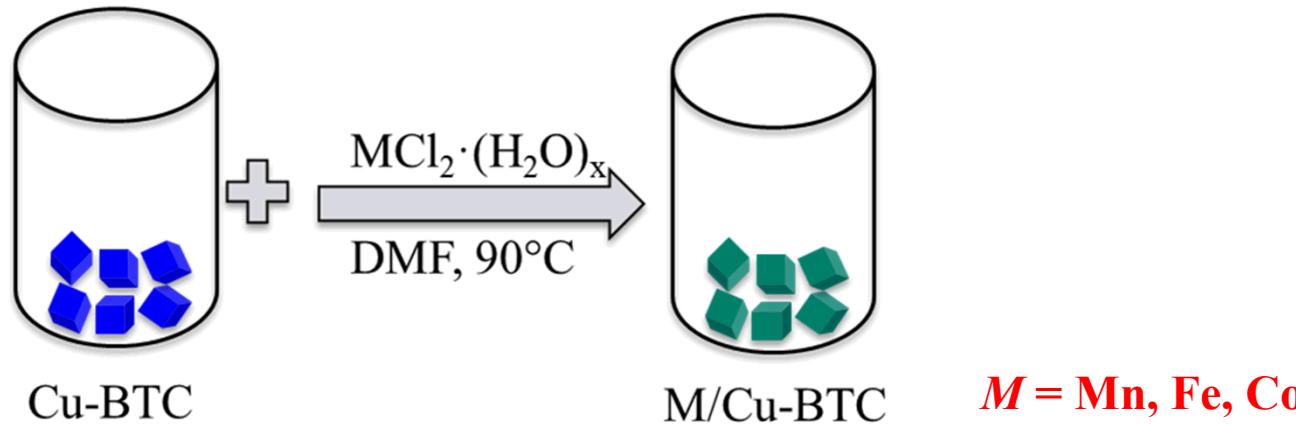
Need/Desire To Retain Porosity of MOF For Studies of Metal-O₂ Bonding Effects

- The effect of Porous analogues of Cu-BTC include: Cr, Mo, Ru, Ni (the Ru and Ni have much lower than expected surface areas, 1000-1100 m²/g)
- Porphyrin-templated Mn-, Fe- and Co- Cu-BTC analogues known, however no measurable accessible porosity (*J. Am. Chem. Soc.* **2012**, *134*, 928–933)

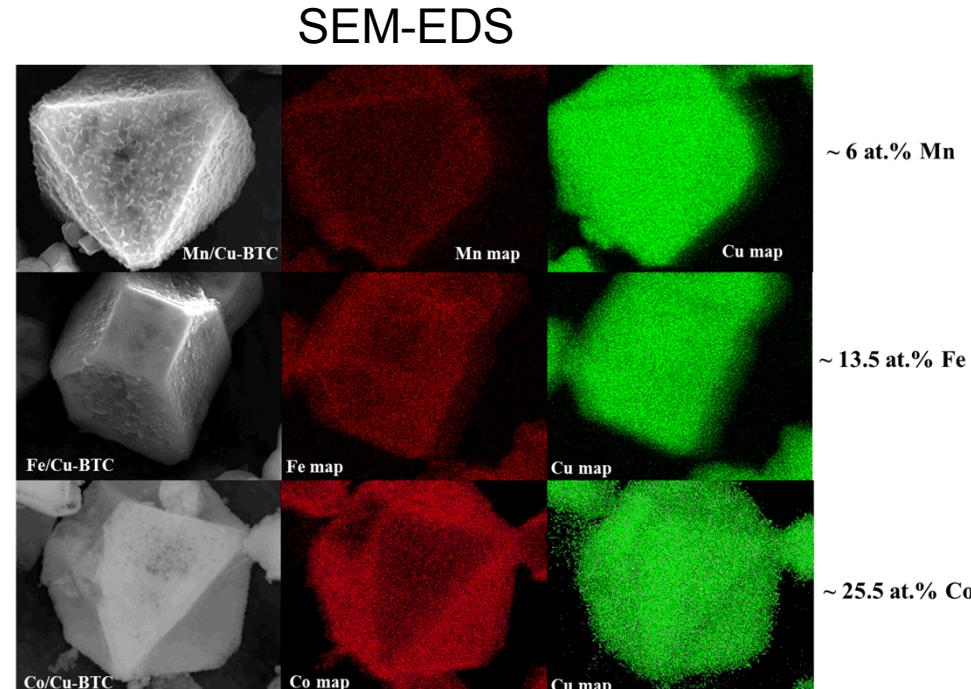
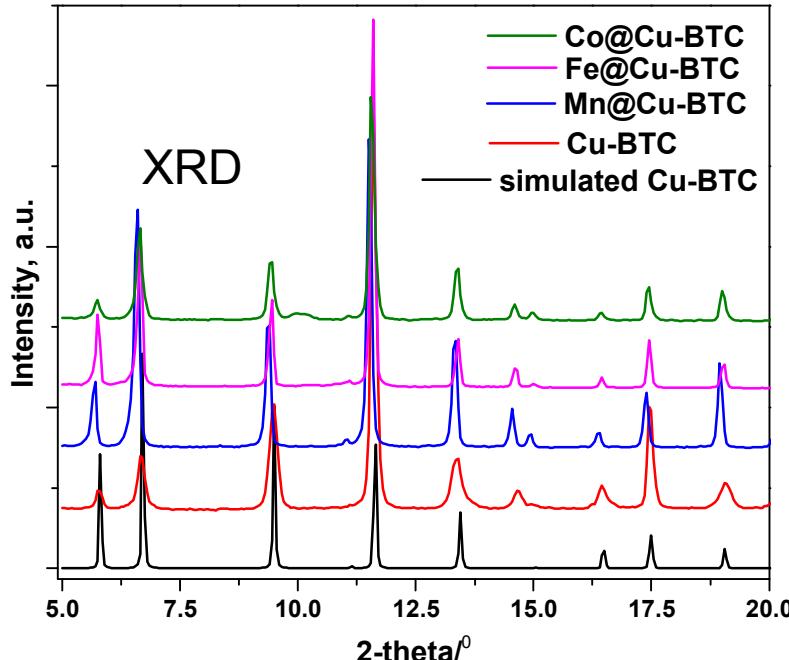


Chui, S. S. Y. et.al *Science* **1999**, *283*, 1148.

Postsynthetic metal ion exchange



Confirmation of In-Framework Metal Substitution – Unit Cell Expansion & Elemental Mapping



	Expansion (\AA)	M-O average bond length (\AA)
Cu-BTC	–	1.7
Co/Cu-BTC	0.043	2.08
Fe/Cu-BTC	0.019	2.0
Mn/Cu-BTC	0.030	2.17

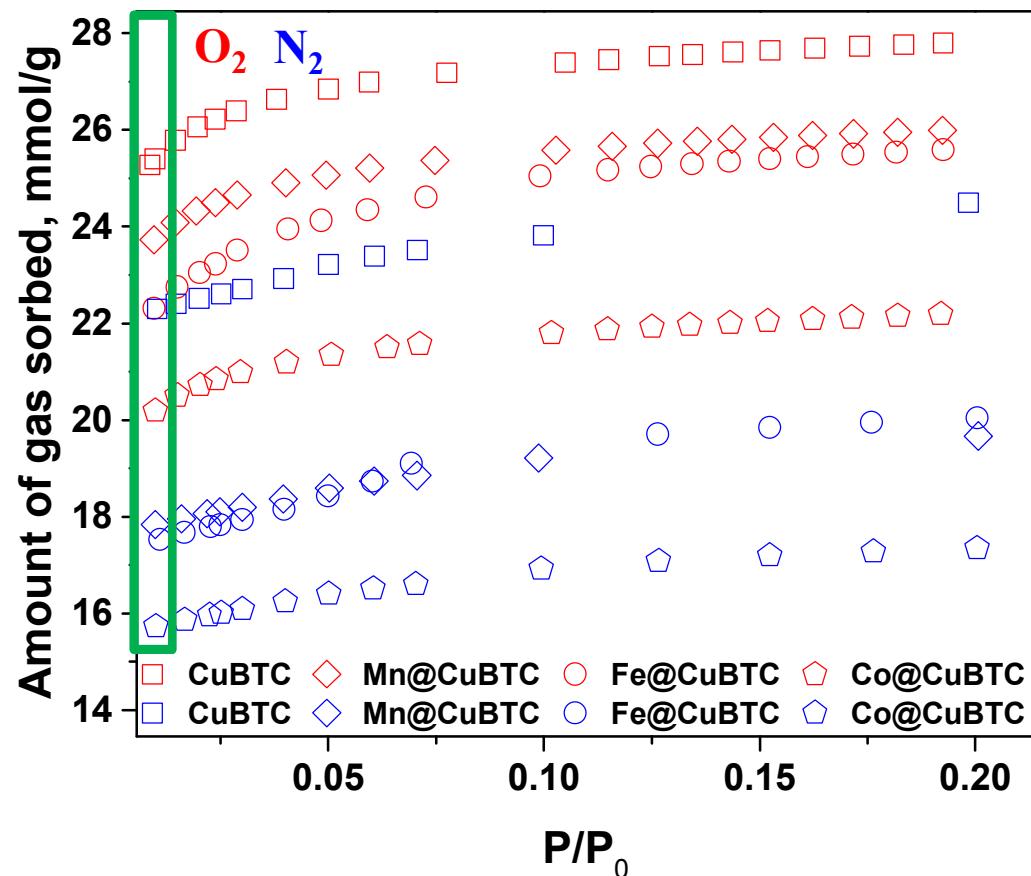


Excellent DFT and Experiment Correlation at Low Temperature and Low Pressure

Cu>Mn>Fe>Co (DFT)
Cu>Mn>Fe>Co (exp)

