SAND2015-7200C

Exceptional service in the national interest

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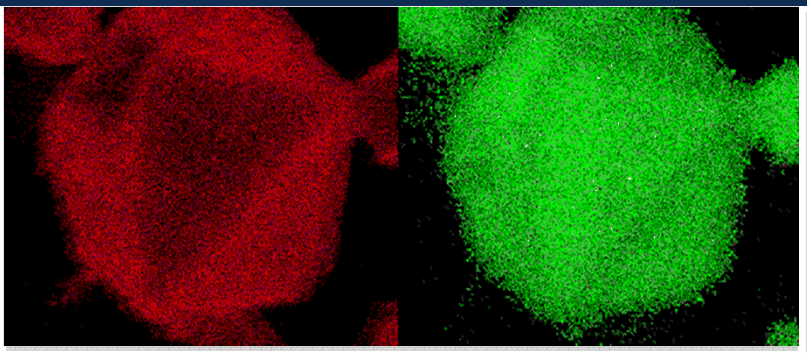

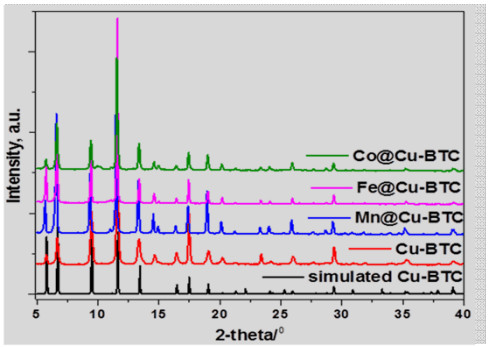

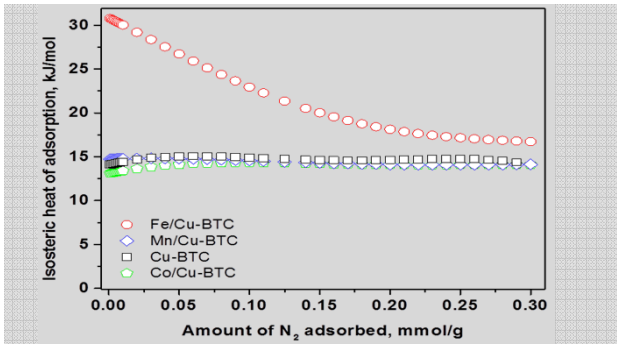

Light Gas Separations with MOFs via Predictive Modeling and Tuned Synthesis

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, USA

6th Microporous and Mesoporous Materials Symposium
Sunset-Black Sea, Bulgaria
September 8, 2015

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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

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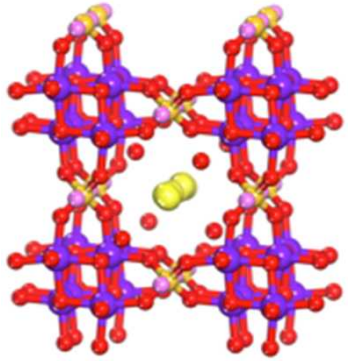
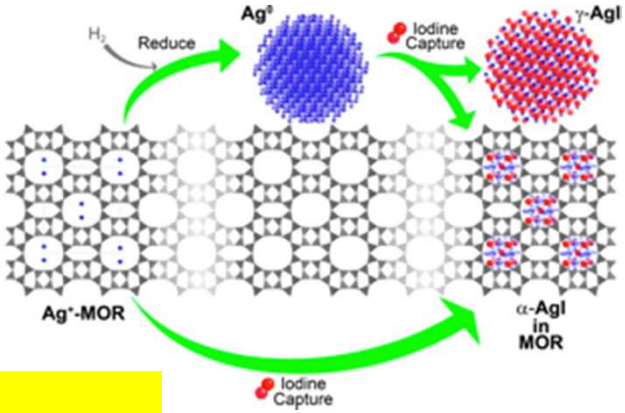
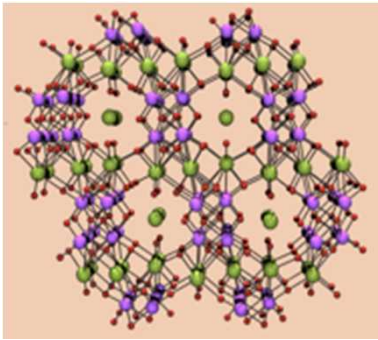


R&D100 1996
JACerS, 2009, *92(9)*, 2144
JACerS, 2011, *94(9)*, 3053
Solvent Extr. & Ion Exch, 2012, *30*, 33

CST, Cs^+ removal from water to Pollucite Waste Form
US Patents *6,479,427; 6,110,378*



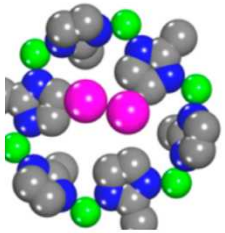
Ag-MOR
I_2(g) capture & mechanisms
JACS, 2010, *132*(26), 8897
J Phys Chem Letters, 2011, *2*, 2742

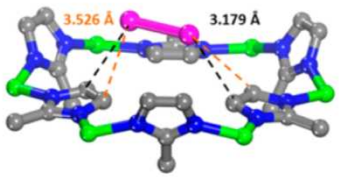


Fundamental Research to Applied to Commercial Products
Design the Separation Material To Develop the Waste Form

