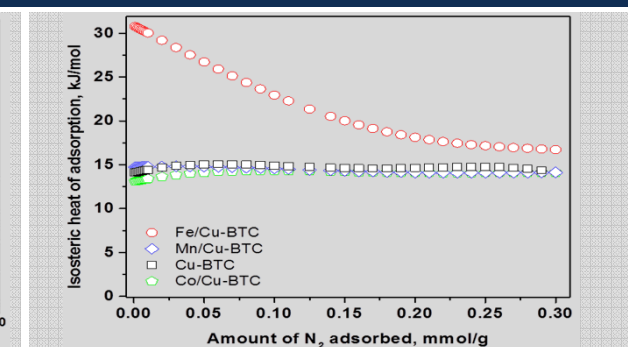
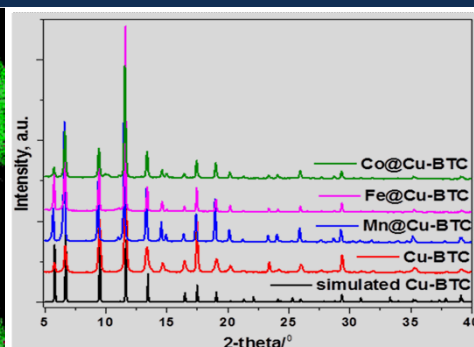
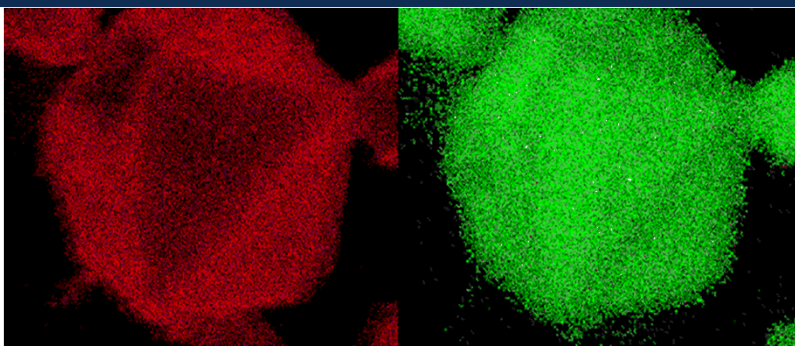


*Exceptional service in the national interest*



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

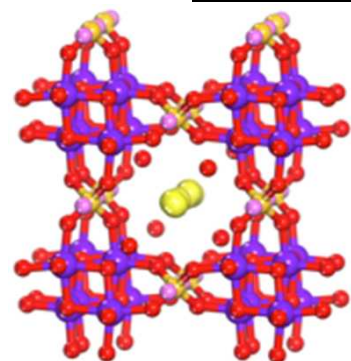
Tina M. Nenoff, Dorina F. Sava Gallis, Marie V. Parkes, Jeffery A. Greathouse, Mark A. Rodriguez,  
Scott M. Paap, and Christopher R. Shaddix  
Sandia National Laboratories, Albuquerque NM & Livermore CA

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<sup>+</sup> removal from  
water to Pollucite Waste Form**

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

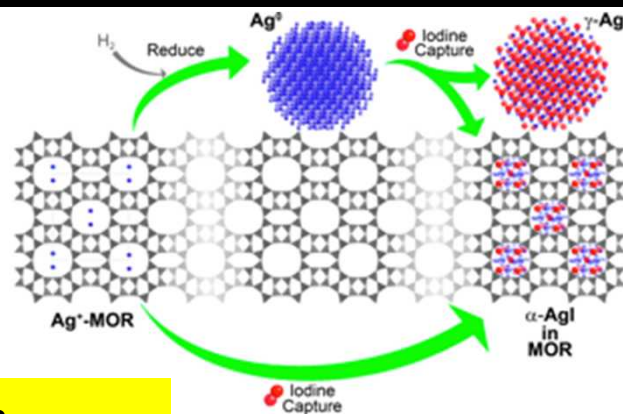
**I<sub>2</sub>/ZIF-8, Isolation  
to Waste Form**

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**



**Ag-MOR**

**I<sub>2</sub>(g) capture &  
mechanisms**

JACS, 2010, 132(26), 8897

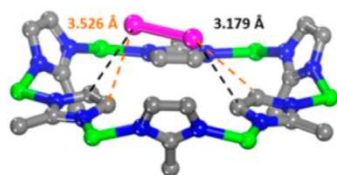
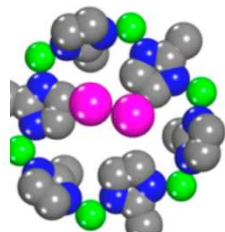
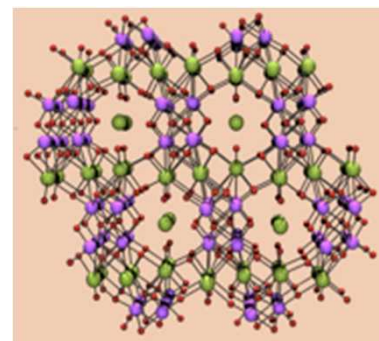
J Phys Chem Letters, 2011,  
2, 2742

**SOMS, Sr<sup>2+</sup> getter,**

**1-step to Perovskite WF**

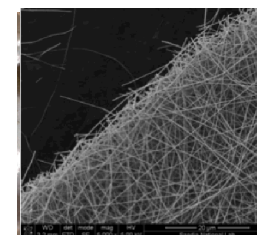
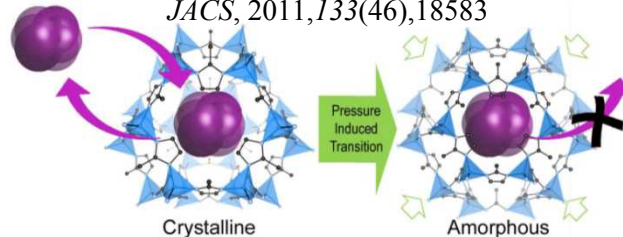
JACS, 2002, 124(3), 1704

US Patent 7,122,164



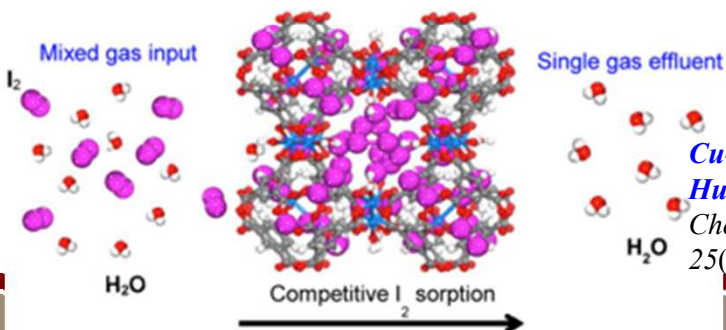
**MOF Amorphization for Gas Storage**

JACS, 2011, 133(46), 18583



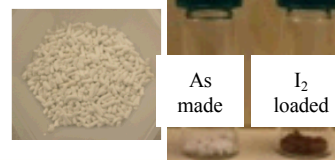
**Nanoporous Nanofibers  
Volatile Gas Removal**

US Patent Application, 2011



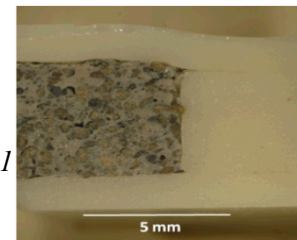
**Cu-BTC: I<sub>2</sub> from  
Humid Gas Stream**

Chem. Mater. 2013,  
25(13), 2591



**Binder Free MOF  
Pelletization**

US Patent  
Pending 2014

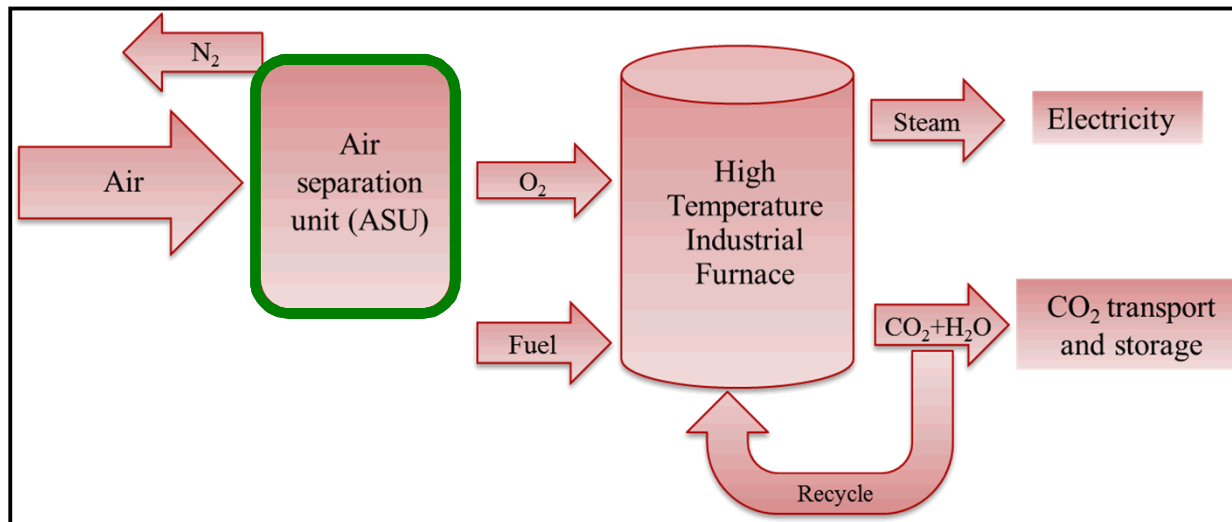


**Universal Core-Shell Iodine  
Glass Waste Form & Getter**

JACerS, 2011, 94(8), 2412

US Patent 8,262,950: 2012

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



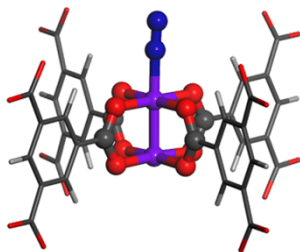
- Oxygen-enriched (oxy-fuel) combustion: burning the fossil fuel in an  $O_2$  rich atmosphere results in a flue gas composed mainly of  $CO_2$  and water (little or no  $SO_x$  and  $NO_x$  emissions)
- The limiting factor of this technology is the efficiency of the cryogenic ASU, a costly and energy 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

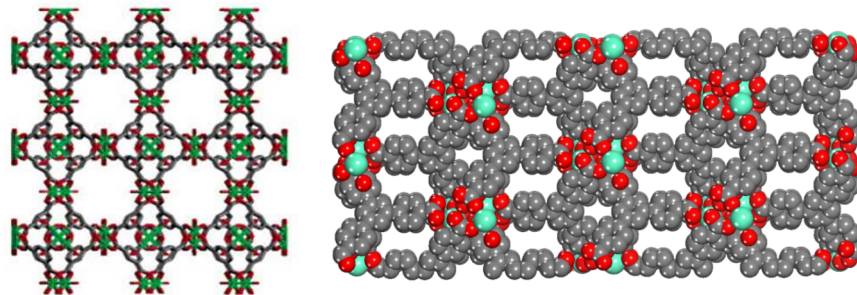
## Predictive molecular modeling

Predictive molecular modeling designed to *measure the binding energy for  $O_2$  and  $N_2$*  on coordinatively unsaturated metal sites in MOFs



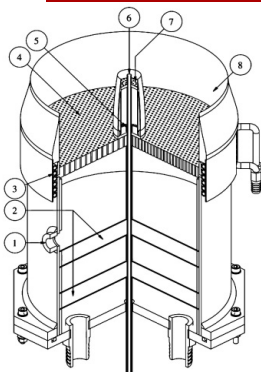
## Materials development

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



Balloon number	Description
1	Flushback over-pressure sensing port
2	Glass bead filled cavity
3	Cooling water coil
4	Collow perforated baseplate
5	Pilot mixture feed exit
6	Central jet exit
7	Pilot perforated baseplate
8	Collow 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

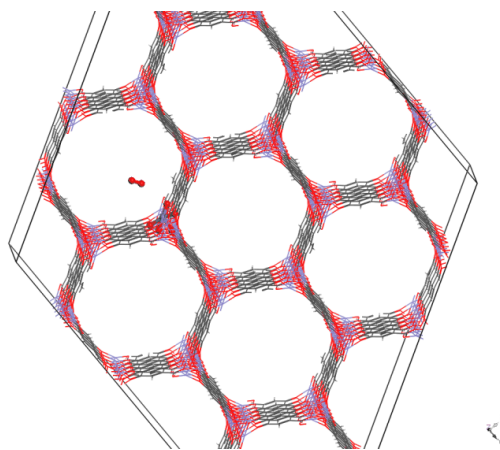
## Systems Analysis

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

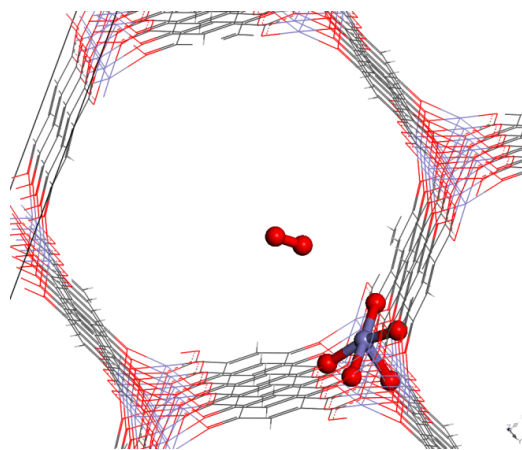
Input information/data from combustion to systems analysis for calculation of percent efficiency improvements



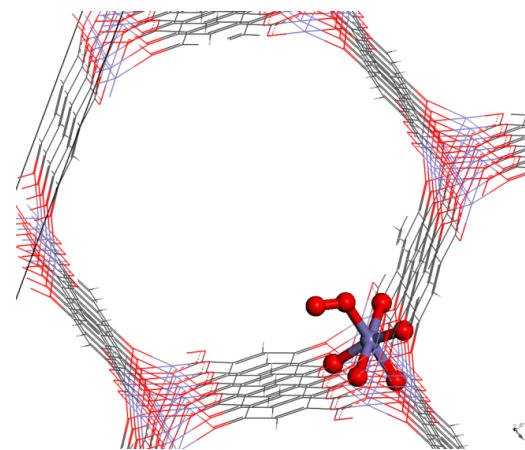
- MOFs with coordinatively unsaturated metal centers are promising materials for O<sub>2</sub>/N<sub>2</sub> separations
- Two prototypical MOFs from this category, Cr<sub>2</sub>(BTC)<sub>3</sub> (*J. Am. Chem. Soc.* **2010**, *132*, 7856–7857) and Fe<sub>2</sub>(DOBDC) (*J. Am. Chem. Soc.* **2011**, *133*, 14814–14822) both show preferential adsorption of O<sub>2</sub> over N<sub>2</sub>
- Plane wave DFT calculations were performed on periodic structures in the Vienna Ab initio Simulation Package (VASP)
- Binding geometries for side-on and bent O<sub>2</sub> and bent and linear geometries for N<sub>2</sub> were evaluated
- Static binding energies for O<sub>2</sub> and N<sub>2</sub> at 0 K