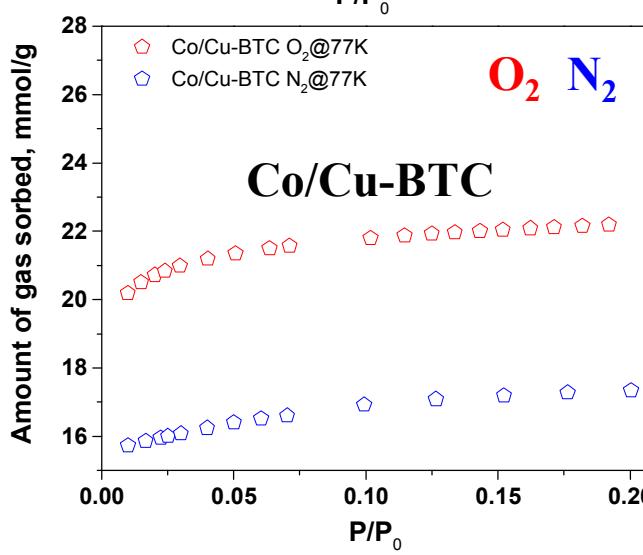
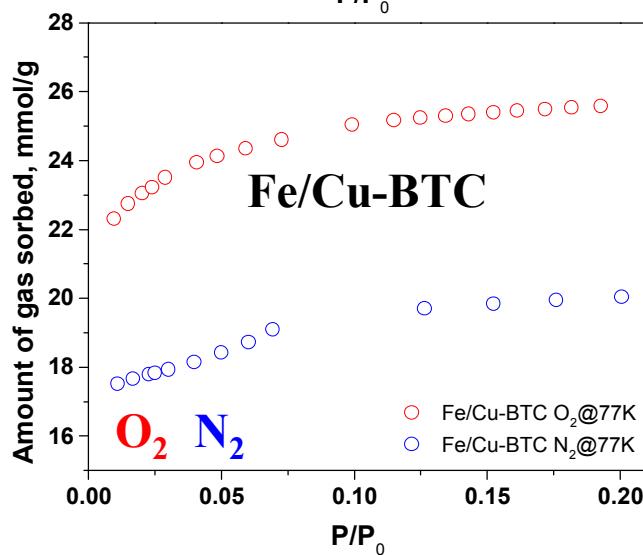
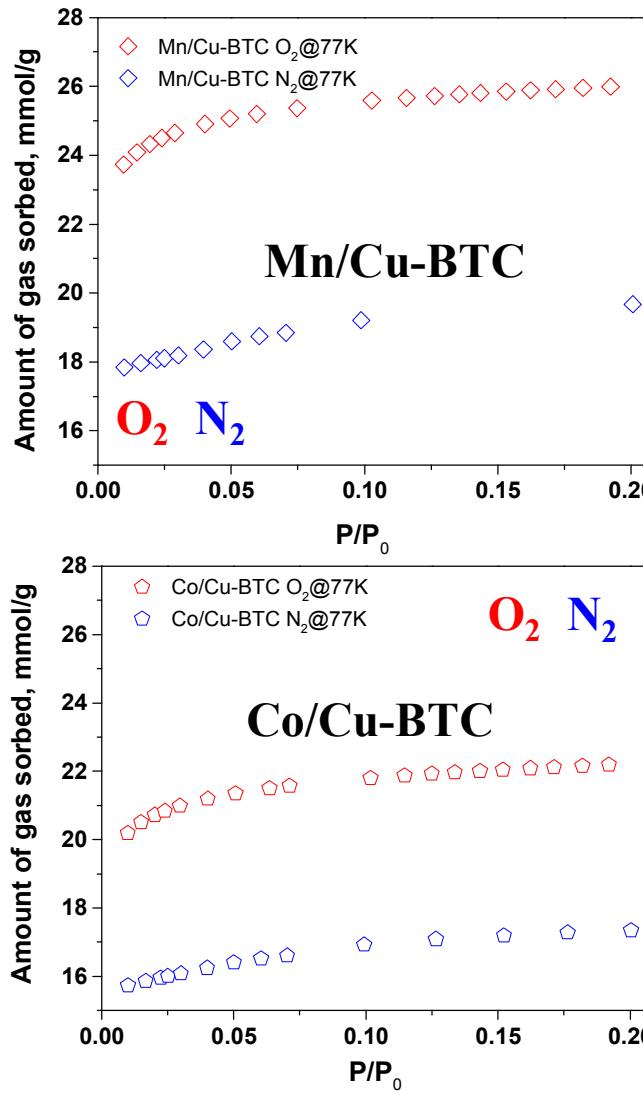
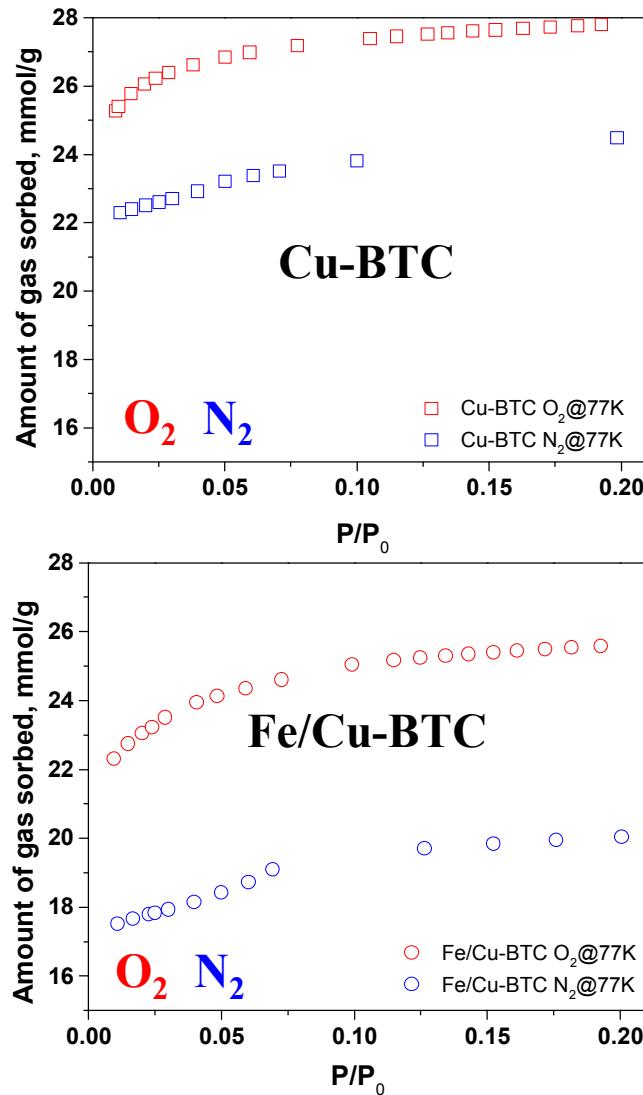
	DFT O ₂ binding energy, kJ/mol	DFT N ₂ binding energy, kJ/mol
Cu-BTC	-116	-105
Mn/Cu-BTC	-113	-97
Fe/Cu-BTC	-110	-92
Co/Cu-BTC	-104	-93

For uptake at the lowest partial pressure measured ($\sim 0.01 P/P_0$)



O₂ (red) and N₂ (blue) adsorption isotherms measured at 77K on pristine Cu-BTC and Mn-, Fe-, and Co-substituted samples

77 K: All Samples have *Higher* O₂ Loadings over N₂

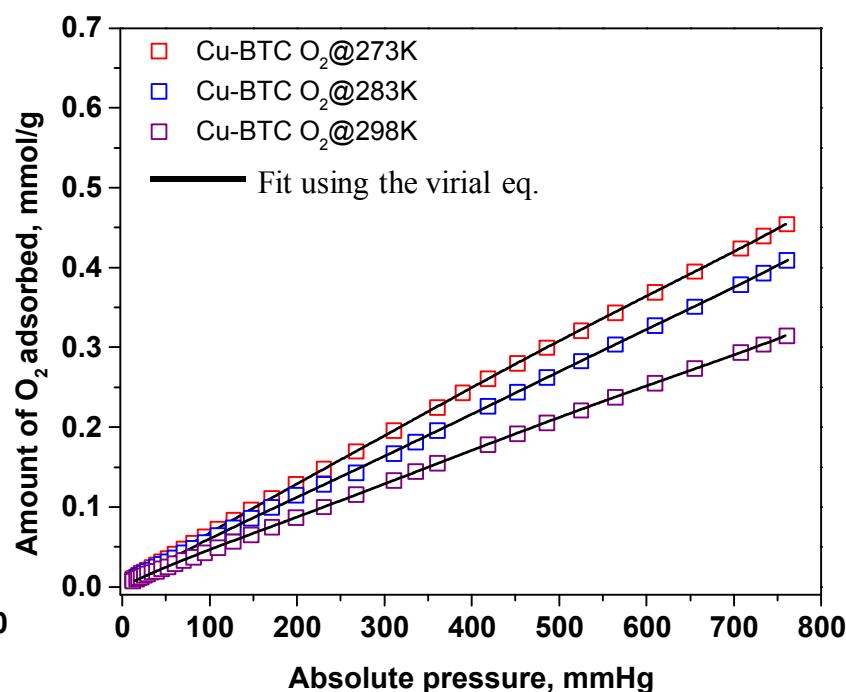
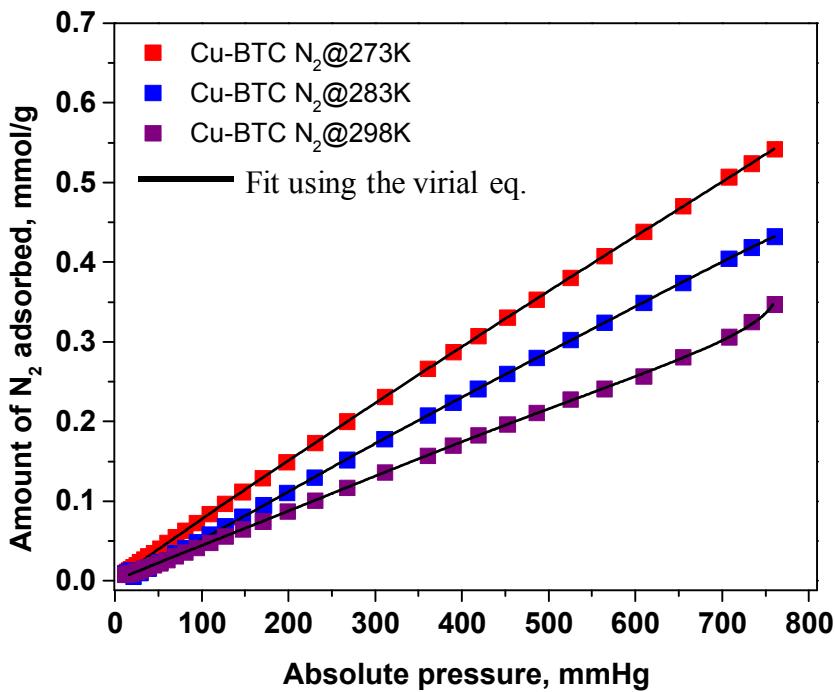


The highest O₂/N₂ selectivity is observed for the Mn/Cu-BTC sample

273-298 K: As Temperature Increases, O₂ Loadings Decrease Relative to N₂

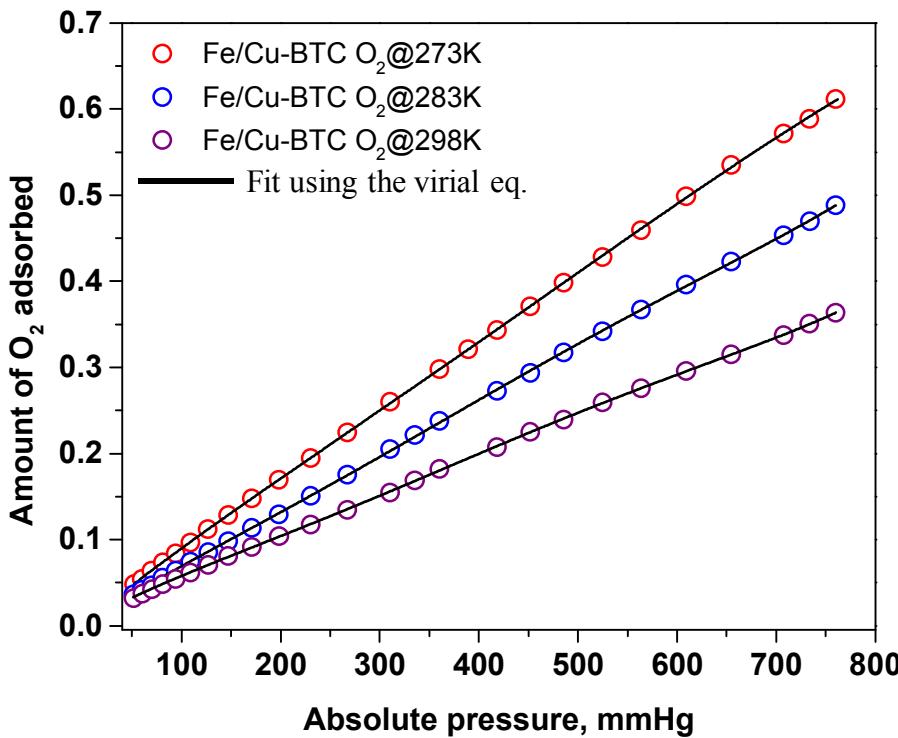
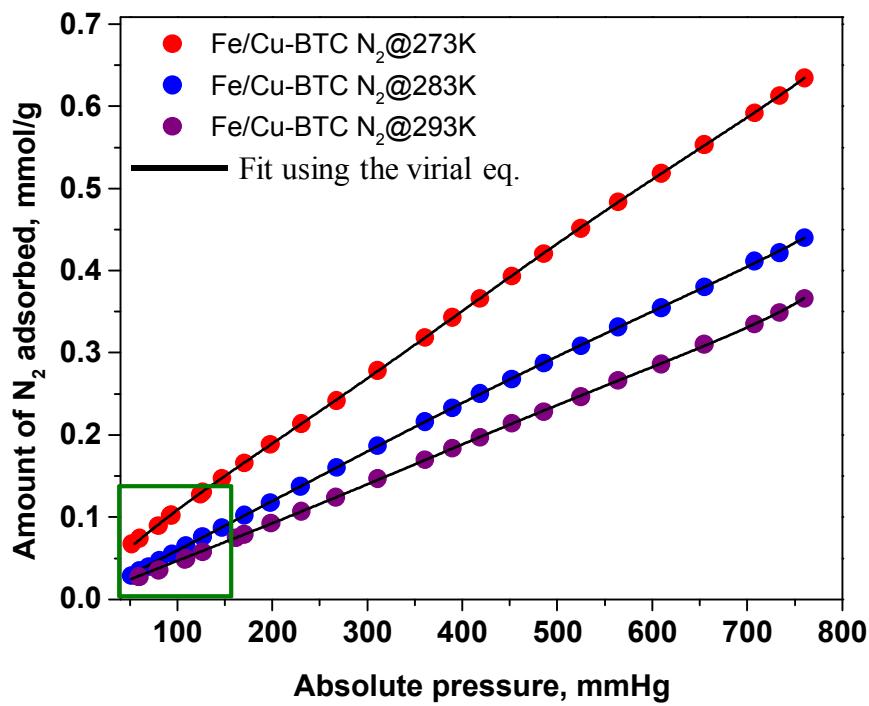
Isotherms in the 273-298K range, *independently* fitted using a modified virial equation:

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i$$



Similar behavior noted for the Mn- and Co/Cu-BTC samples

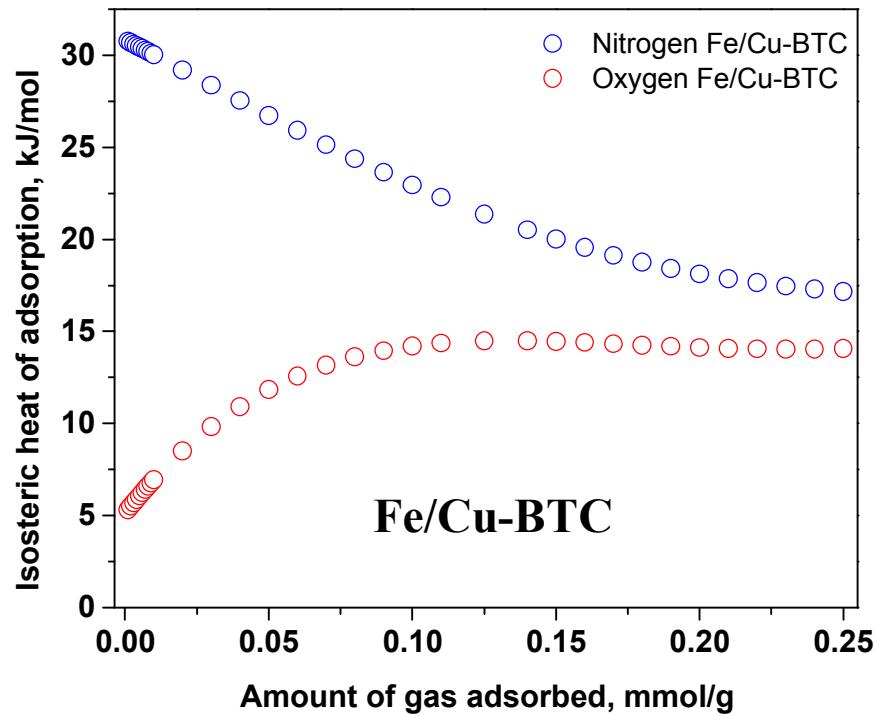
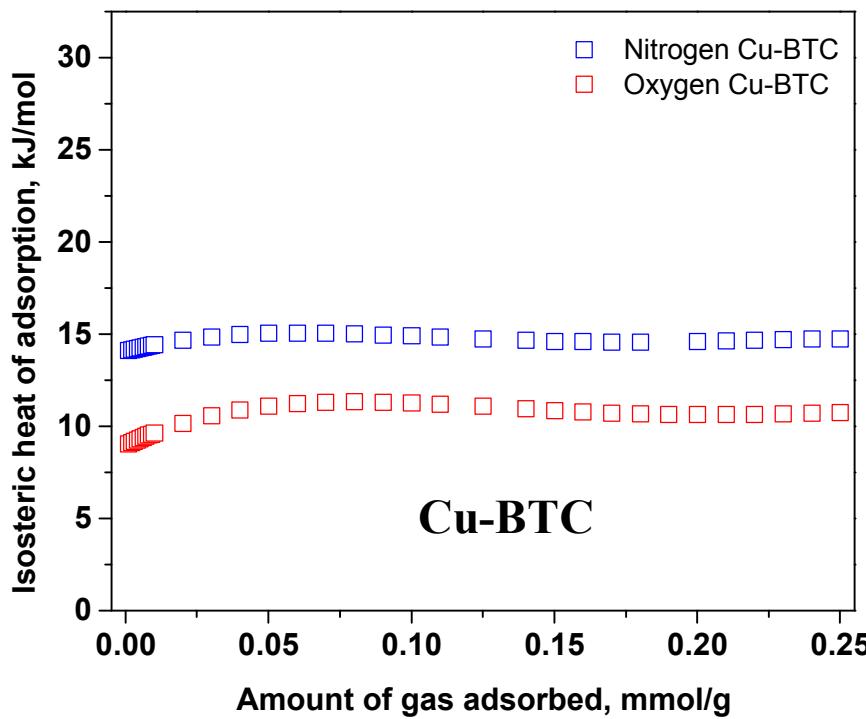
N_2 @273 K in Fe/Cu-BTC Trend Deviation: Slightly Higher N_2 Uptake at Lowest Loading Levels (at lowest pressures)



N_2 and O_2 adsorption isotherms measured at 273, 283, and 298K on Fe/Cu-BTC

Similar N_2 and O_2 uptake for Fe/Cu-BTC in the room temperature range

Isosteric Heats of Adsorption for O₂ (red) and N₂ (blue) Comparison of Cu-BTC vs Fe/Cu-BTC Data

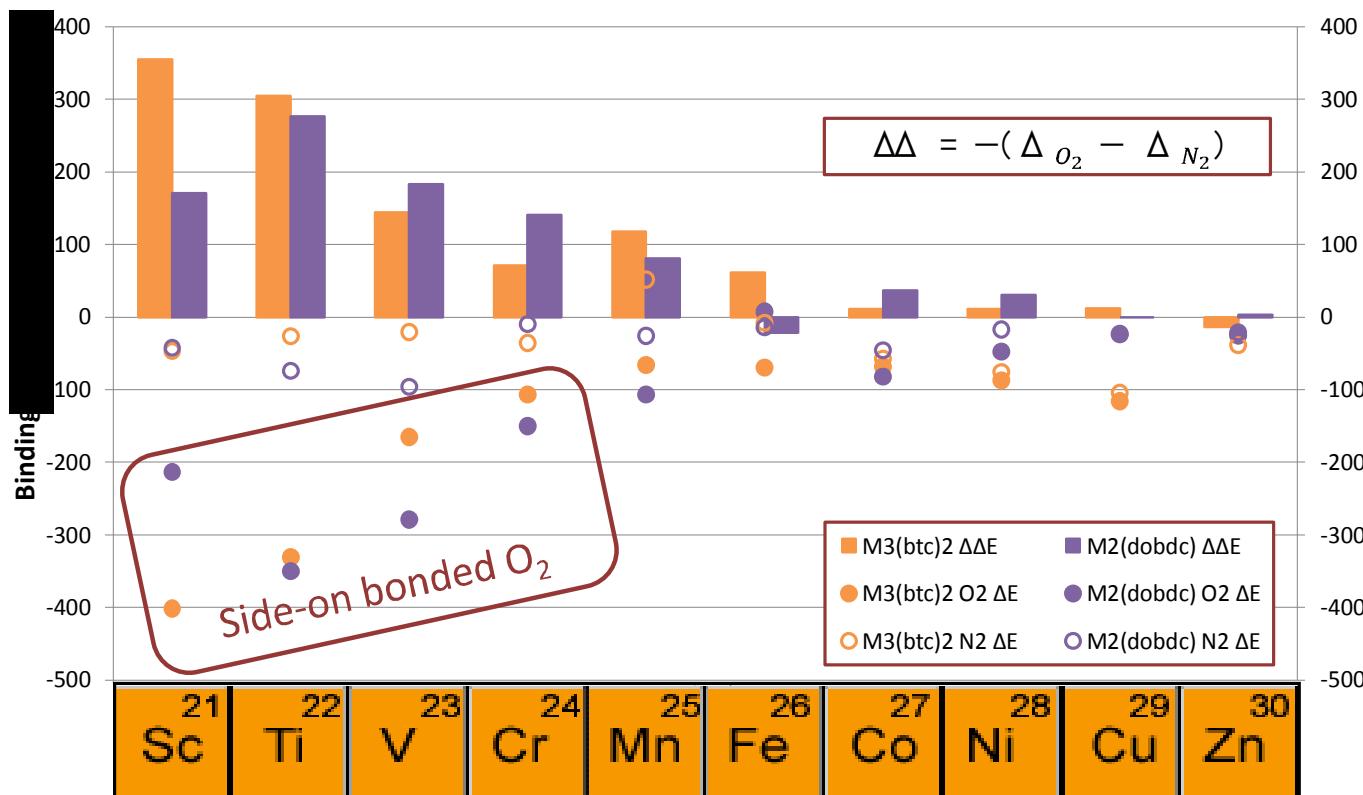


The 0 K DFT *binding energy* calculations **do not correlate** as well with experimental data from **273-298 K**

Is it the framework morphology / channel structure or the choice of metal center?

Transition to Quantum Calculations to Estimate Metal-Oxygen Binding Energy

Binding Energy Calculated as a Function of Metal Site



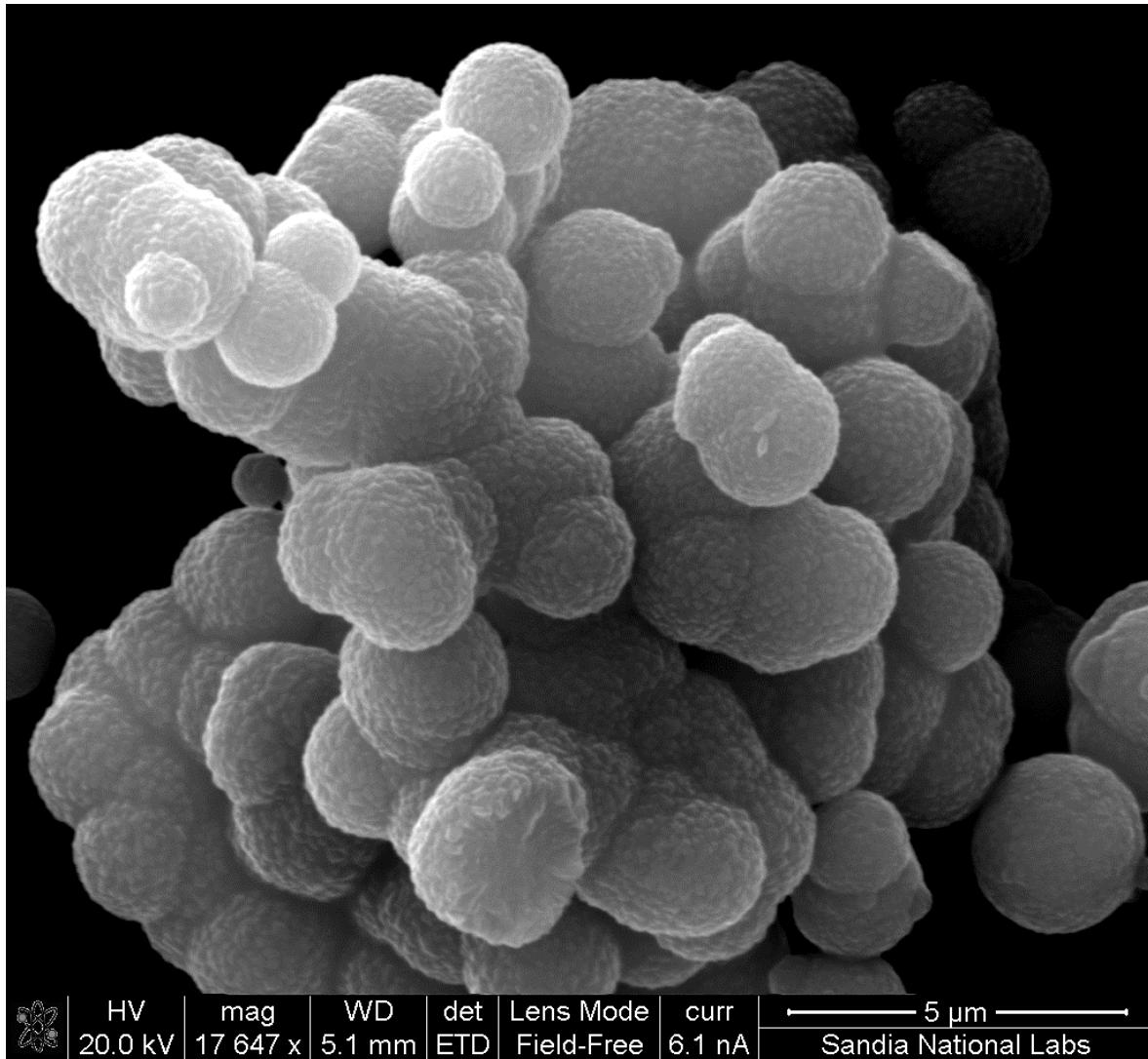
Parkes, M.; Sava Gallis, D. F.; Greathouse, J.A.; Nenoff, T.M.

“Screening MOFs for O₂/N₂ Separations: Role of MOF Metal Center”,
J. Phys Chem C, 2015, 119, 6556.

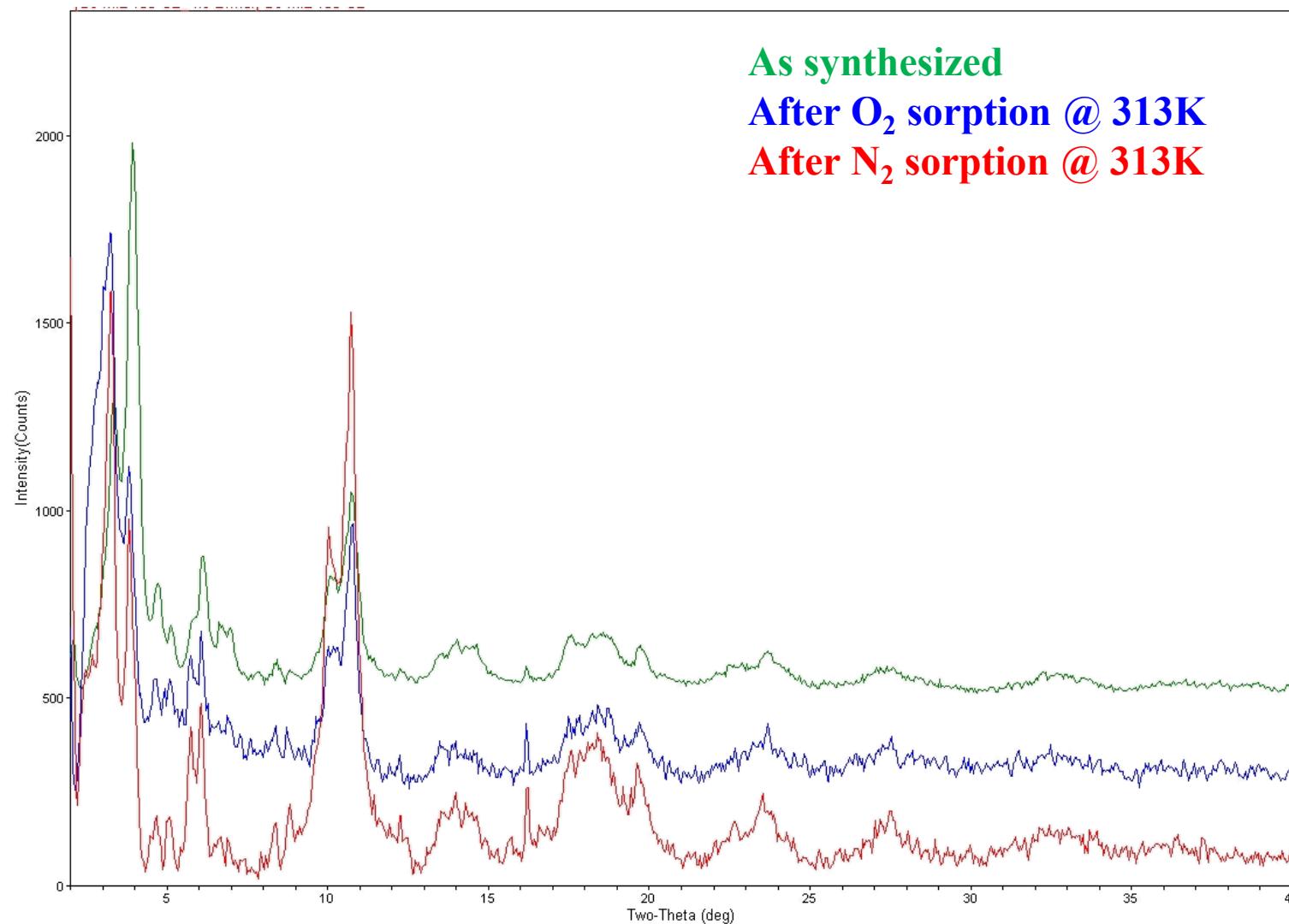
Marie Parkes, Sanibel Conference, Top Prize - Poster, 2014

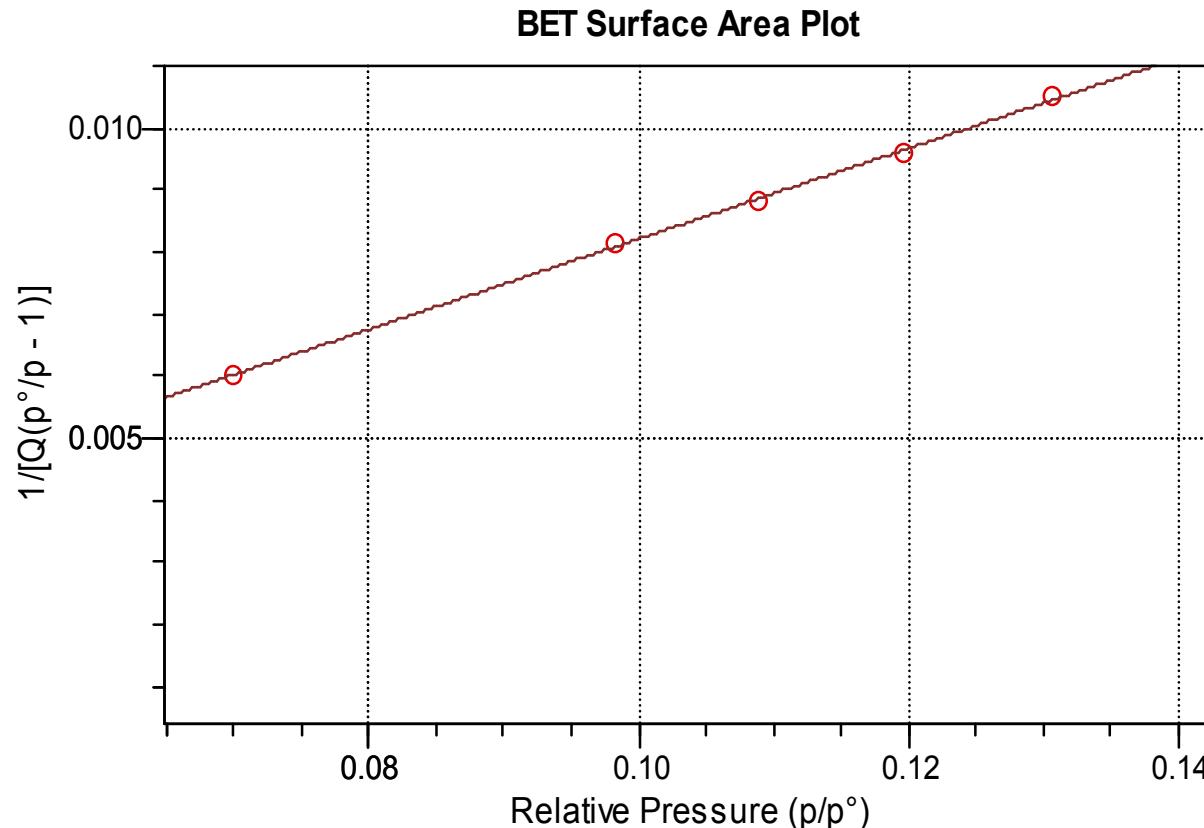
Modeling Designed / Inspired MOF Synthesis

SMOF-8



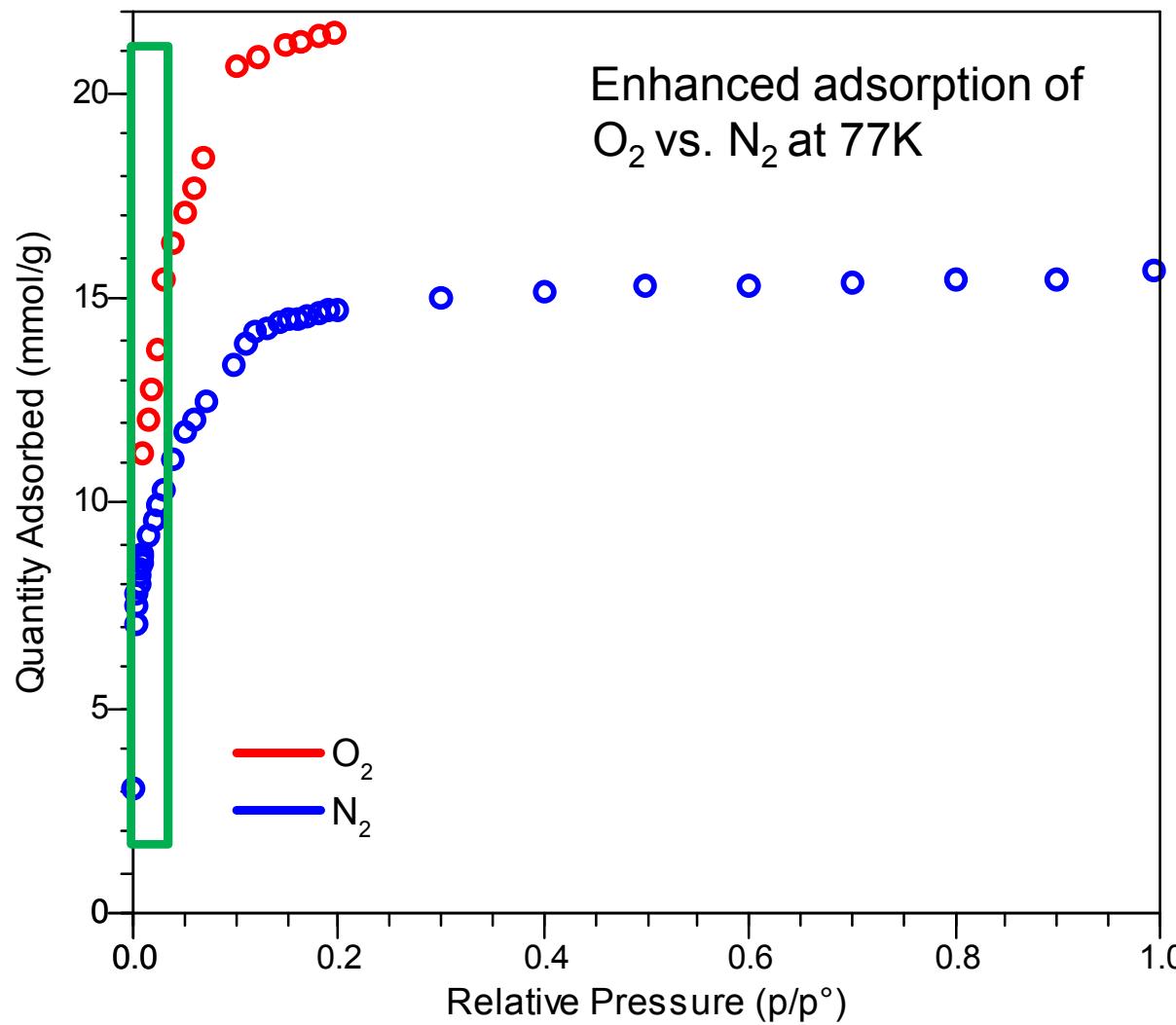
SMOF-8: Stable MOF framework over Wide Temperature Range and with Exposure to Variety of Gases