MOF with O<sub>2</sub> in pore

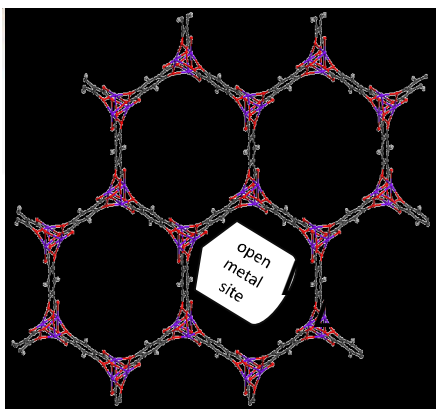


O<sub>2</sub> ready to bind to metal

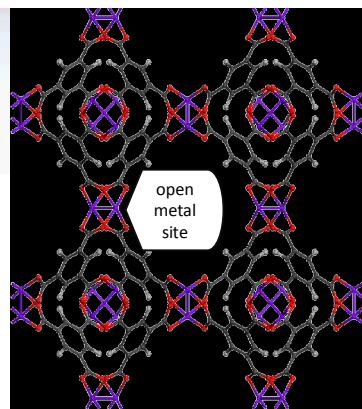


O<sub>2</sub> bound to metal

# DFT modeling of of Oxygen Adsorption in Varied Metal-Centered MOFs



$M_2(\text{dobdc})$



$M_3(\text{btc})_2$

**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** ( $\Delta E_{O_2}$ ,  $\Delta E_{N_2}$ ) were calculated by

$$\Delta E_{O_2} = E_{MOF+O_2} - E_{MOF} - E_{O_2}$$

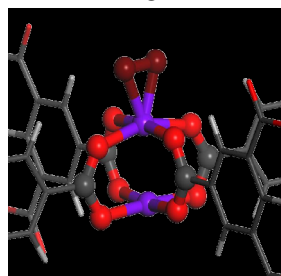
The **differences in binding energies** ( $\Delta \Delta E$ ) for oxygen and nitrogen were calculated by

$$\Delta \Delta E = -(\Delta E_{O_2} - \Delta E_{N_2})$$

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

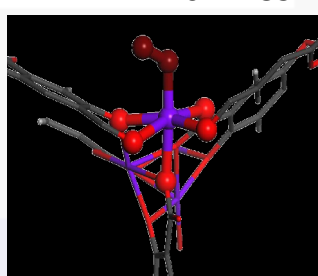
## Attention Paid to Bonding Geometries

**Side-on bonding**  
 $\angle M-X-X$   $67^\circ - 71^\circ$



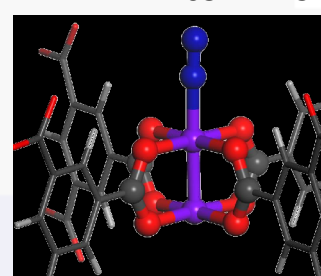
$\text{Cr}_3(\text{btc})_2(\text{O}_2)$

**Bent bonding**  
 $\angle M-X-X$   $116^\circ - 159^\circ$



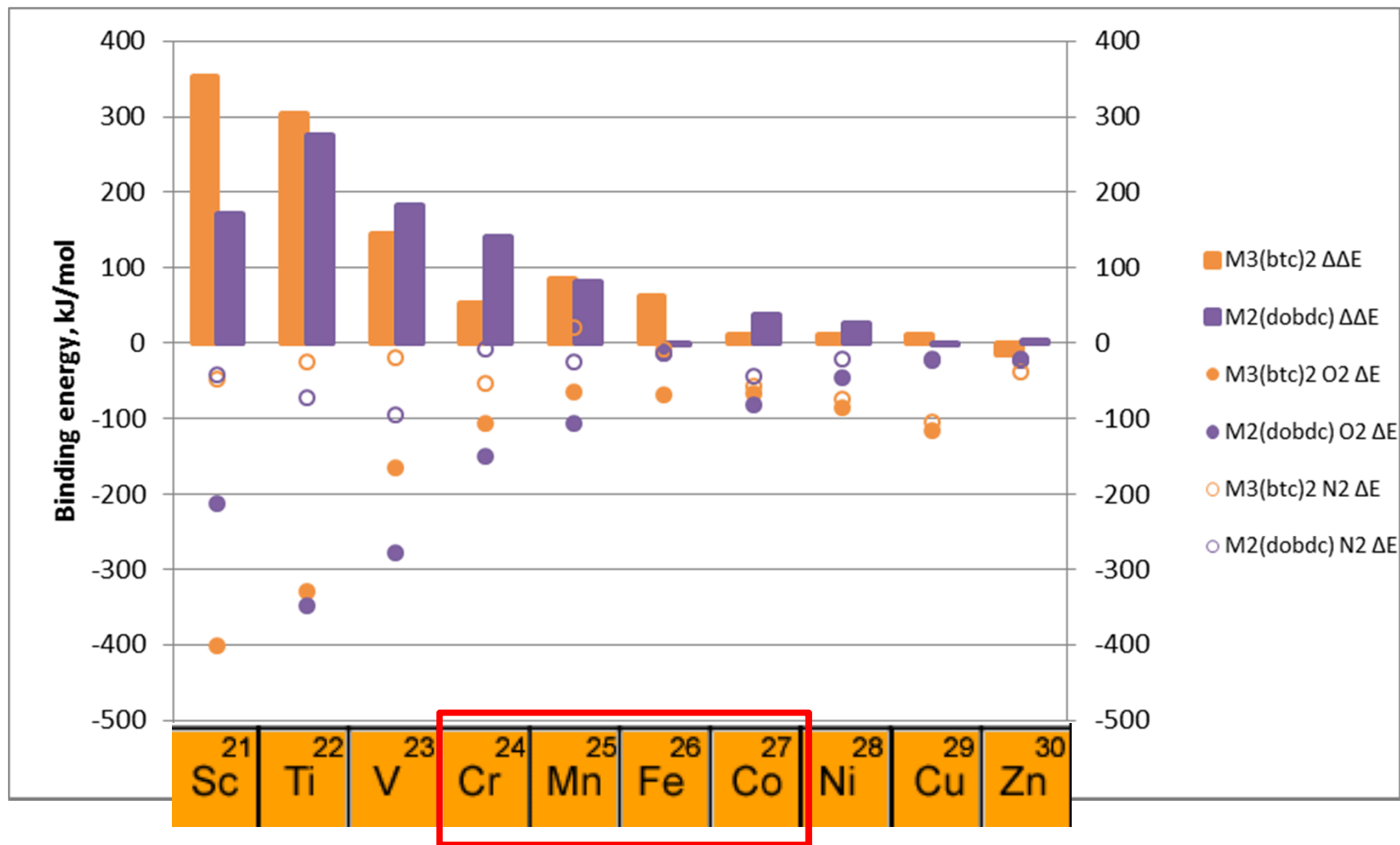
$\text{Mn}_2(\text{dobdc})(\text{O}_2)$

**Linear bonding**  
 $\angle M-X-X$   $165^\circ - 179^\circ$

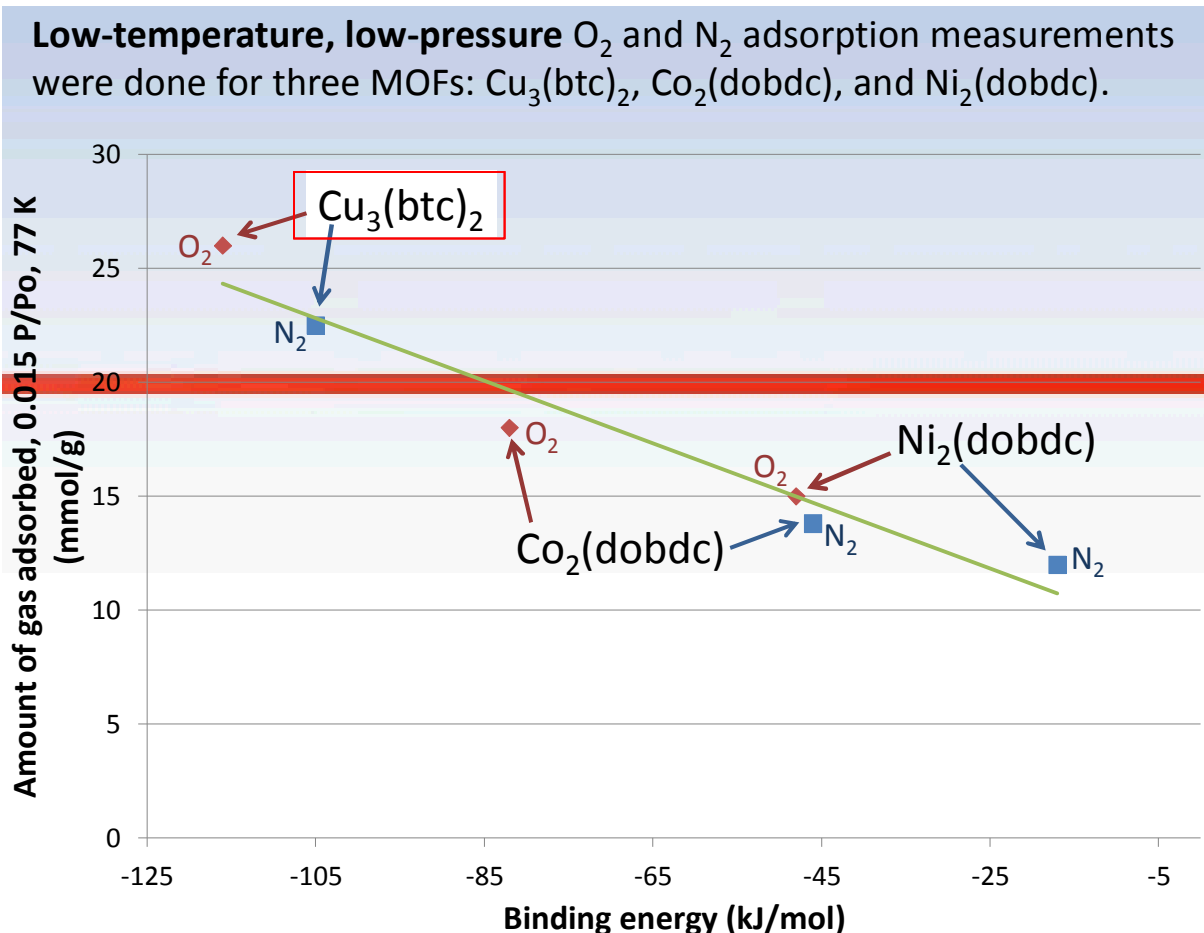


$\text{Fe}_3(\text{btc})_2(\text{N}_2)$

# O<sub>2</sub> and N<sub>2</sub> binding energies trends across the first row transition metal series



# Transition to Quantum Calculations to Estimate Metal-Oxygen Binding Energy



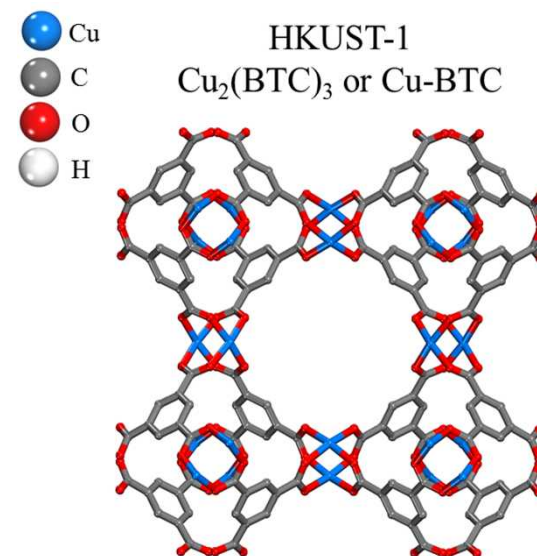
**Excellent correlation** between simulated binding energies and low-temperature, low-pressure experimental gas uptake.



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

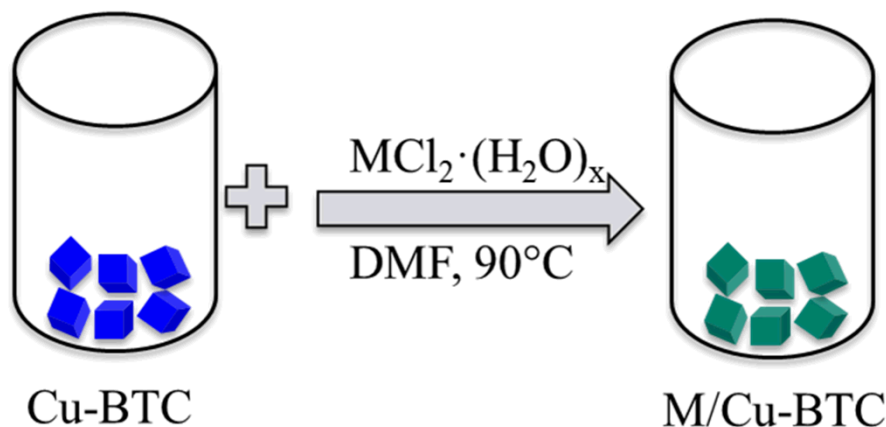
## Need/Desire To Retain Porosity of MOF For Studies of Metal-O<sub>2</sub> Bonding Effects

- 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 m<sup>2</sup>/g)
- Porphyrin-templated Mn-, Fe- and Co- Cu-BTC analogues known, however no measurable accessible porosity (*J. Am. Chem. Soc.* **2012**, 134, 928–933)



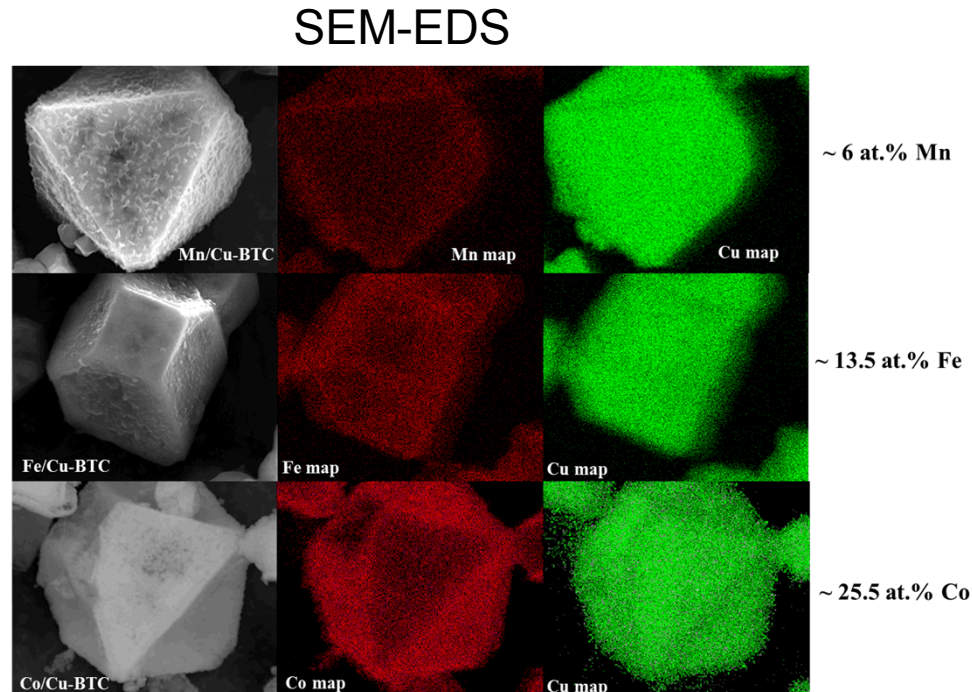
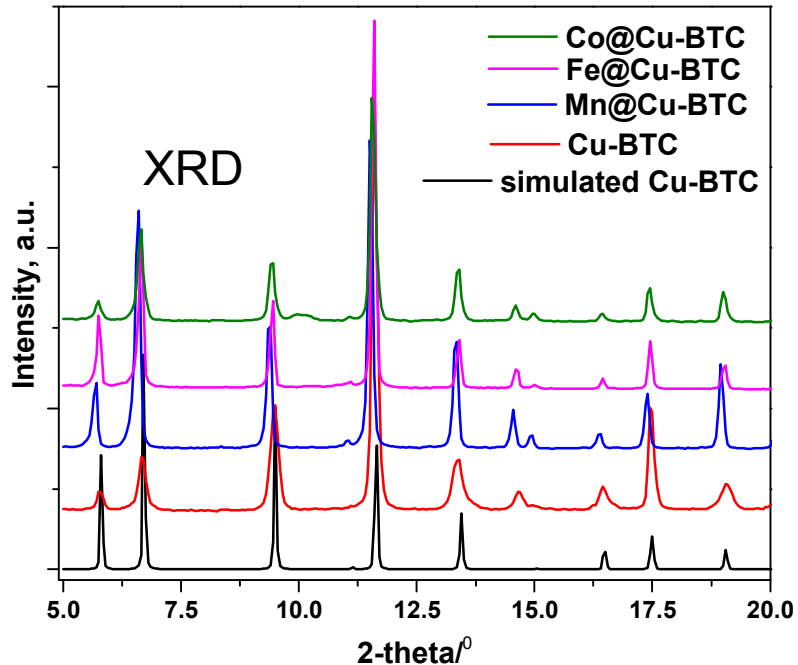
Chui, S. S. Y et.al Science **1999**, 283, 1148.