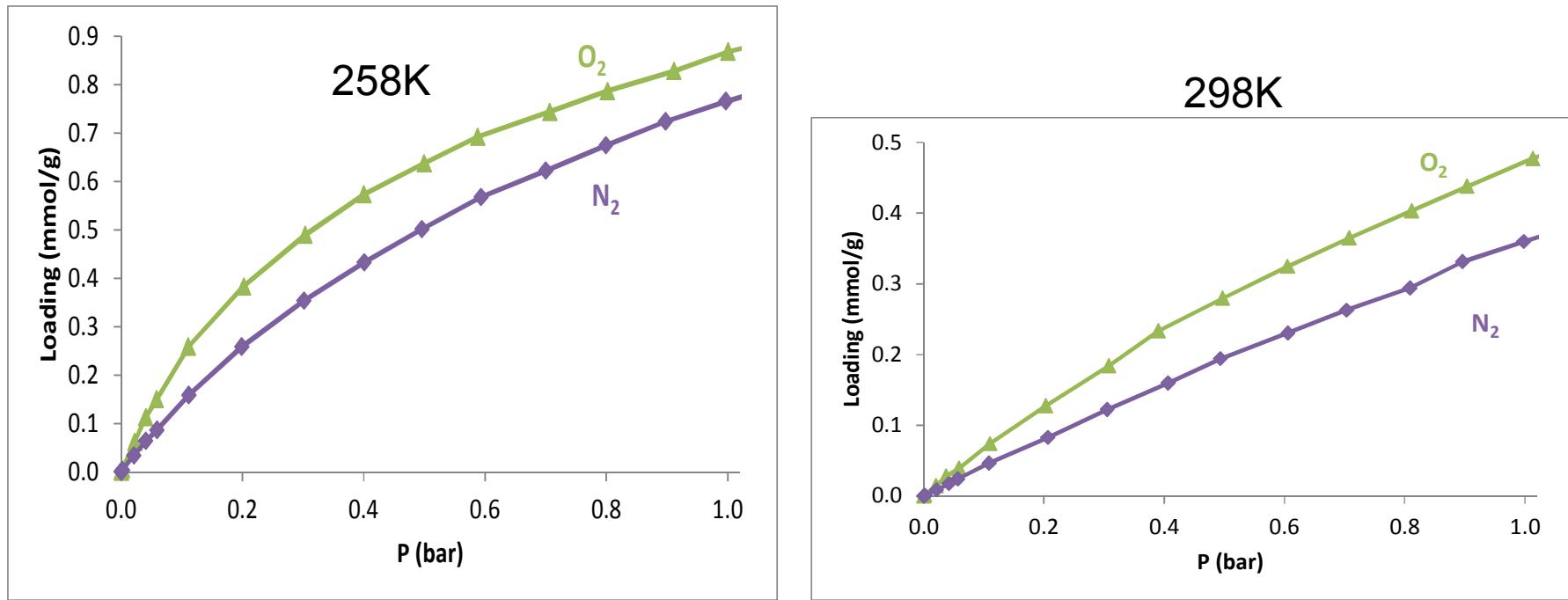


BET surface area: $1321.7194 \pm 24.4623 \text{ m}^2/\text{g}$

SMOF-8: Metal-Center has a role at 77K



SMOF-8: GCMC Isotherm Calculations at 258K and 298K

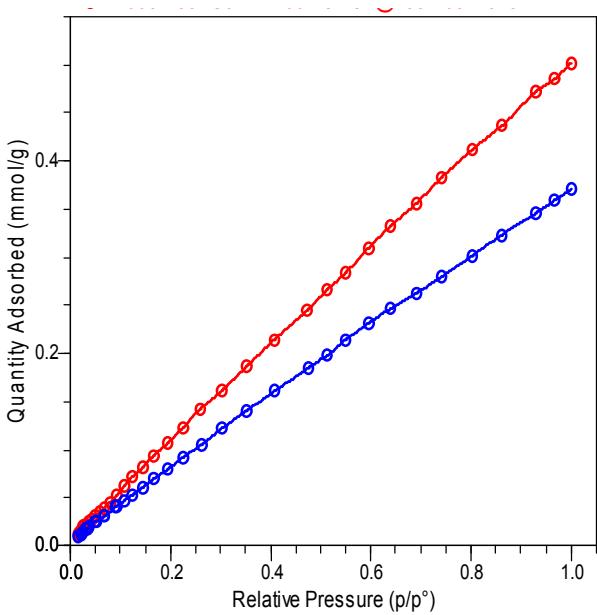


0 – 1 bar.

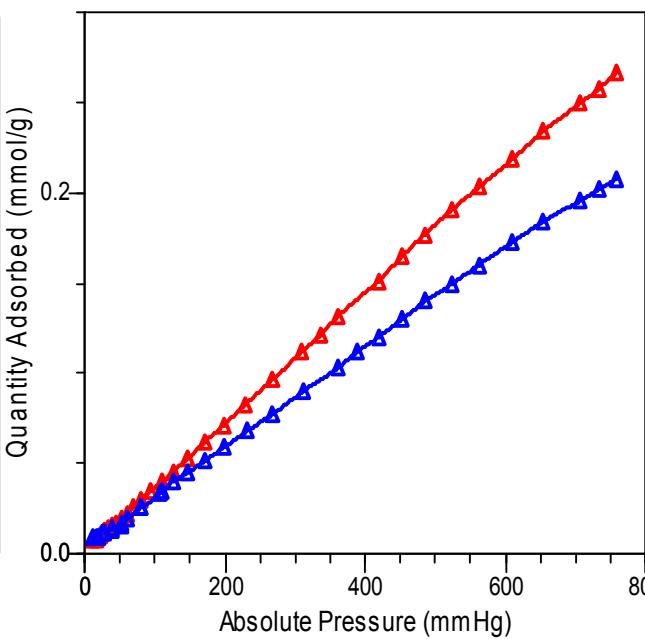
Preferred O_2 uptake but O_2/N_2 selectivity increases between 258K and 298K

SMOF-8: Enhanced Quantity of O₂ vs N₂ Adsorbed over Wide Temperature Range (at least to 313K)

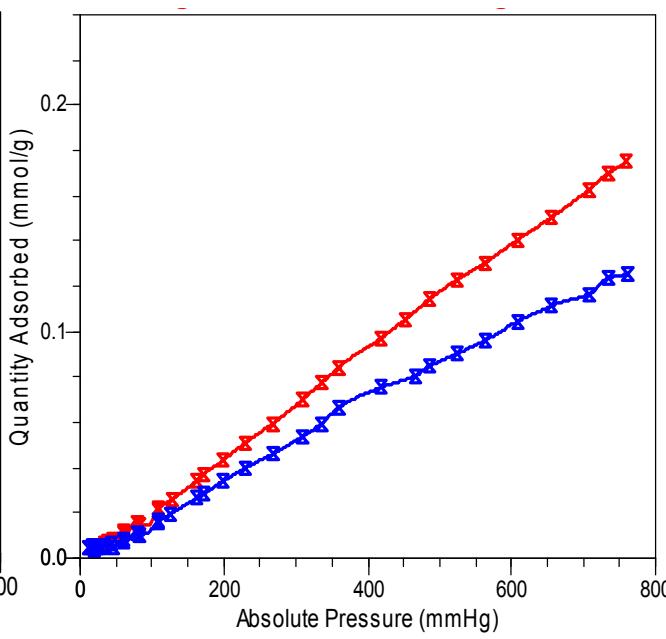
SMOF-8
O₂ vs. N₂ @258K



SMOF-8
O₂ vs. N₂ @298K



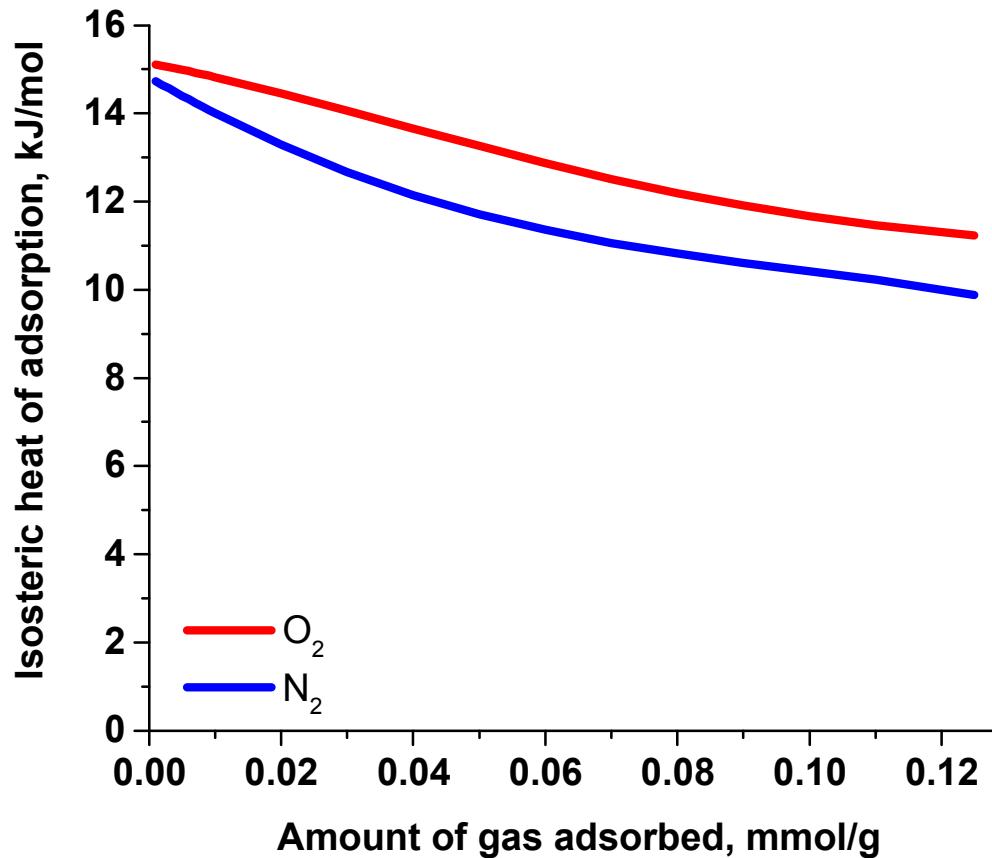
SMOF-8
O₂ vs. N₂ @313K



Isotherm trends mimic those predicted by GCMC

SMOF-8: Isosteric Heat of Adsorption (kJ/mol)

Qst derived from 258K, 298K and 313 K
Independent Virial Fit HOA



Conclusions and future work

- Successfully synthesized partially substituted Co-, Fe- and Mn- analogues of Cu-BTC
- Assessed the effect on metal substitution on the O₂ and N₂ adsorption capacity at both cryogenic and close to room temperature ranges
- For the Co-, Mn- and original Cu-BTC, O₂ preferentially adsorbs over N₂ at 77K. **However**, the trend is reversed at 298K, where N₂ preferentially adsorbs over O₂
- Based on predictive modeling, we studied early transition metal metal-center MOFs for enhanced O₂ sorption.
- SMOF-8: Early transition metal MOFs show preference for O₂ vs N₂ over wide temperature range (up to at least 313K), as confirmed by isosteric heats of adsorption higher in SMOF-8 for O₂ versus N₂
- Next Steps: Data to Technoeconomic Analysis and Burner Design for Oxyfuel combustion applications

Thank You

Sandia National Laboratories' Sites



Albuquerque, New Mexico



Kauai Test Facility
Hawaii



**Tonopah Test
Range,
Nevada**



Yucca Mountain
Nevada



WIPP,
New Mexico



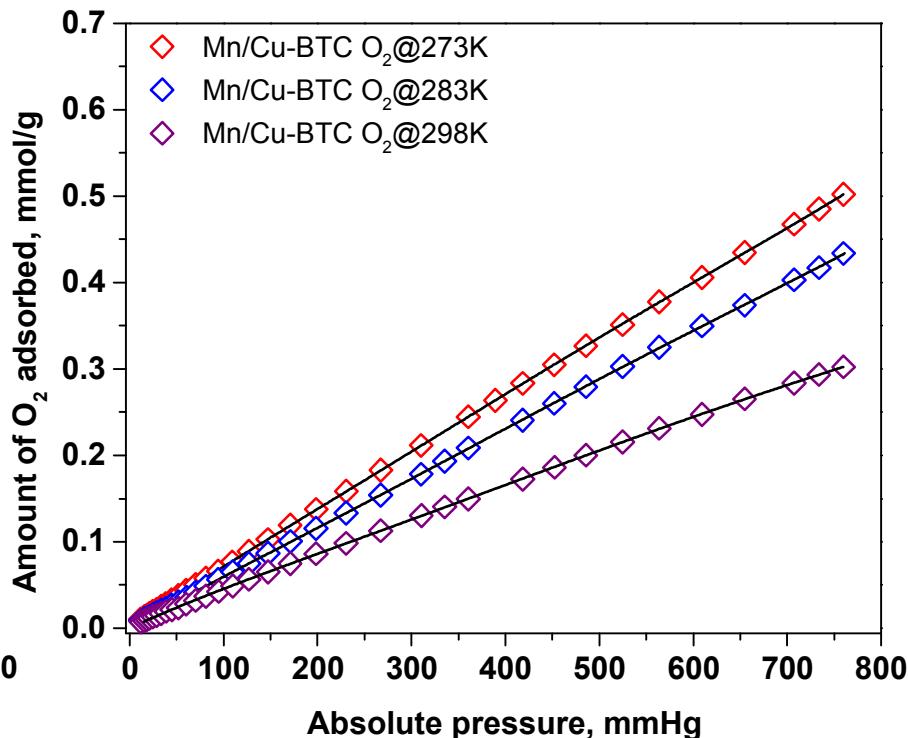
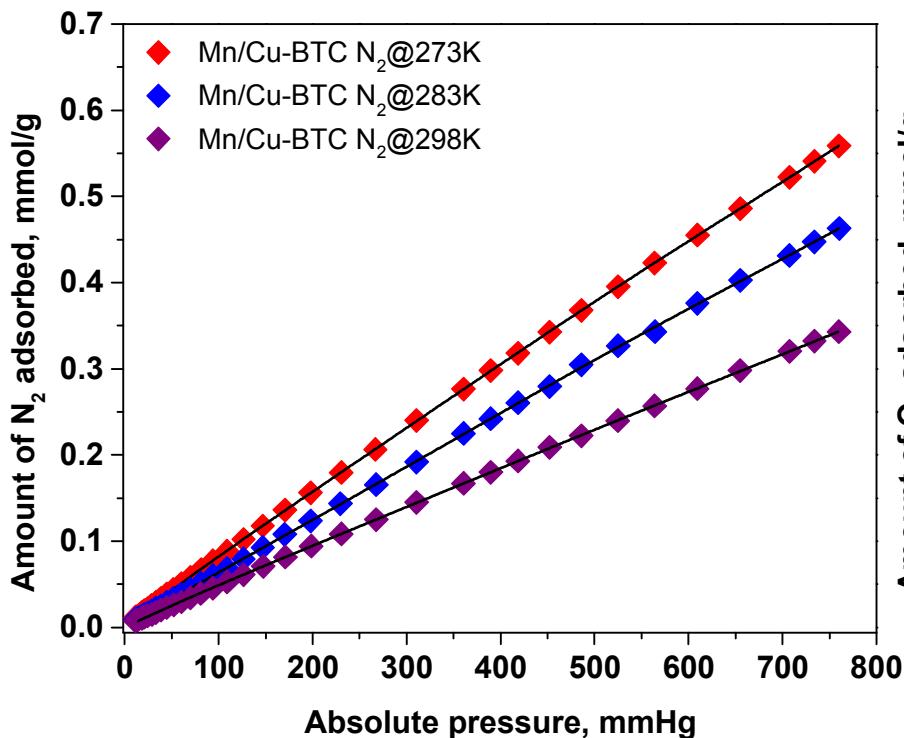
Pantex, Texas



Livermore, California

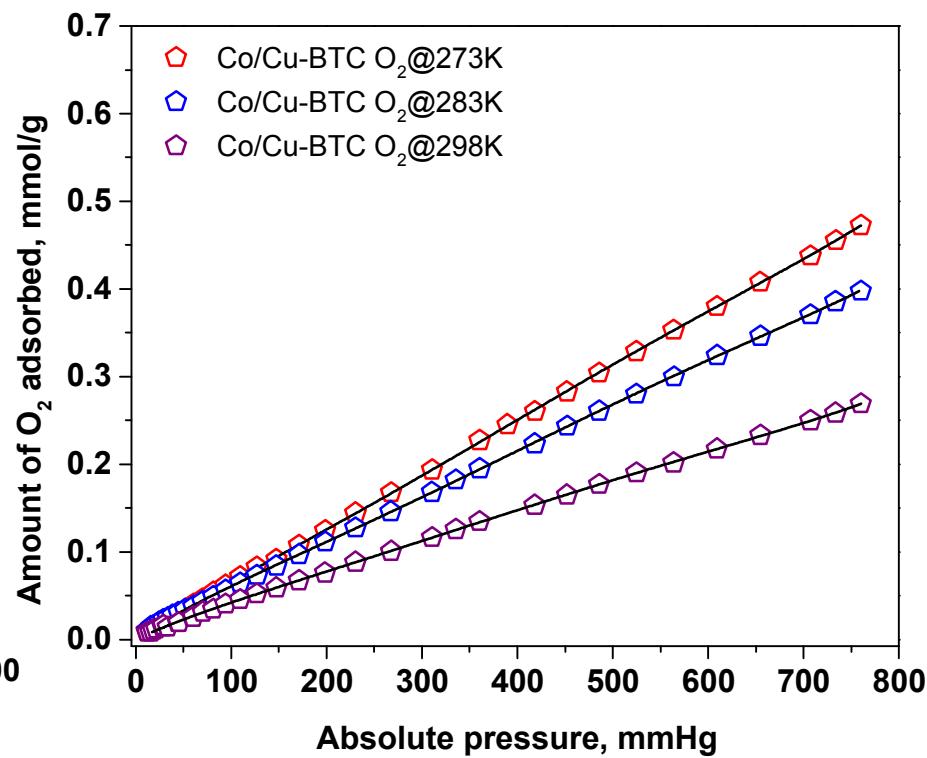
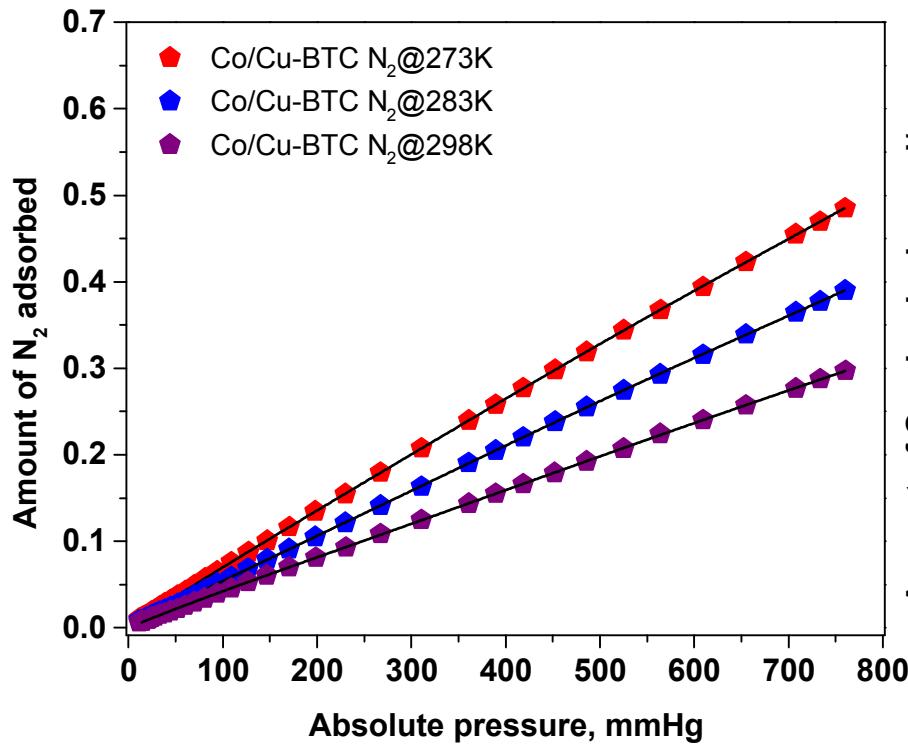
Thank You

N_2 and O_2 adsorption isotherms measured at 273, 283, and 298K on pristine Mn/Cu-BTC



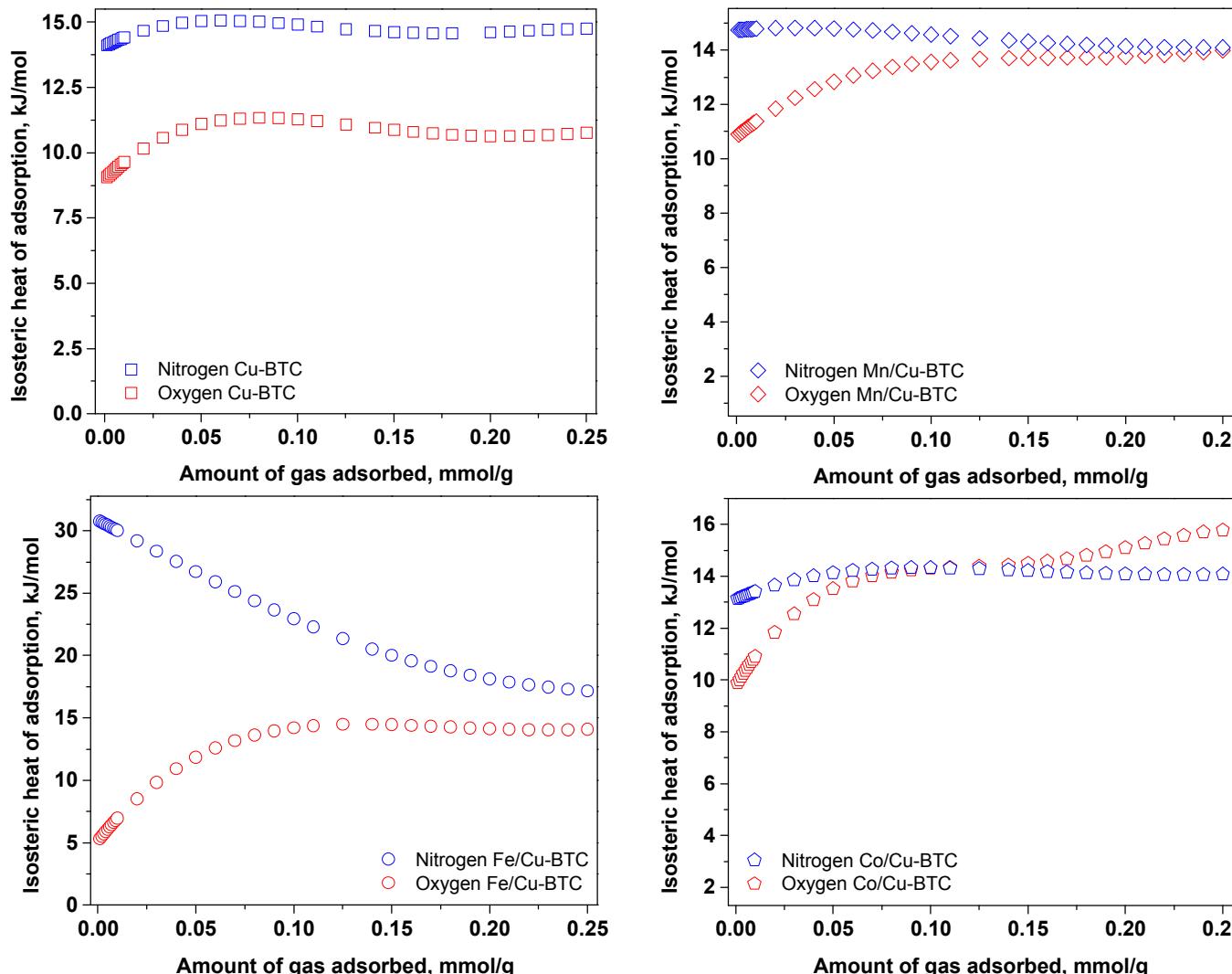
In the room temperature range, slightly higher affinity for N_2 over O_2 is noted

N_2 and O_2 adsorption isotherms measured at 273, 283, and 298K on pristine Co/Cu-BTC