## Postsynthetic metal ion exchange

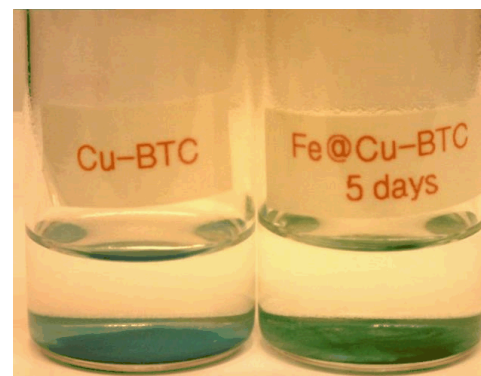


***M* = Mn, Fe, Co**

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



	Expansion (Å)	M-O average bond length (Å)
Cu-BTC	—	1.7
Co/Cu-BTC	<b>0.043</b>	2.08
Fe/Cu-BTC	<b>0.019</b>	2.0
Mn/Cu-BTC	<b>0.030</b>	2.17

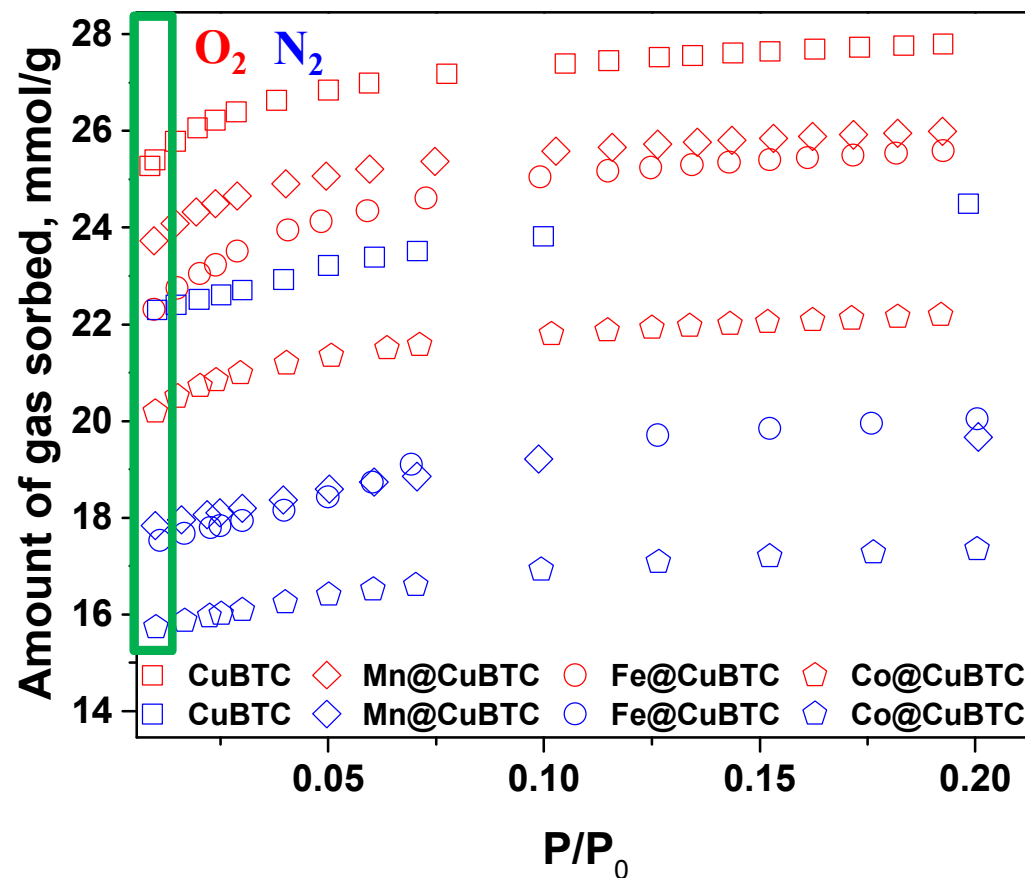


# Excellent DFT and Experiment Correlation at Low Temperature and Low Pressure

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

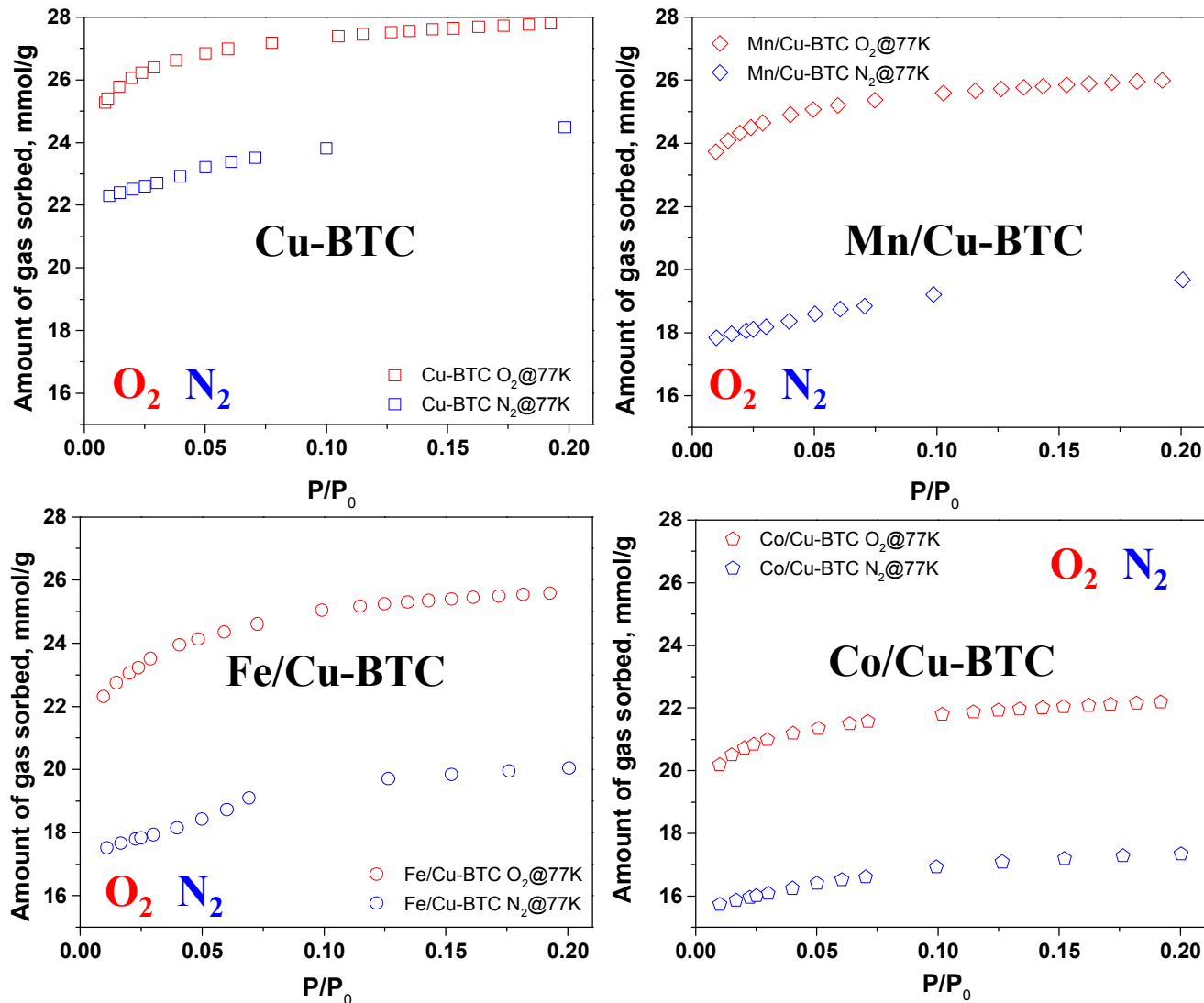
	DFT O <sub>2</sub> binding energy, kJ/mol	DFT N <sub>2</sub> binding energy, kJ/mol
Cu-BTC	-116	-105
Mn/Cu-BTC	-113	-97
Fe/Cu-BTC	-110	-92
Co/Cu-BTC	-104	-93

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



$O_2$  (red) and  $N_2$  (blue) adsorption isotherms measured at 77K on pristine Cu-BTC and Mn-, Fe-, and Co-substituted samples

# 77 K: All Samples have *Higher* O<sub>2</sub> Loadings over N<sub>2</sub>

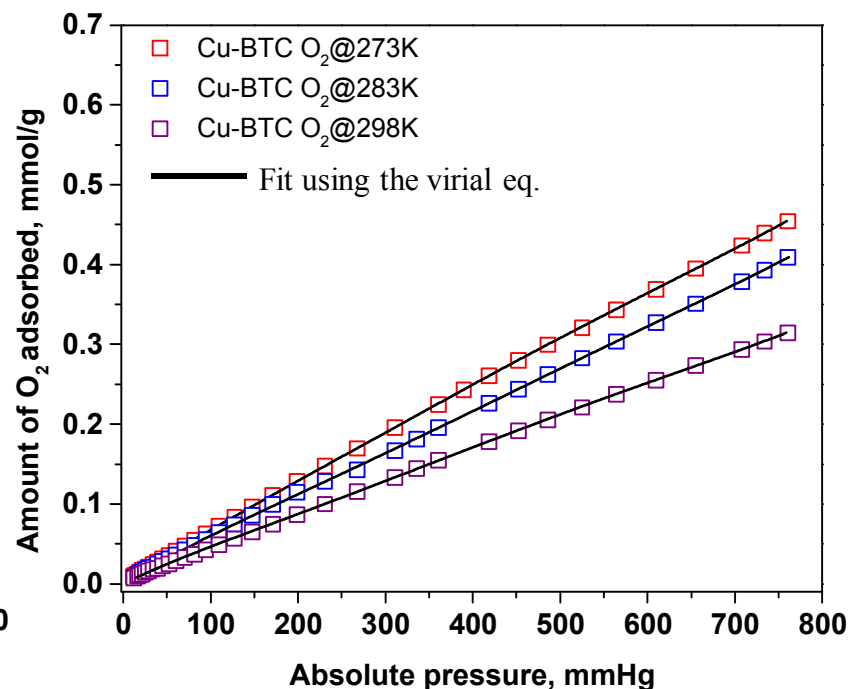
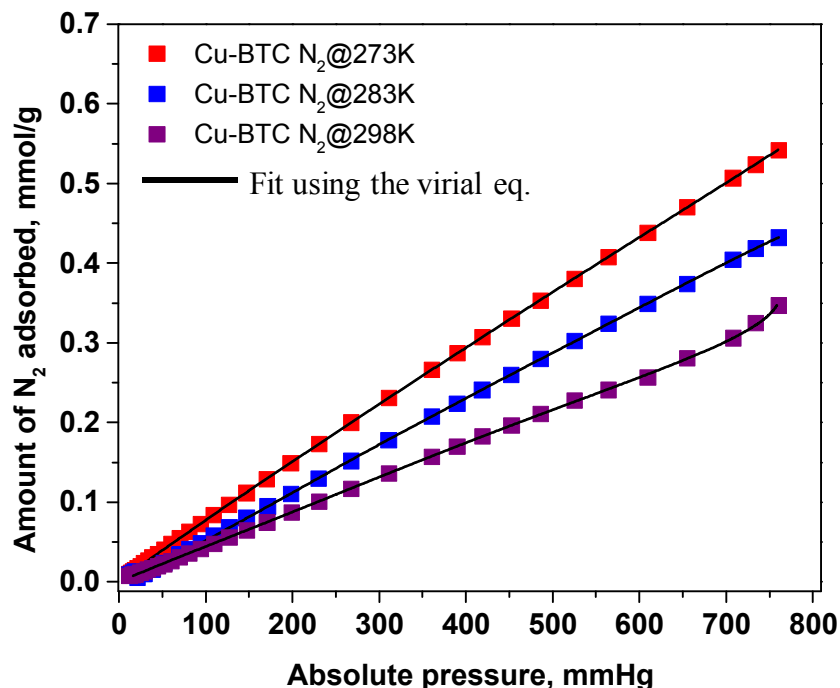


The highest O<sub>2</sub>/N<sub>2</sub> selectivity is observed for the Mn/Cu-BTC sample