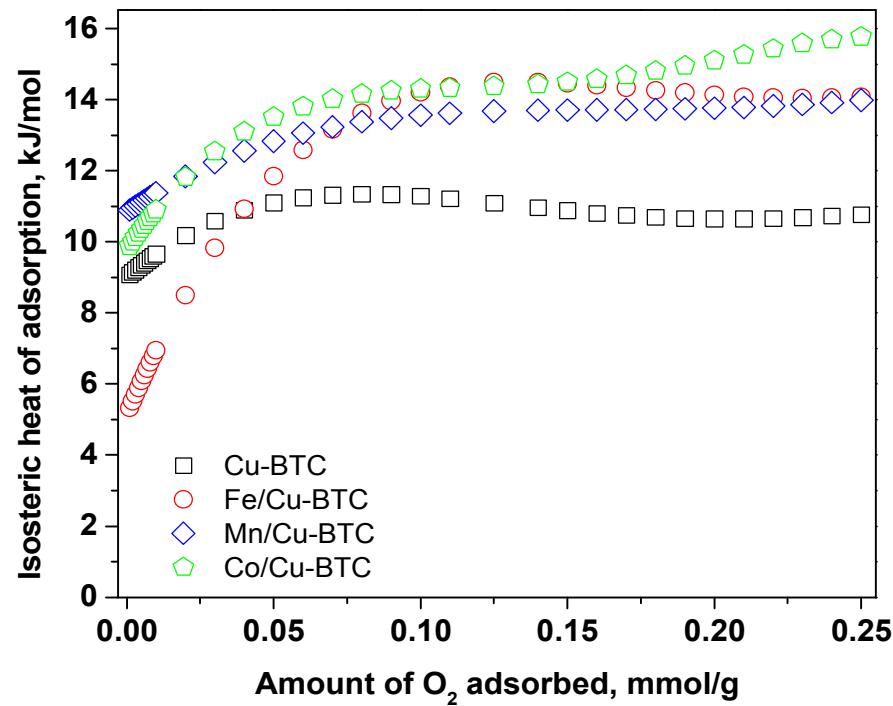
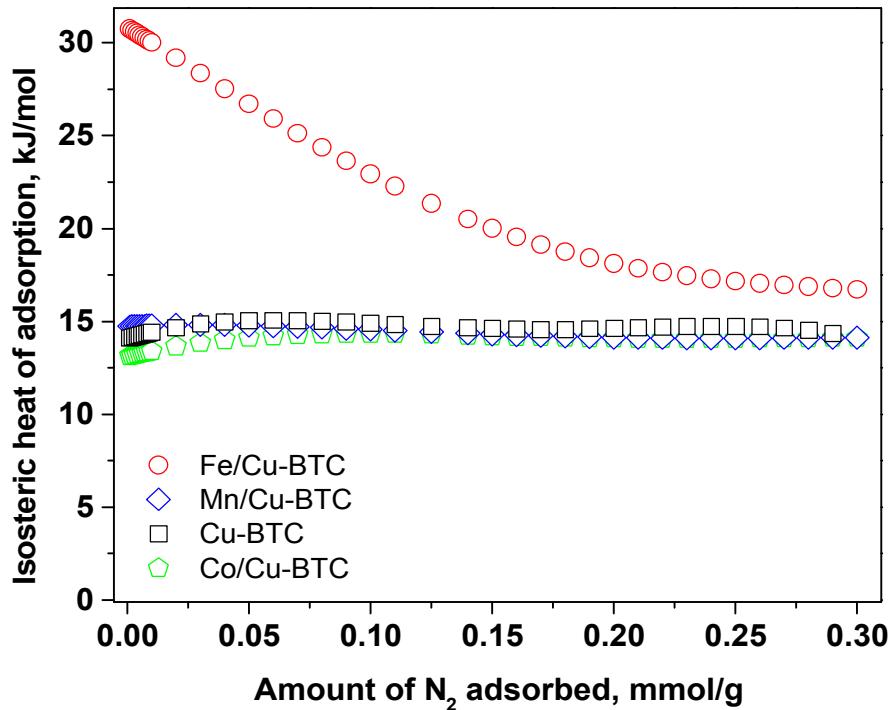


In the room temperature range, slightly higher affinity for N_2 over O_2 is noted

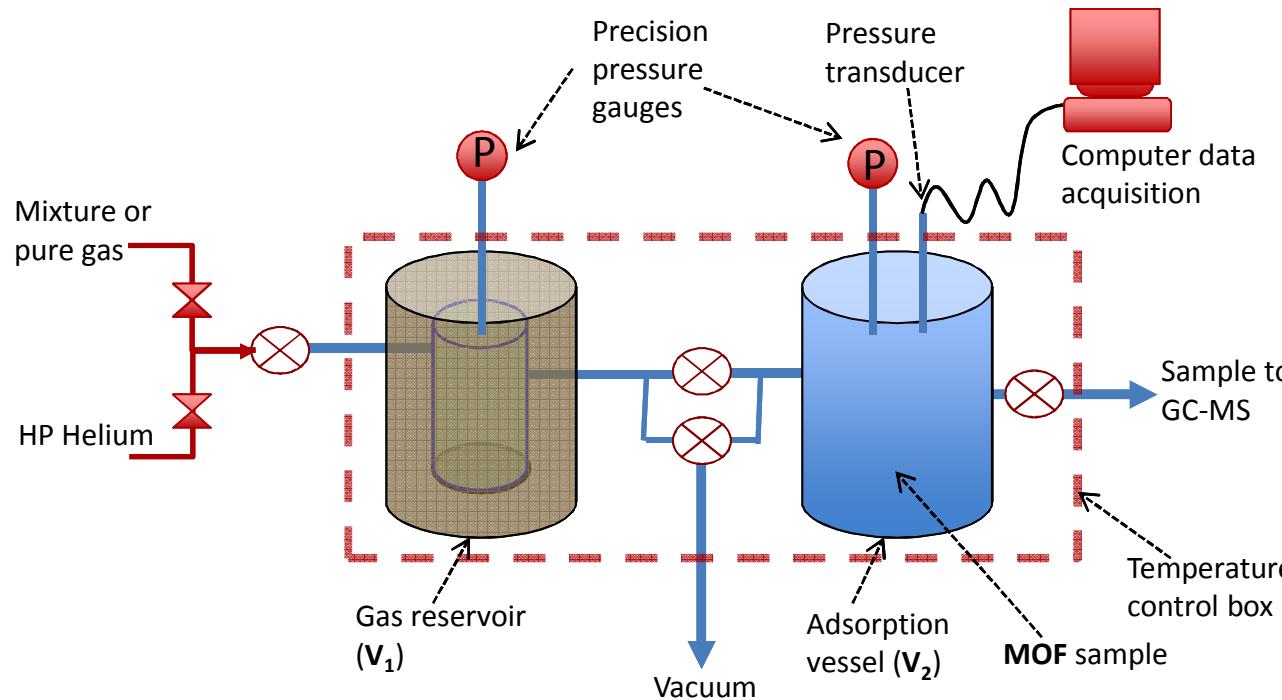
Significantly higher binding energy of N₂ over O₂ is noted for the Fe/Cu-BTC sample



Isosteric heats of adsorption for O₂ (red) and N₂ (blue) obtained from the fitted 273, 283 and 298K adsorption isotherms



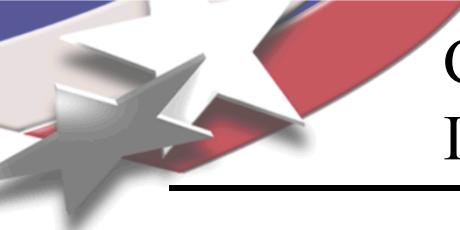
O₂/N₂ Gas mixture adsorption measurements containing 20% O₂ and 80% N₂



Room temperature (294K) in pressure range of 1.77 to 5.2 bars.

Samples tested for adsorption of O₂/N₂ mixture containing 20% O₂ and 80% N₂ at 21, 35, and 48.5°C, respectively.

P_{eq} , bar	Amount adsorbed., cm ³ (STP).g ^{-1.bar⁻¹}		a_{O_2/N_2}
	O ₂	N ₂	
1.77	6.568	7.109	0.924
3.50	5.910	6.384	0.926
5.00	5.346	5.558	0.962



Combustion Studies plus MOF O₂ Separations for Improved Combustion Process Efficiency

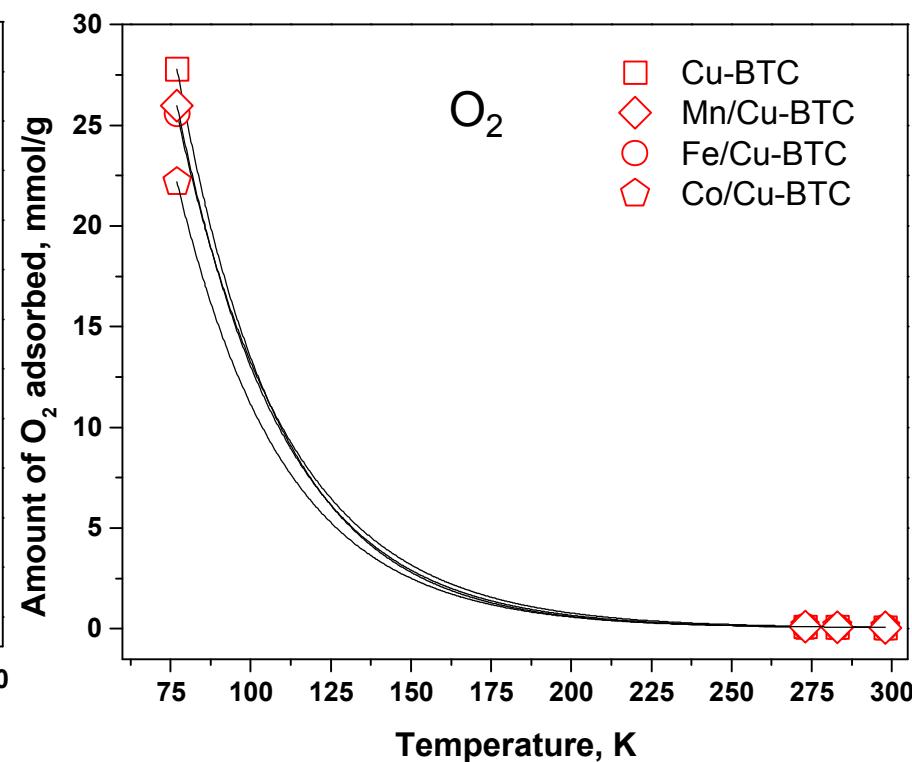
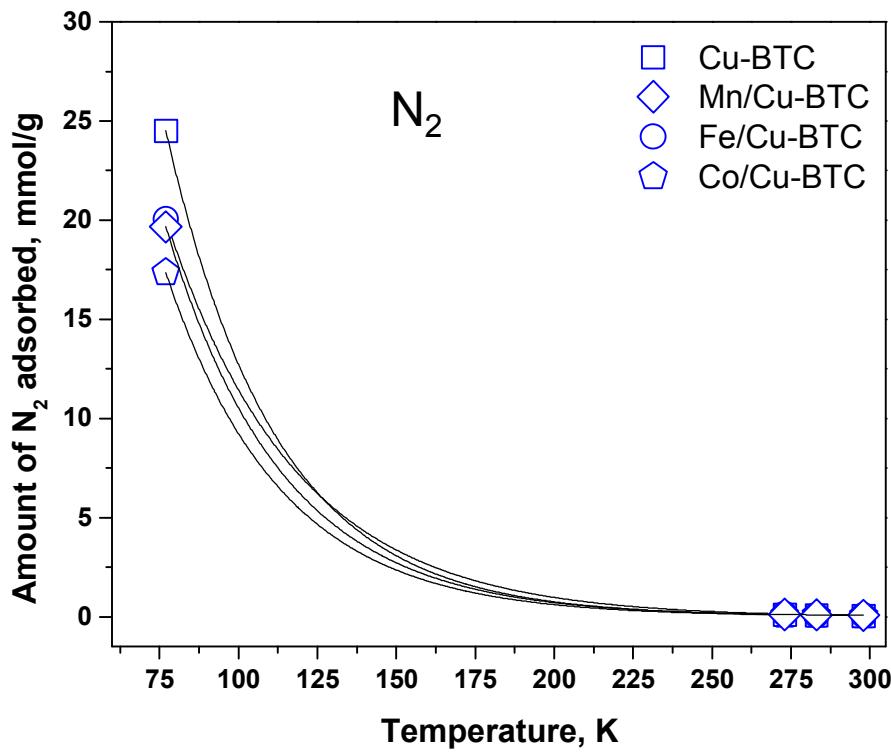
LDRD: Combine Experiment MOFs Gas Separations Data into Flame / Combustion Testing

5% improved efficiency ← heat/radiation improvement w/oxyfuel ← enhanced O₂/N₂ via MOF

- 1) Study of non-premixed oxygen-enriched and oxy-fuel flames using a non-premixed turbulent jet flame burner
- 2) Measurement of radiant flux for accurate determination of flame radiation
- 3) Measurement of soot concentration in flames planar laser-induced incandescence measurements (LII)
- 4) Allow for the calculation of the contribution of the soot to total radiant heat transfer of the flames
- 5) **Data input to Systems Analysis for calculations of efficiency improvements of combined developed MOFs into Oxyfuel Process Stream**