# 273-298 K: As Temperature Increases, O<sub>2</sub> Loadings Decrease Relative to N<sub>2</sub>

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

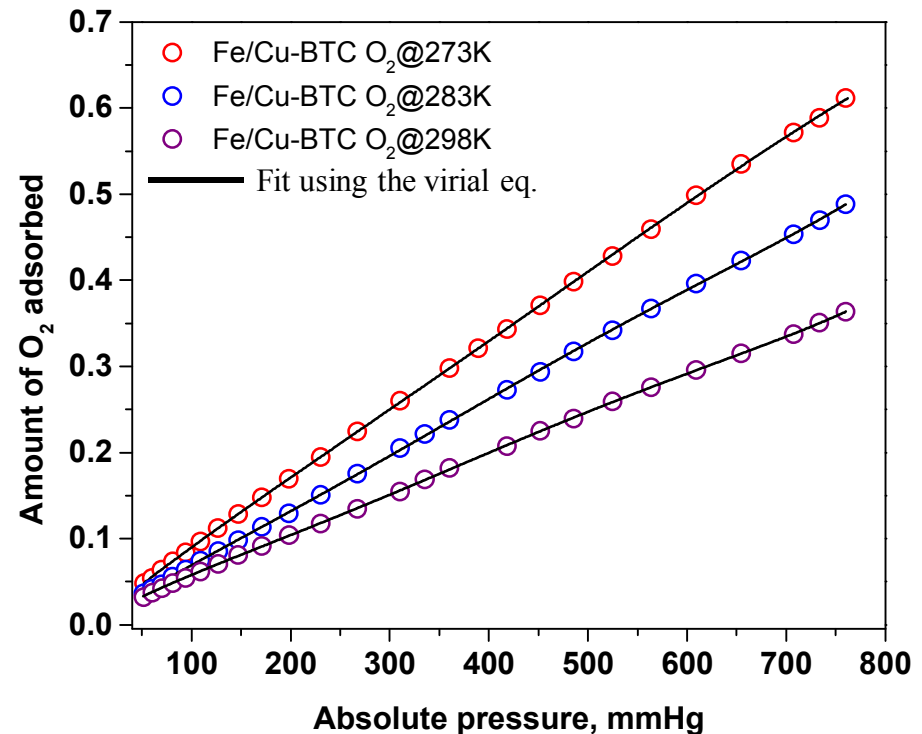
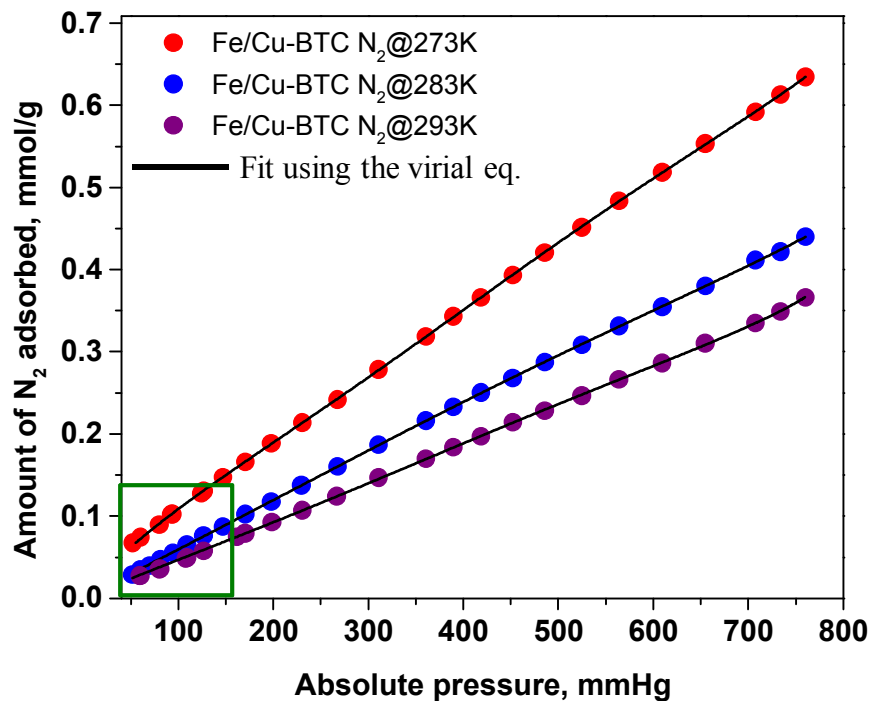
$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i$$



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)

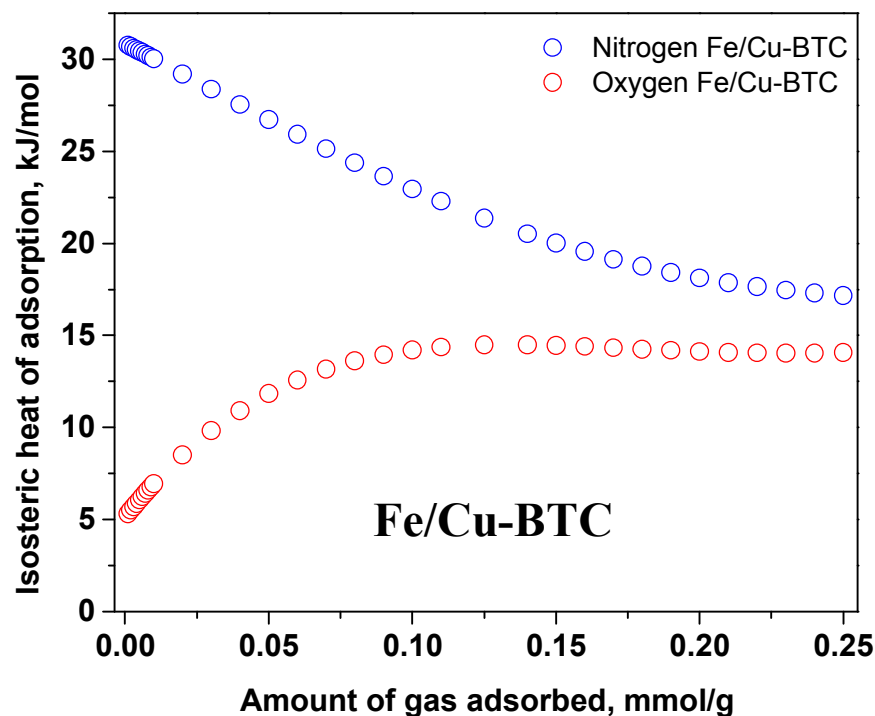
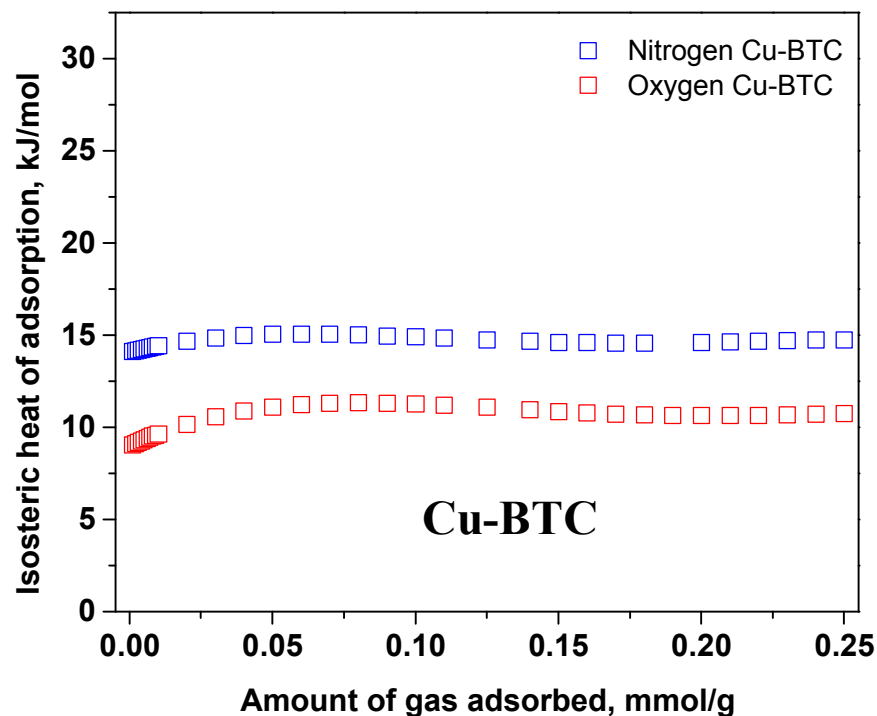


$N_2$  and  $O_2$  adsorption isotherms measured at 273, 283, and 298K on Fe/Cu-BTC

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

# Isosteric Heats of Adsorption for O<sub>2</sub> (red) and N<sub>2</sub> (blue)

## Comparison of Cu-BTC vs Fe/Cu-BTC Data

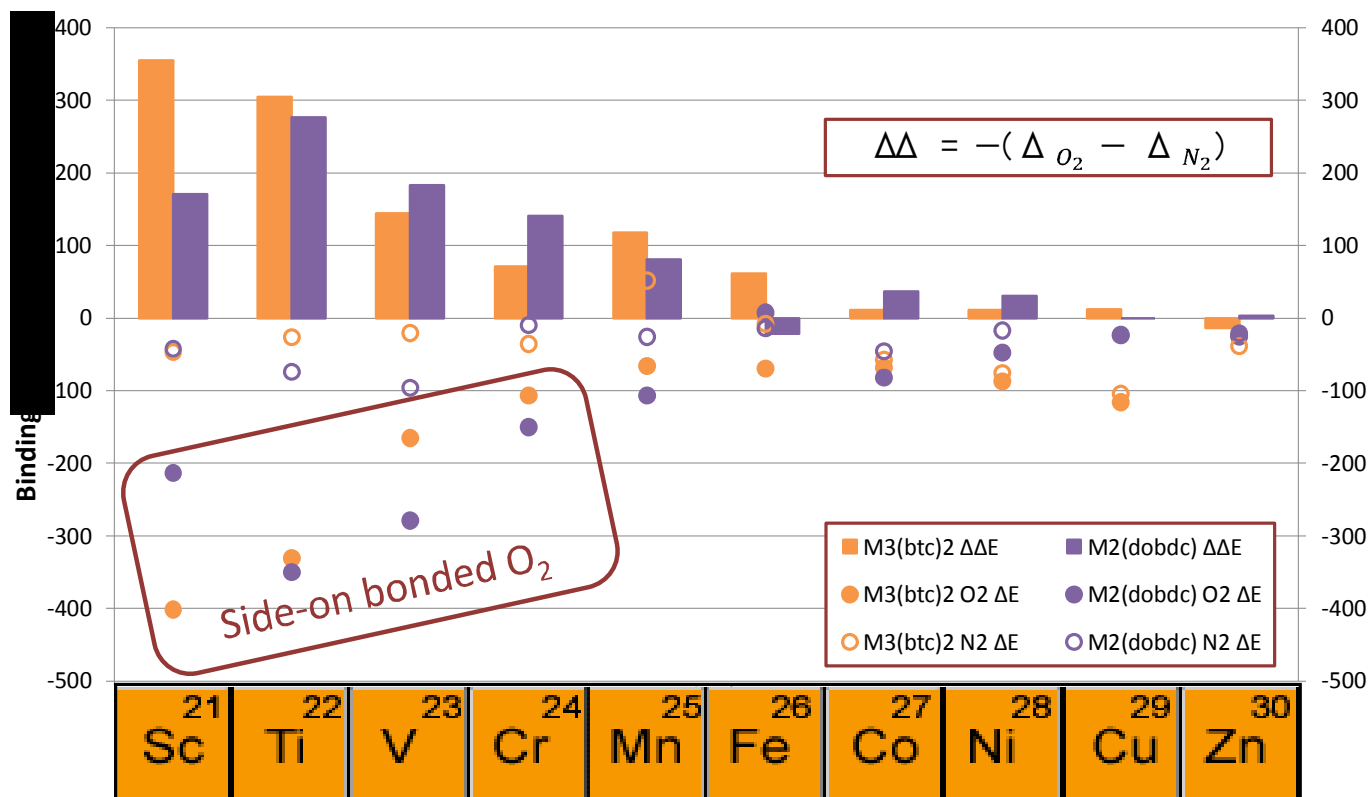


The 0 K DFT *binding energy* calculations **do not correlate** as well with experimental data from **273-298 K**

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

# Transition to Quantum Calculations to Estimate Metal-Oxygen Binding Energy

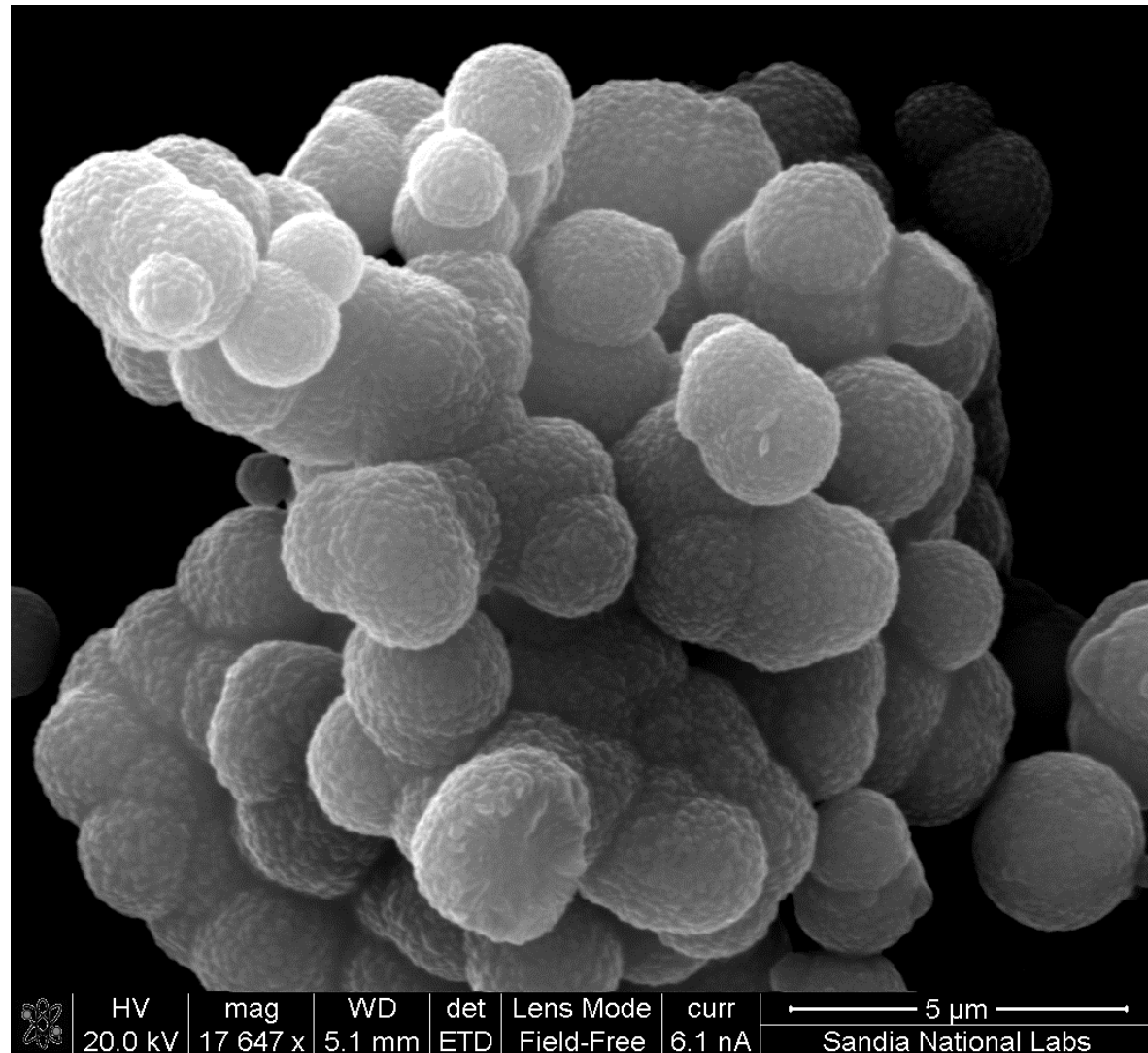
Binding Energy Calculated as a Function of Metal Site



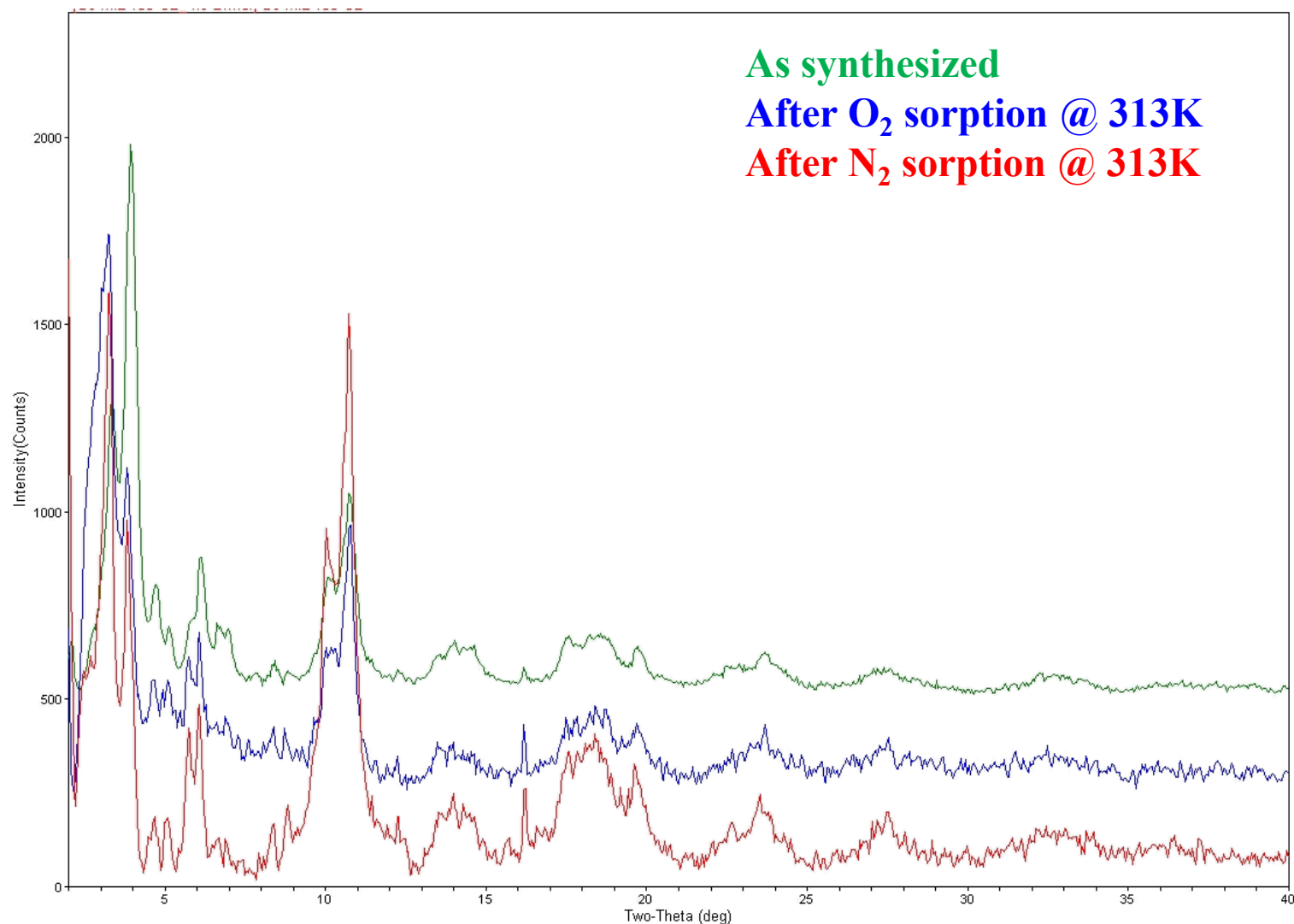
Parkes, M.; Sava Gallis, D. F.; Greathouse, J.A.; Nenoff, T.M.  
 “Screening MOFs for O<sub>2</sub>/N<sub>2</sub> Separations: Role of MOF Metal Center”,  
*J. Phys Chem C*, **2015**, *119*, 6556.

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

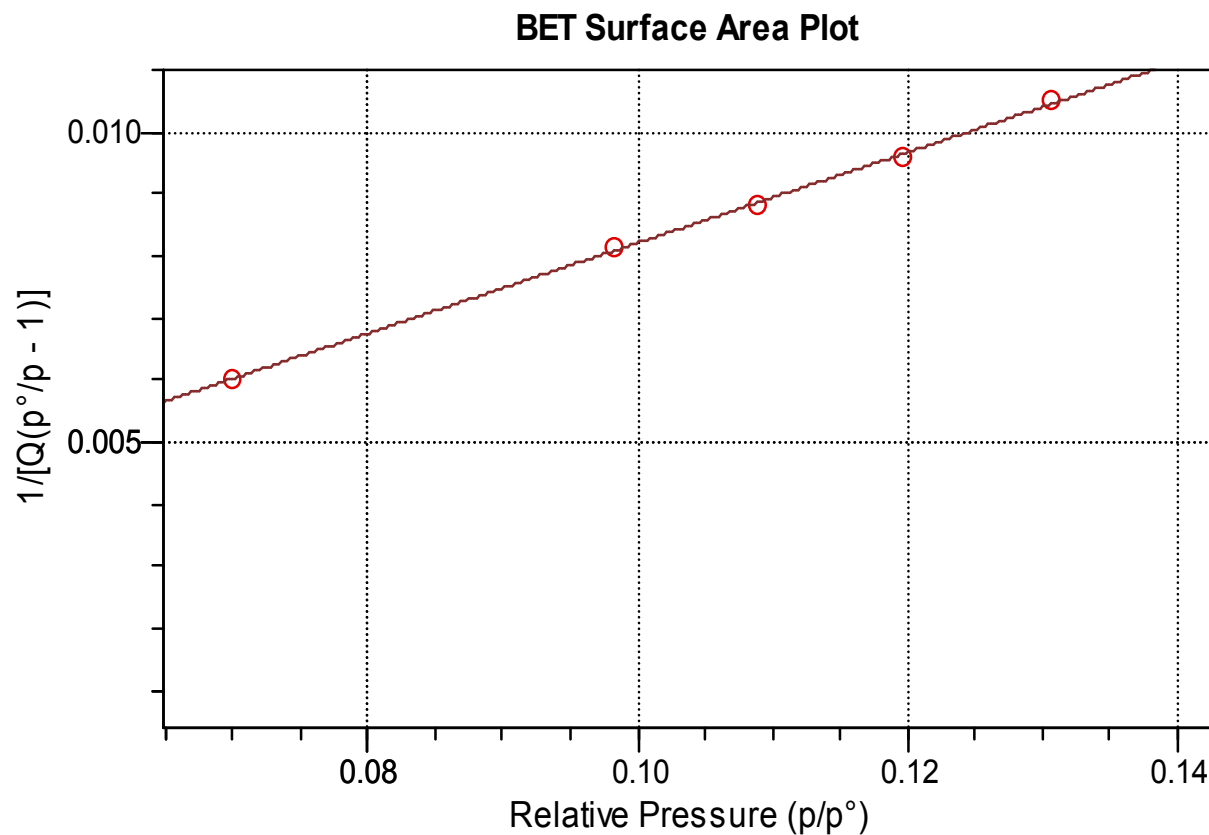
SMOF-8



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

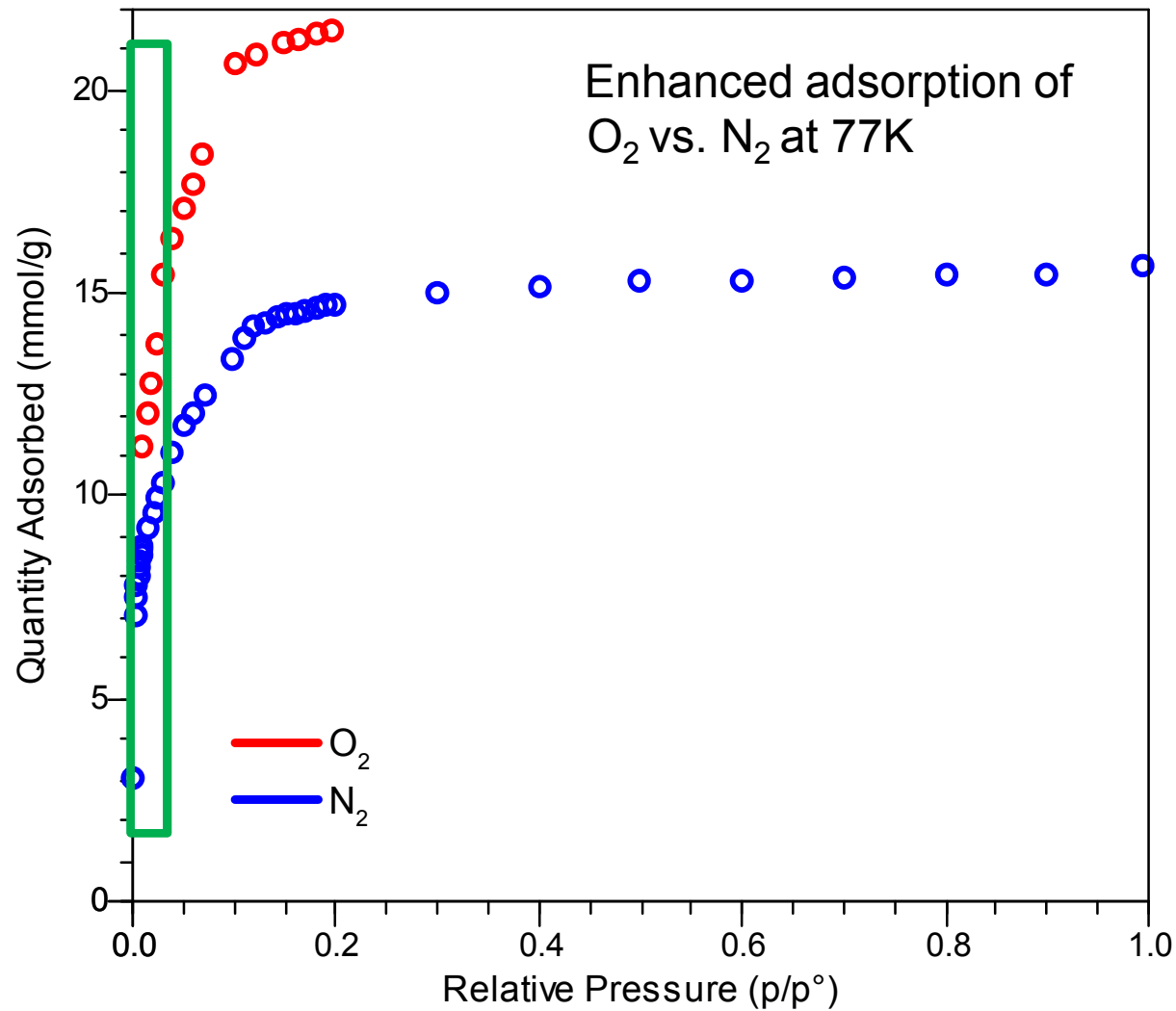


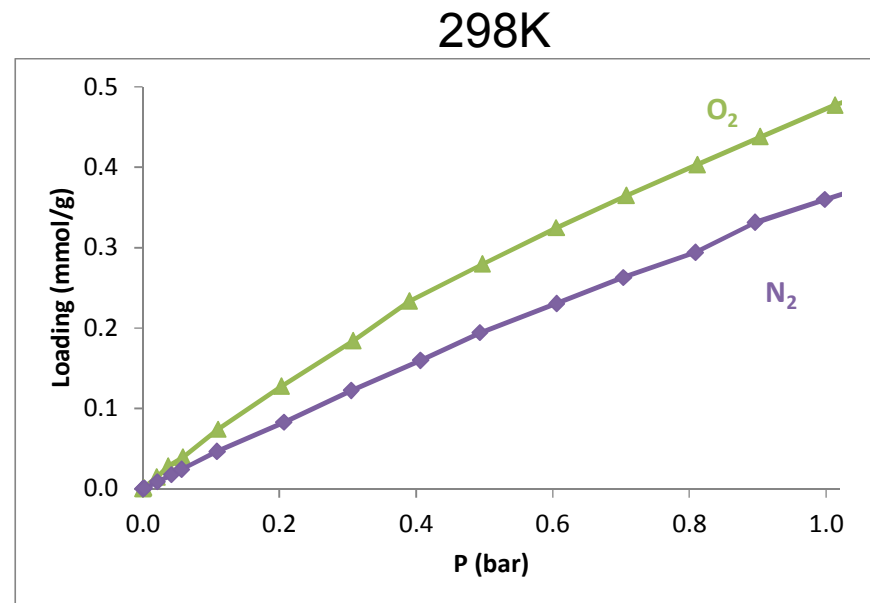
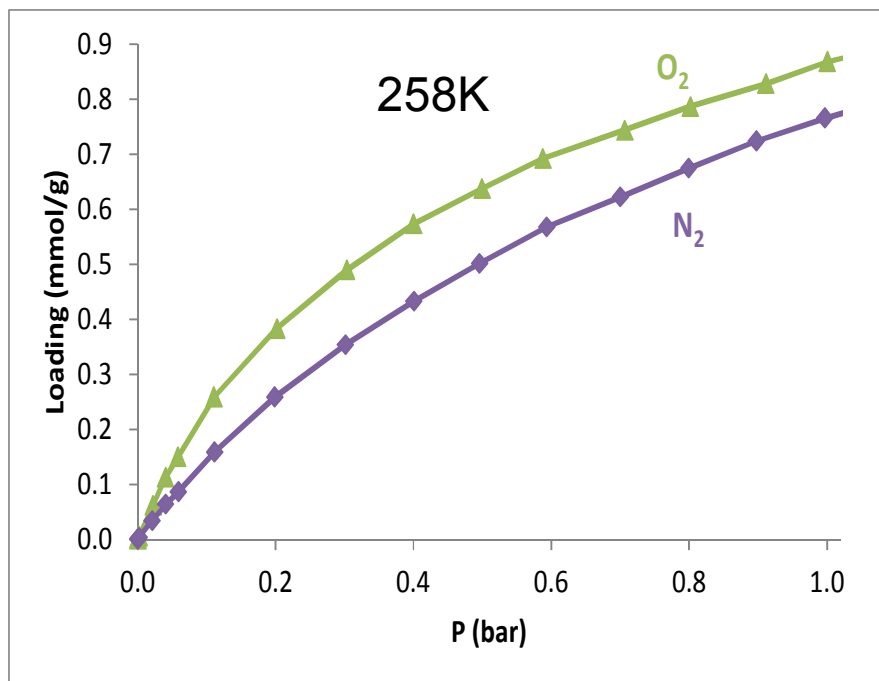




BET surface area:  $1321.7194 \pm 24.4623 \text{ m}^2/\text{g}$

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





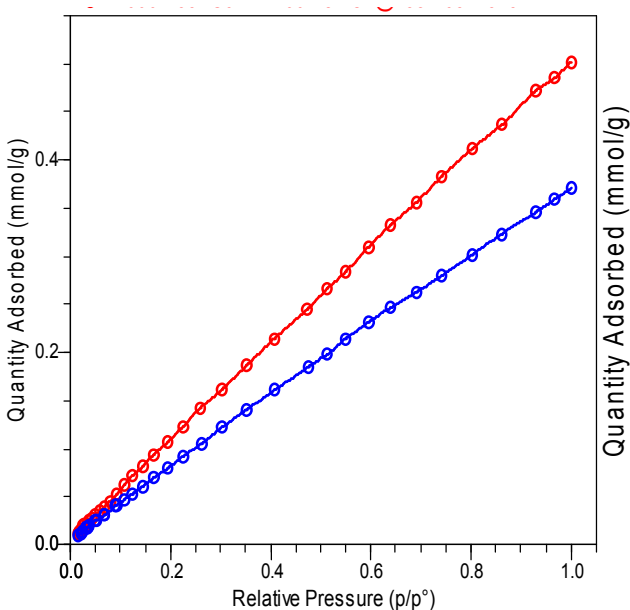
0 – 1 bar.