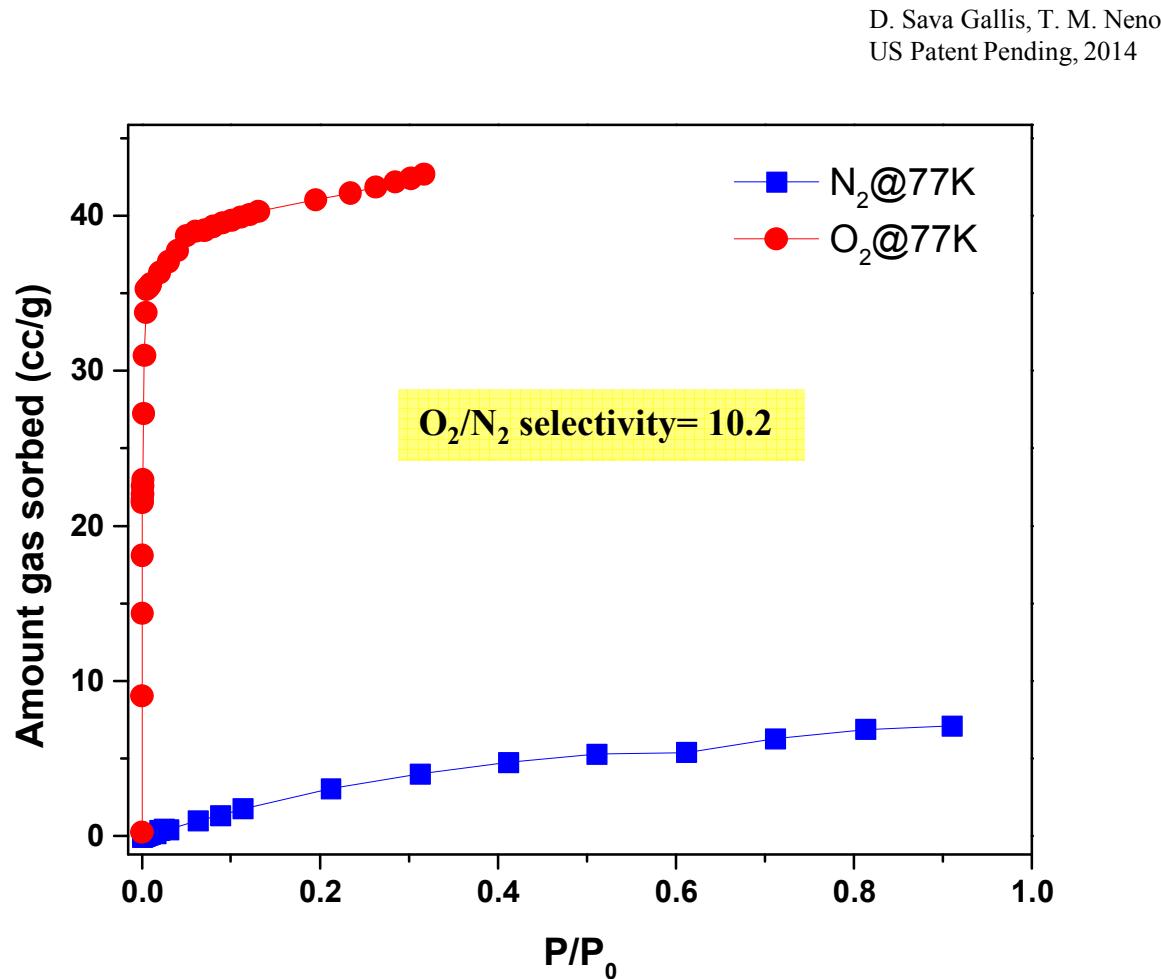
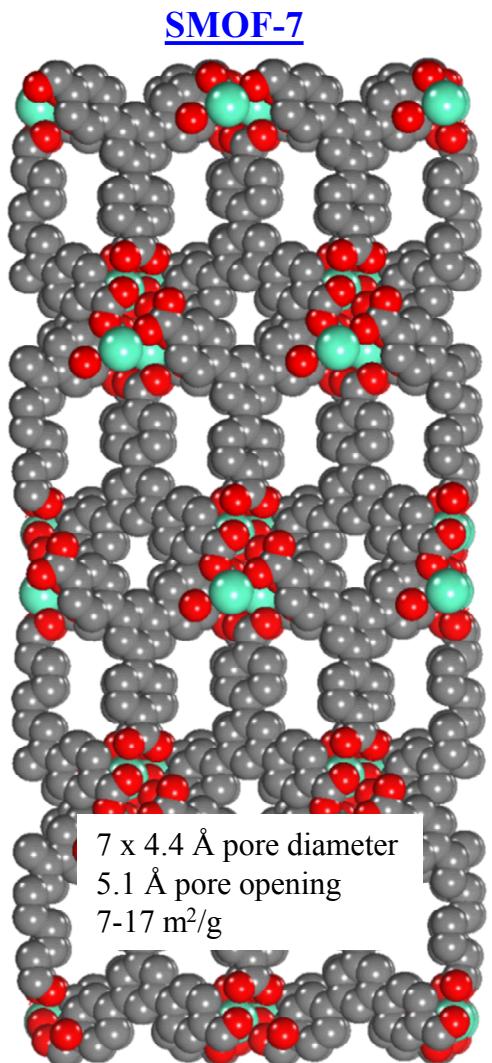
At 77K, Metal Sites Play an Important Role, while at 273 - 298 K Metal Sites have a *Smaller Effect*

The temperature dependency of the N_2 and O_2 uptake at ~ 0.2 atm and 77, 273, 283, and 298 K

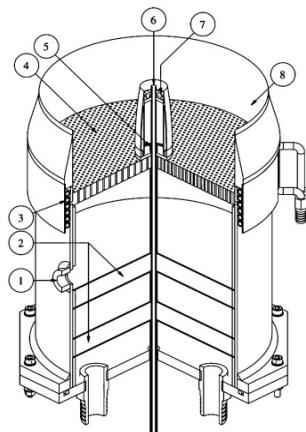


Distinct transition point temperature where the metal sites dependence on the O_2 and N_2 uptake is inverted

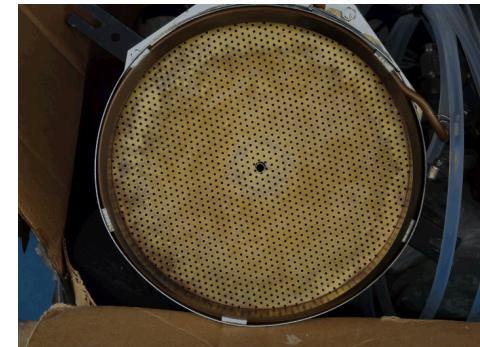
SMOF-7: O₂ vs. N₂ Single Gas Sorption Isotherm, at 77K



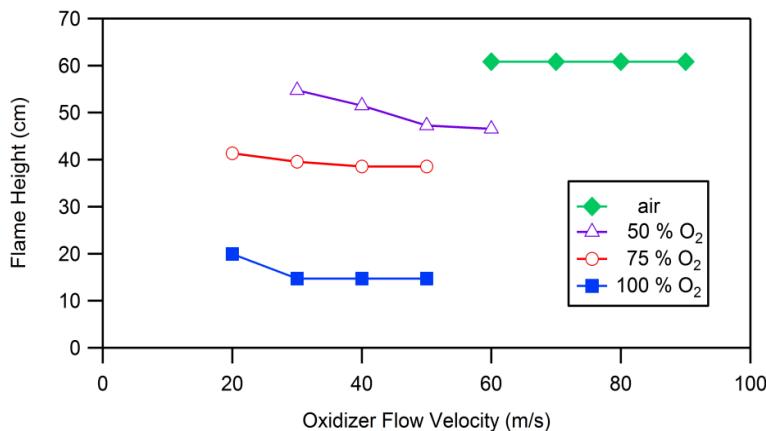
Coupling of Burner design and Oxy-fuel Combustion to Radiant Heat Transfer



Balloon number	Description
1	Flameback over-pressure sensing port
2	Glass bell jar filled cavities
3	Cooling water coil
4	Co-flow perforated baseplate
5	Pilot mixture feed exit
6	Central jet exit
7	Pilot perforated baseplate
8	Co-flow collar



- Newly designed and constructed burner with smaller diameter inside tube for CH₄ into oxider jet flow
- Allows either premixed or non-premixed methane-air flame
- Designed specifically for pure O₂ and enriched O₂ stream as determined by gas separations data from MOFs and economic life cycle analyses



LDRD calculated/predicted flame heights when using a 1/8", 0.020 wall stainless steel tube to deliver methane to the Dunn burner.

The volumetric flow of methane is always equal to $\frac{1}{2}$ the flow of oxygen, to maintain stoichiometric combustion conditions.

Preliminary Investigation of Oxygen-Enriched NG Flames

Performed preliminary testing performed with oxidizers of pure oxygen and with 50% O₂ in N₂, using an overall equivalence ratio of 1, with a constant methane flow

- Velocity (Re) of oxidizer flow is 50% lower when using pure O₂, making for taller flame (slower mixing)
- Soot formation is enhanced when using pure O₂ (higher temperatures, slower mixing)



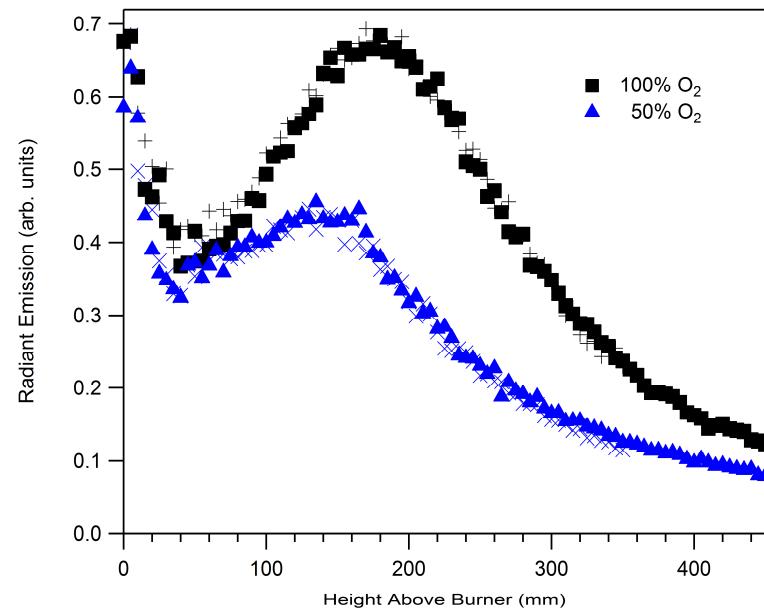
50% O₂ in N₂



100% O₂

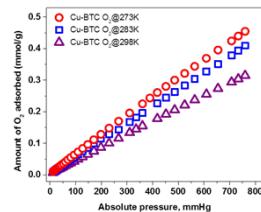
Radiant emission measurements have been performed along the flame centerline

- Data for 100% O₂ shows significantly more thermal radiation
- Flame temperatures are higher when using pure O₂ (more radiation from flame products)
- Some soot is formed in the 100% O₂ flame

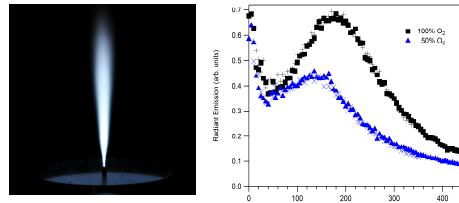


Systems Analysis of MOF-based Air Separation

MOF adsorption
isotherms (N₂ & O₂)
(from MOF team)



Optimal O₂:N₂ ratio
for combustion
(from combustion team)

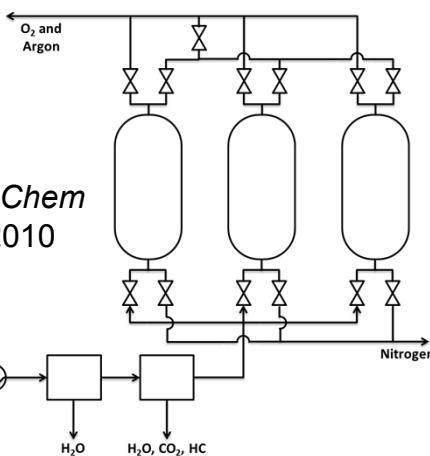


Can MOF-based
PSA reduce energy
consumption by 5%
vs. conventional PSA
air separation?

Construct and
validate model of
PSA process

Adjust PSA model
parameters to yield
desired O₂:N₂ ratio

Estimate energy
consumption based
on PSA parameters



Key PSA model parameters:

- Vessel dimensions
- Operating pressures
- Cycle time
- Feed rate

PSA energy consumption is
dominated by compressor(s)
→ Operating pressures and
flow rates are primary
drivers