Preferred O<sub>2</sub> uptake but O<sub>2</sub>/N<sub>2</sub> selectivity increases between 258K and 298K

# SMOF-8: Enhanced Quantity of O<sub>2</sub> vs N<sub>2</sub> Adsorbed over Wide Temperature Range (at least to 313K)

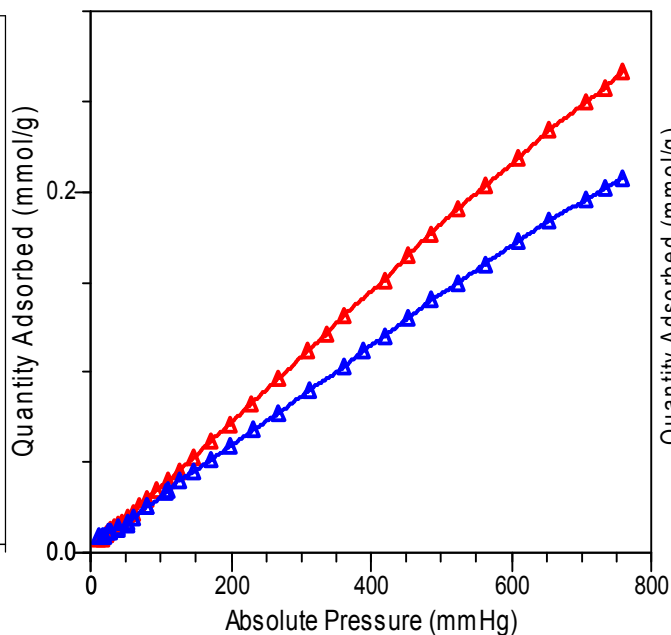
SMOF-8

O<sub>2</sub> vs. N<sub>2</sub> @258K



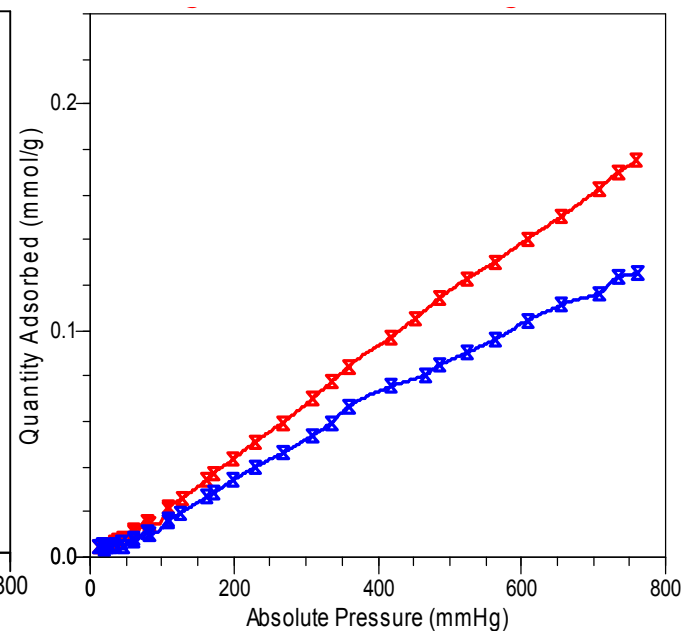
SMOF-8

O<sub>2</sub> vs. N<sub>2</sub> @298K



SMOF-8

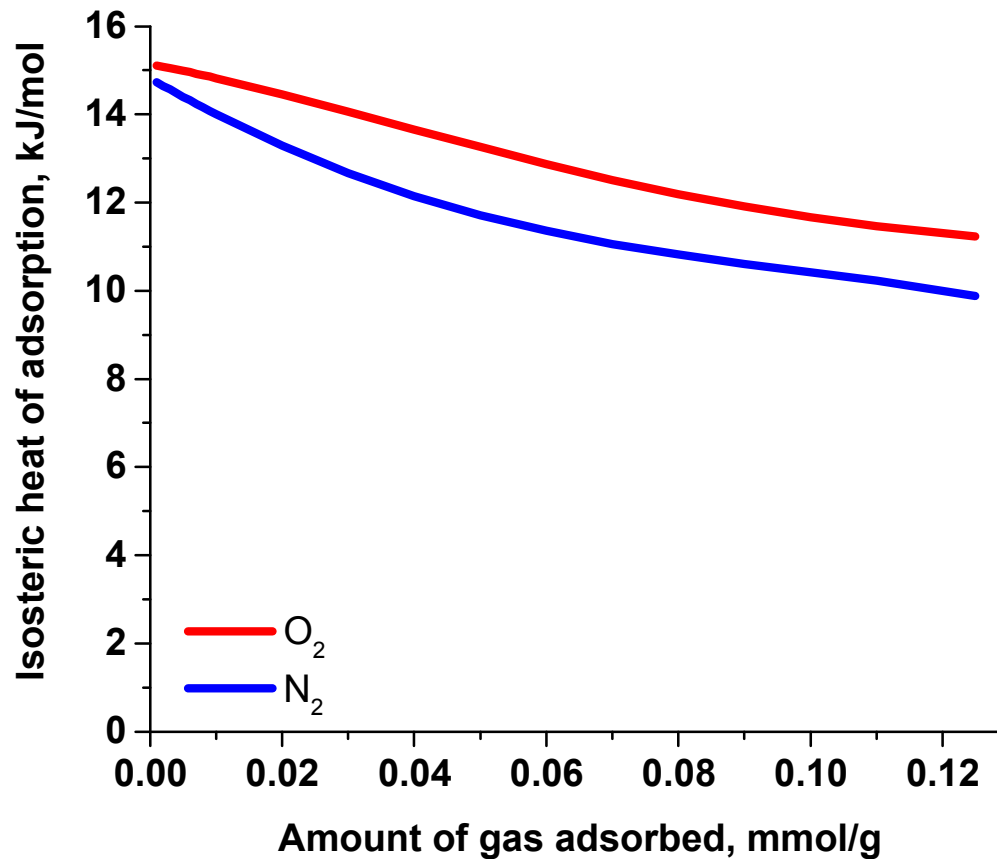
O<sub>2</sub> vs. N<sub>2</sub> @313K



Isotherm trends mimic those predicted by GCMC

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

Q<sub>st</sub> derived from 258K, 298K and 313 K  
Independent Virial Fit HOA





- Successfully synthesized partially substituted  
Co-, Fe- and Mn- analogues of Cu-BTC
- Assessed the effect on metal substitution on the O<sub>2</sub> and N<sub>2</sub> adsorption capacity at both cryogenic and close to room temperature ranges
- For the Co-, Mn- and original Cu-BTC, O<sub>2</sub> preferentially adsorbs over N<sub>2</sub> at 77K. *However*, the trend is reversed at 298K, where N<sub>2</sub> preferentially adsorbs over O<sub>2</sub>
- Based on predictive modeling, we studied early transition metal metal-center MOFs for enhanced O<sub>2</sub> sorption.
- SMOF-8: Early transition metal MOFs show preference for O<sub>2</sub> vs N<sub>2</sub> over wide temperature range (up to at least 313K), as confirmed by isosteric heats of adsorption higher in SMOF-8 for O<sub>2</sub> versus N<sub>2</sub>
- Next Steps: Data to Technoeconomic Analysis and Burner Design for Oxyfuel combustion applications

# Thank You

## Sandia National Laboratories' Sites



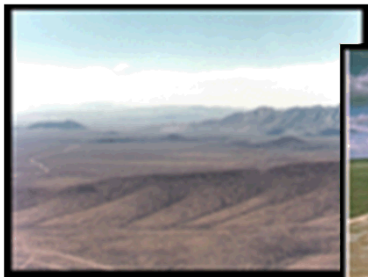
**Albuquerque, New Mexico**



**Kauai Test Facility  
Hawaii**



**Tonopah Test  
Range,  
Nevada**



**Yucca Mountain  
Nevada**



**WIPP,  
New Mexico**



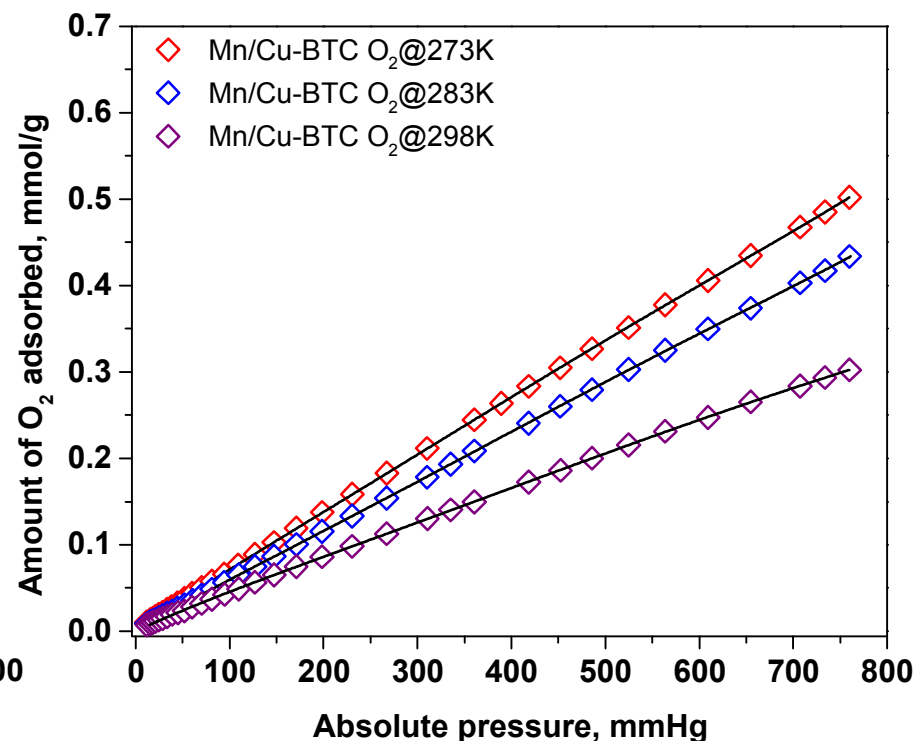
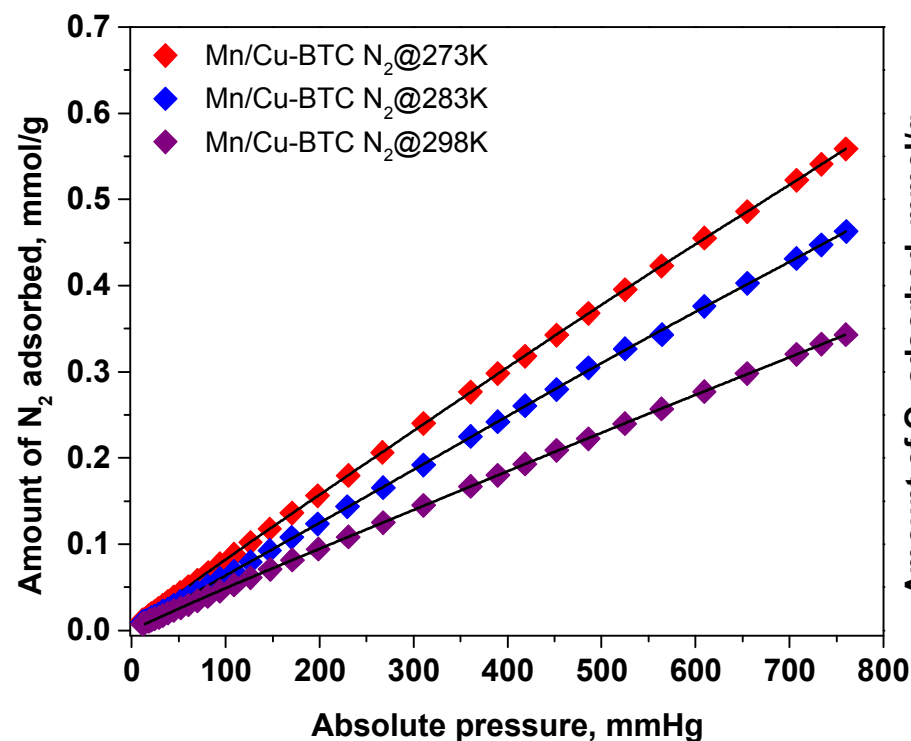
**Pantex, Texas**



**Livermore, California**

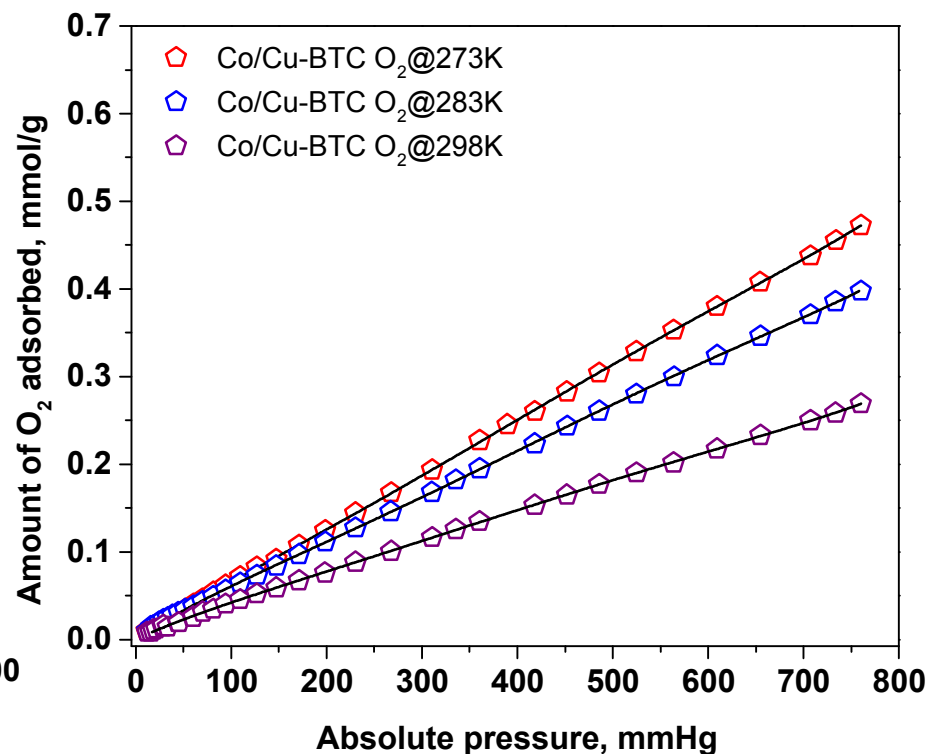
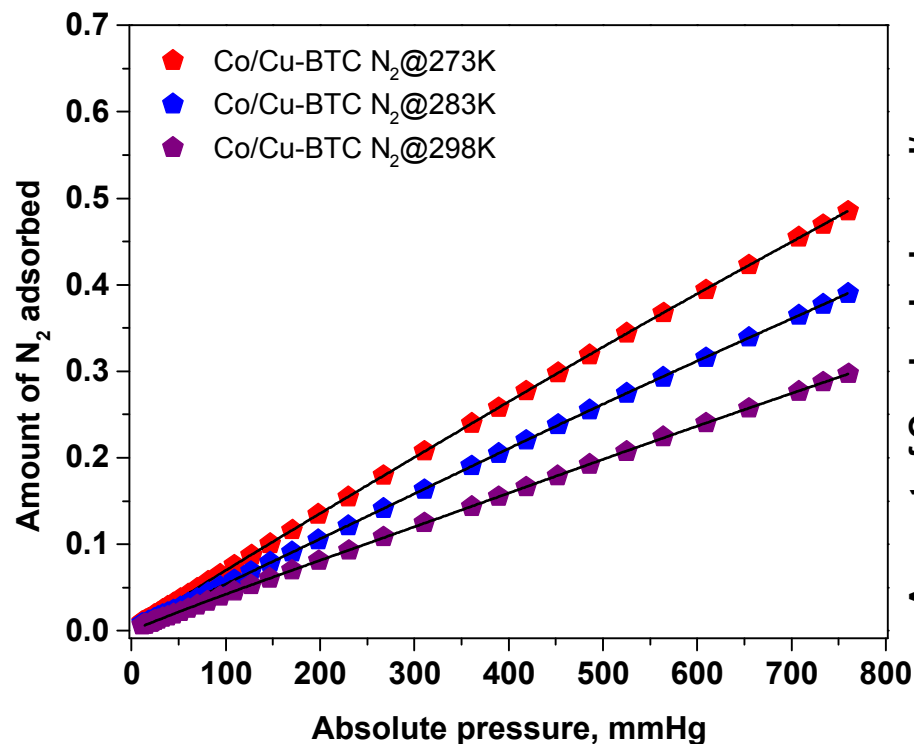
**Thank You**

# $\text{N}_2$ and $\text{O}_2$ adsorption isotherms measured at 273, 283, and 298K on pristine Mn/Cu-BTC



In the room temperature range, slightly higher affinity for  $\text{N}_2$  over  $\text{O}_2$  is noted

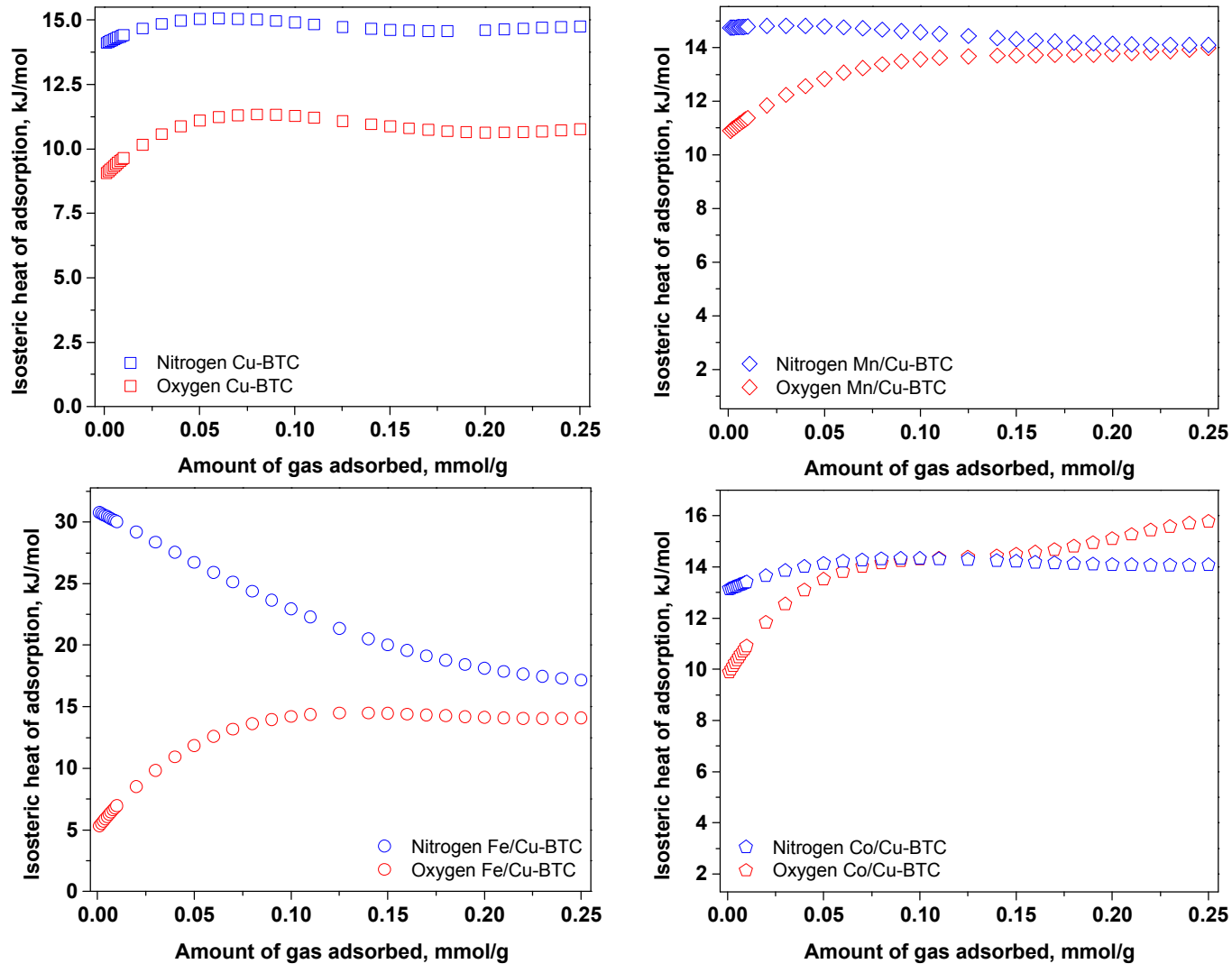
# $\text{N}_2$ and $\text{O}_2$ adsorption isotherms measured at 273, 283, and 298K on pristine Co/Cu-BTC



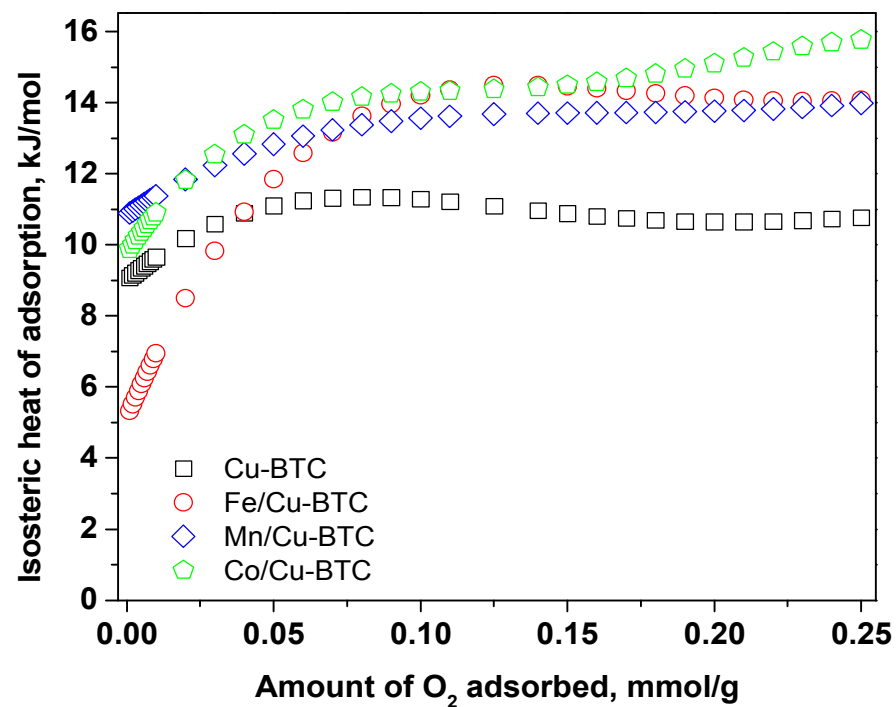
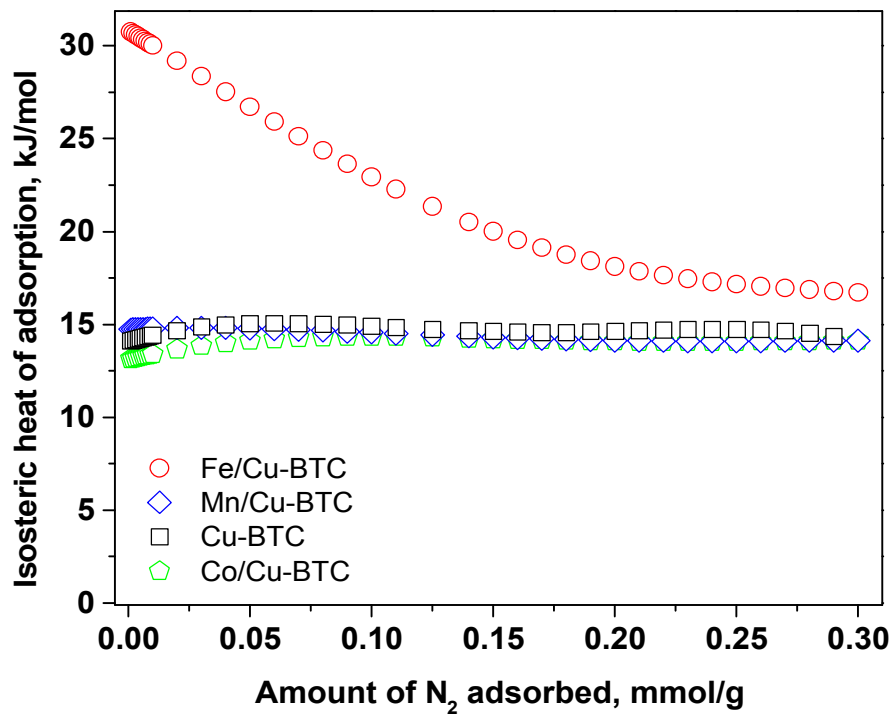
In the room temperature range, slightly higher affinity for  $\text{N}_2$  over  $\text{O}_2$  is noted



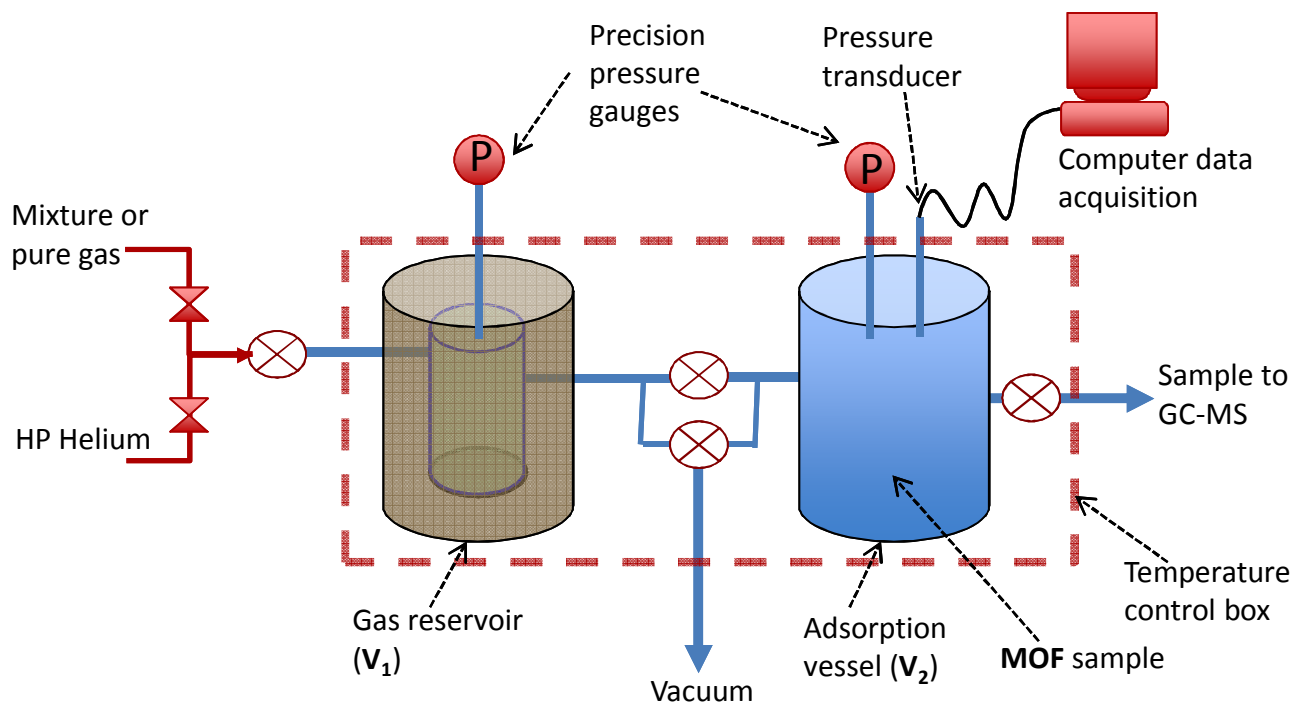
# Significantly higher binding energy of $N_2$ over $O_2$ is noted for the Fe/Cu-BTC sample



Isosteric heats of adsorption for  $O_2$  (red) and  $N_2$  (blue) obtained from the fitted 273, 283 and 298K adsorption isotherms



# O<sub>2</sub>/N<sub>2</sub> Gas mixture adsorption measurements containing 20% O<sub>2</sub> and 80% N<sub>2</sub>



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

Samples tested for adsorption of O<sub>2</sub>/N<sub>2</sub> mixture containing 20% O<sub>2</sub> and 80% N<sub>2</sub> at 21, 35, and 48.5°C, respectively.

P <sub>eq</sub> , bar	Amount adsorbed., cm <sup>3</sup> (STP).g <sup>-1</sup> .bar <sup>-1</sup>		aO <sub>2</sub> /N <sub>2</sub>
	O <sub>2</sub>	N <sub>2</sub>	
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 O<sub>2</sub> Separations for Improved Combustion Process Efficiency

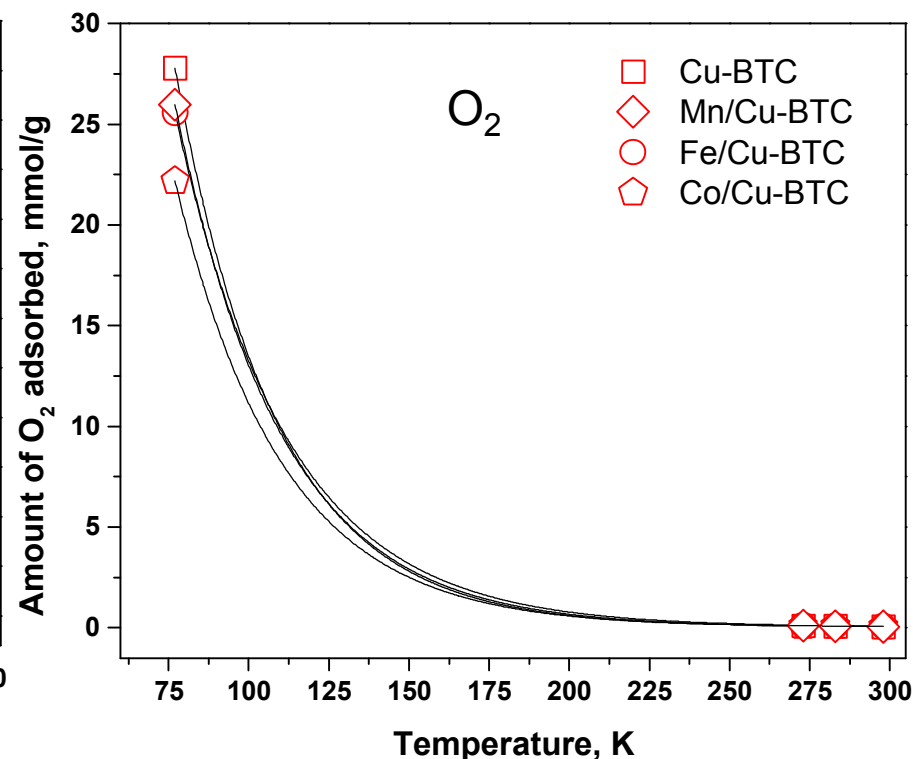
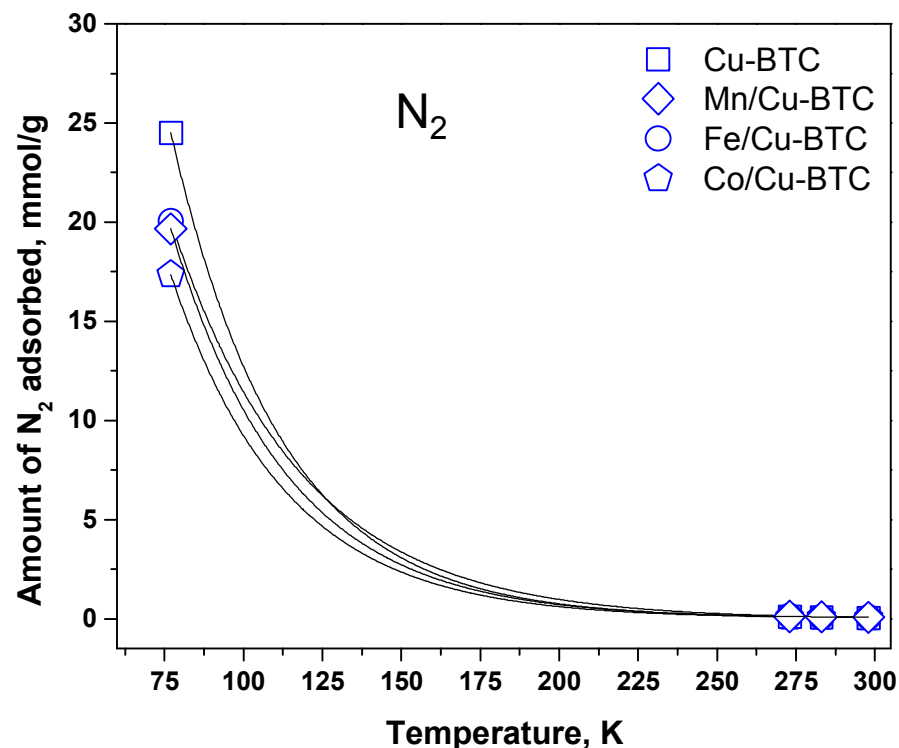
*LDRD: Combine Experiment MOFs Gas Separations Data into Flame / Combustion Testing*

*5% improved efficiency ← heat/radiation improvement w/oxyfuel ← enhanced O<sub>2</sub>/N<sub>2</sub> 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<sub>2</sub> and O<sub>2</sub> uptake at ~ 0.2 atm and 77, 273, 283, and 298 K

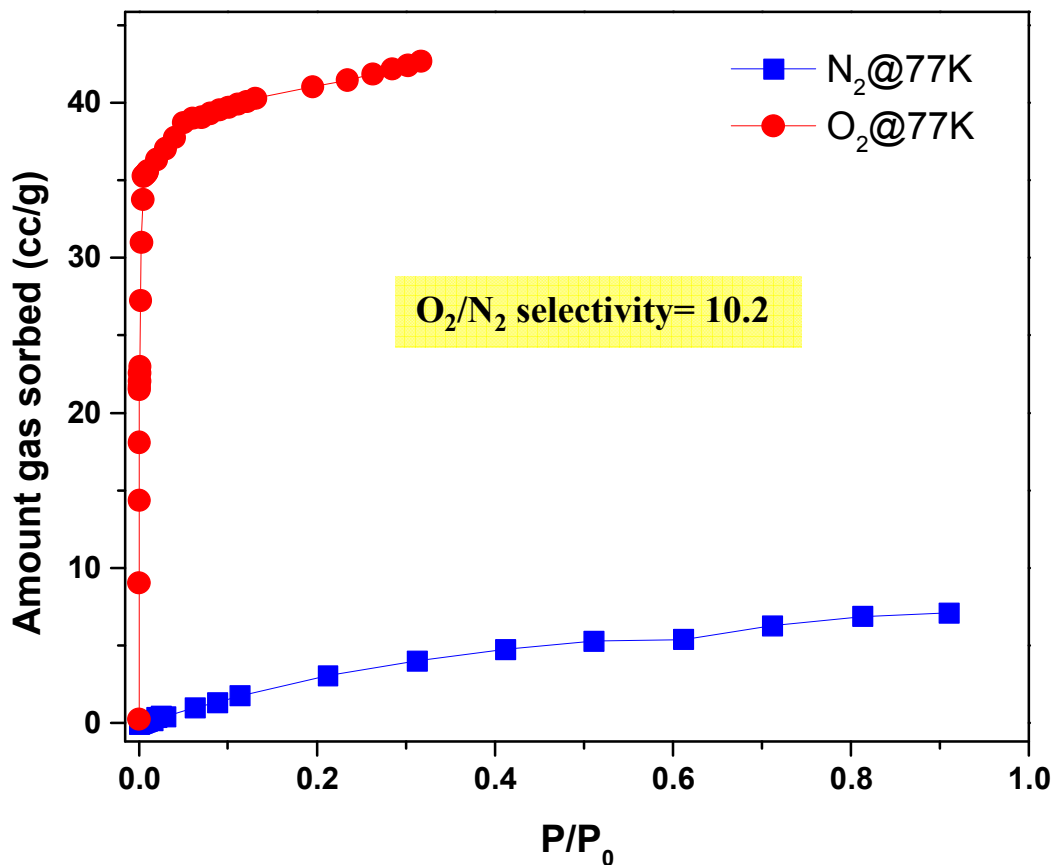
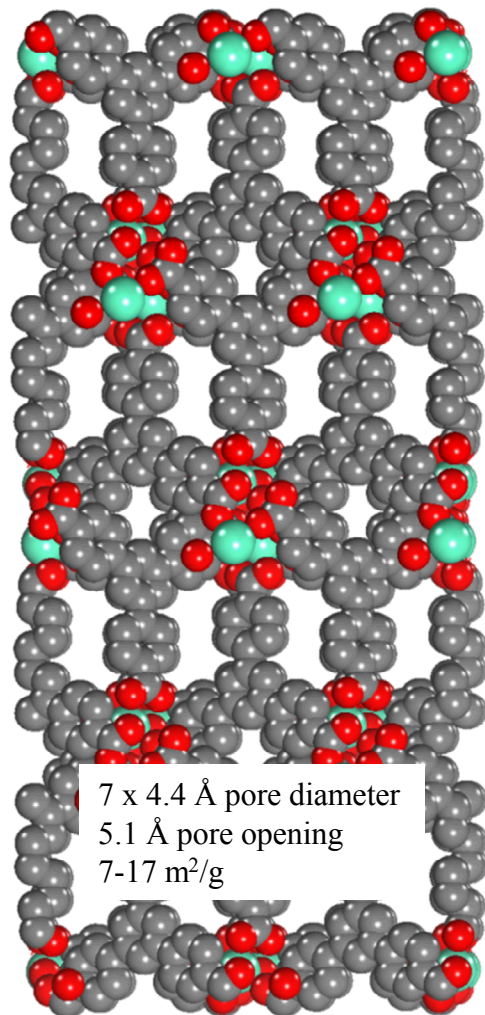


Distinct transition point temperature where the metal sites dependence on the O<sub>2</sub> and N<sub>2</sub> uptake is inverted

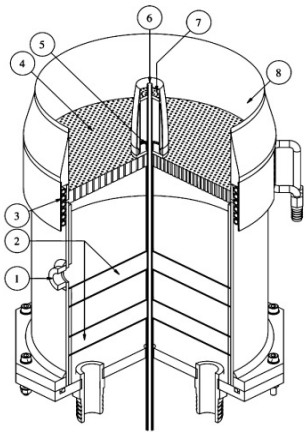
# SMOF-7: O<sub>2</sub> vs. N<sub>2</sub> Single Gas Sorption Isotherm, at 77K

D. Sava Gallis, T. M. Nenoff,  
US Patent Pending, 2014

## SMOF-7



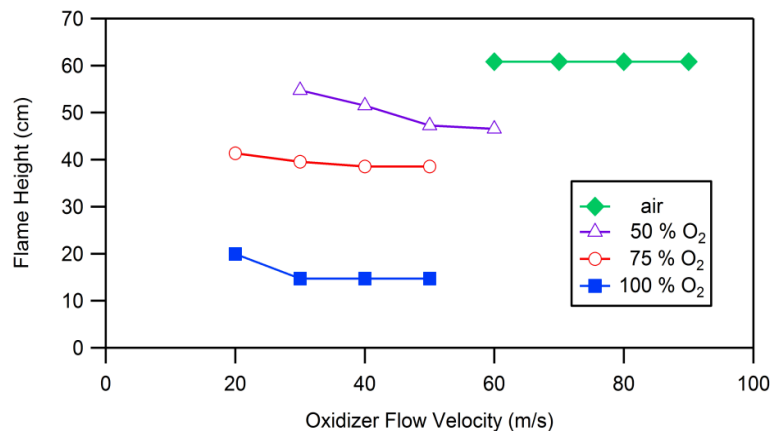
# Coupling of Burner design and Oxy-fuel Combustion to Radiant Heat Transfer



Balloon number	Description
1	Flashback over-pressure sensing port
2	Glass bead filled cavities
3	Cooling water coil
4	Coflow perforated baseplate
5	Pilot mixture feed exit
6	Central jet exit
7	Pilot perforated baseplate
8	Coflow collar



- Newly designed and constructed burner with smaller diameter inside tube for  $\text{CH}_4$  into oxidizer jet flow
- Allows either premixed or non-premixed methane-air flame
- Designed specifically for pure  $\text{O}_2$  and enriched  $\text{O}_2$  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.

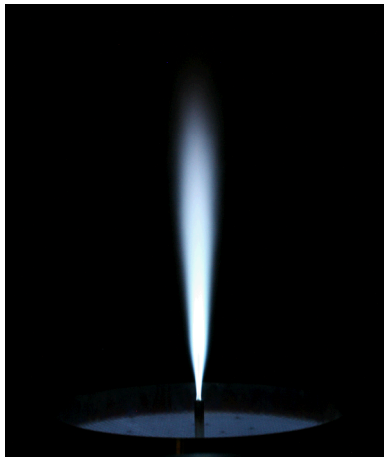
The volumetric flow of methane is always equal to  $\frac{1}{2}$  the flow of oxygen, to maintain stoichiometric combustion conditions.



# Preliminary Investigation of Oxygen-Enriched NG Flames

Performed preliminary testing performed with oxidizers of pure oxygen and with 50% O<sub>2</sub> in N<sub>2</sub>, using an overall equivalence ratio of 1, with a constant methane flow

- Velocity (Re) of oxidizer flow is 50% lower when using pure O<sub>2</sub>, making for taller flame (slower mixing)
- Soot formation is enhanced when using pure O<sub>2</sub> (higher temperatures, slower mixing)



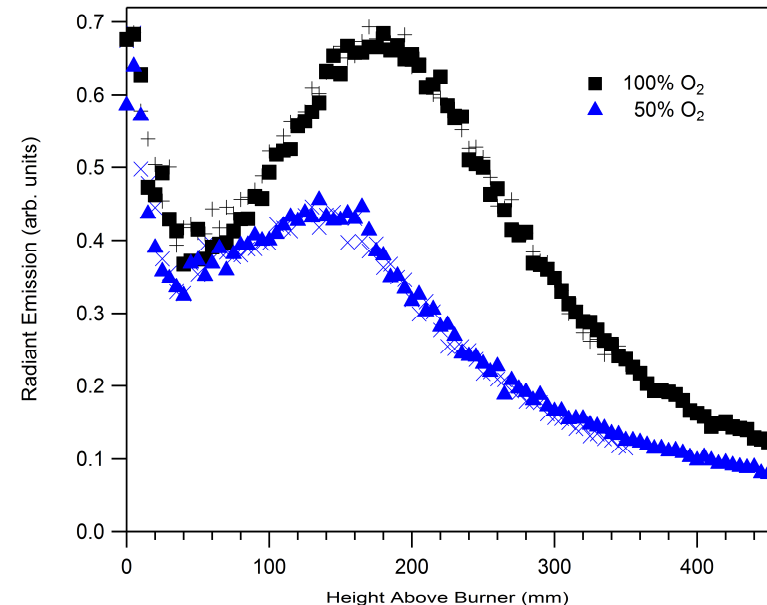
50% O<sub>2</sub> in N<sub>2</sub>



100% O<sub>2</sub>

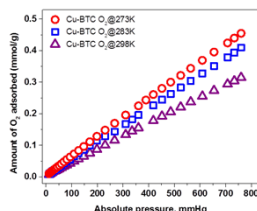
Radiant emission measurements have been performed along the flame centerline

- Data for 100% O<sub>2</sub> shows significantly more thermal radiation
- Flame temperatures are higher when using pure O<sub>2</sub> (more radiation from flame products)
- Some soot is formed in the 100% O<sub>2</sub> flame

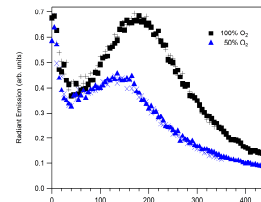
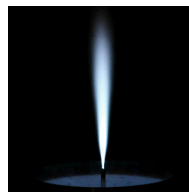


# Systems Analysis of MOF-based Air Separation

MOF adsorption  
isotherms ( $N_2$  &  $O_2$ )  
(from MOF team)



Optimal  $O_2:N_2$  ratio  
for combustion  
(from combustion team)



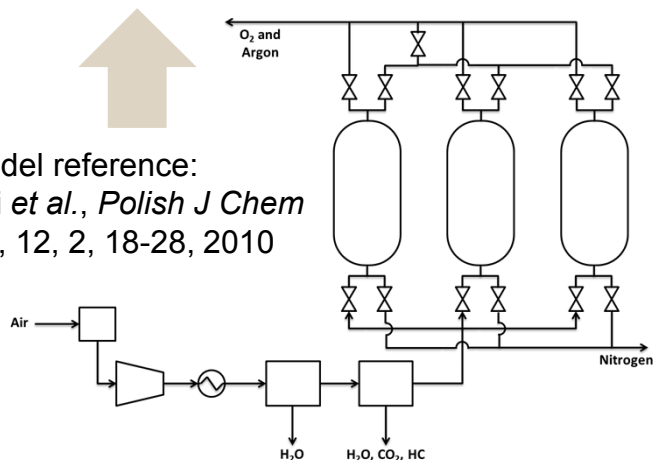
*Can MOF-based  
PSA reduce energy  
consumption by 5%  
vs. conventional PSA  
air separation?*

Construct and  
validate model of  
PSA process

Adjust PSA model  
parameters to yield  
desired  $O_2:N_2$  ratio

Estimate energy  
consumption based  
on PSA parameters

PSA model reference:  
Beeyani *et al.*, *Polish J Chem  
Technol*, 12, 2, 18-28, 2010



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