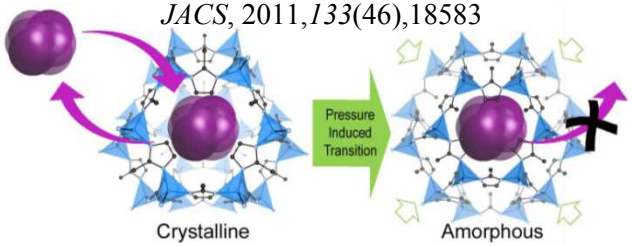
I_2/ZIF-8, Isolation to Waste Form
JACS, 2011,*133(32)*,12398
US Patent filed 2012
JACS 2013, *135*, 16256

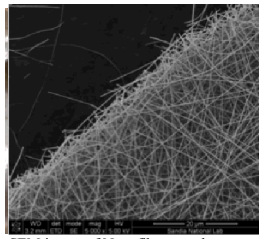
SOMS, Sr^{2+} getter, 1-step to Perovksite WF
JACS, 2002,*124(3)*, 1704
US Patent *7,122,164*



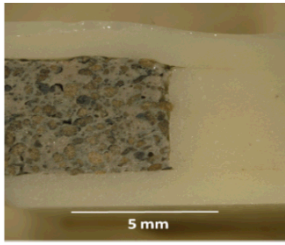


MOF Amorphization for Gas Storage
JACS, 2011,*133*(46),18583

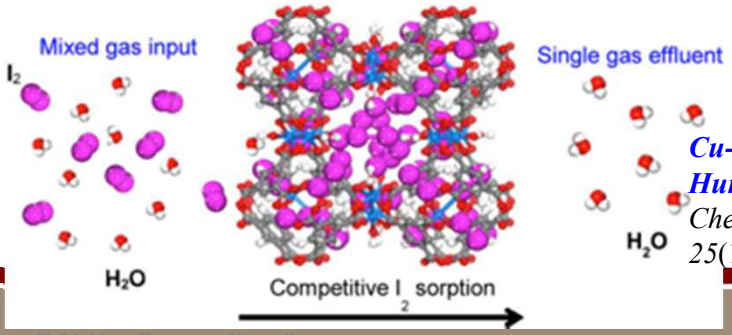




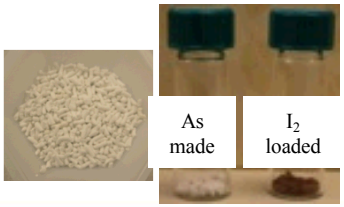
Nanoporous Nanofibers Volatile Gas Removal
US Patent Application,2011



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



Cu-BTC: I_2 from Humid Gas Stream
Chem. Mater. 2013, *25*(13), 2591



Binder Free MOF Pelletization
US Patent Pending 2014

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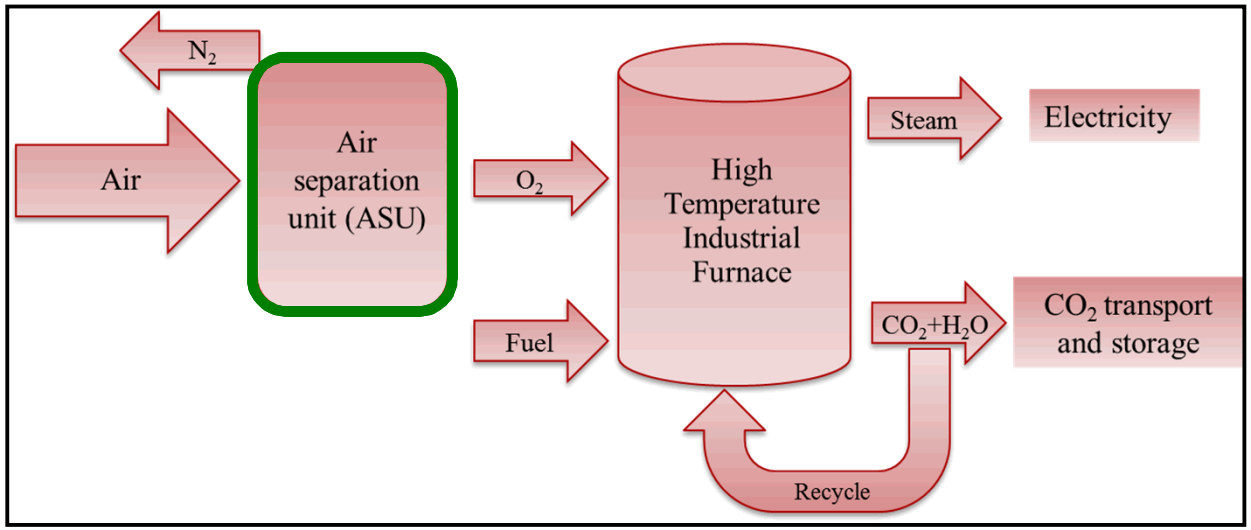
O_2/N_2 air separations with MOFs to Increase the Efficiency of the *ASU*



- 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

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

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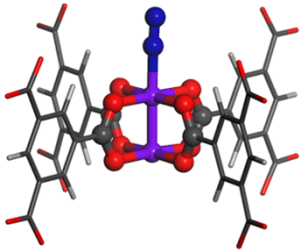
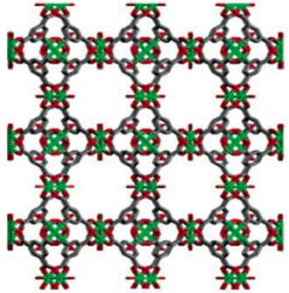
Predictive molecular modeling

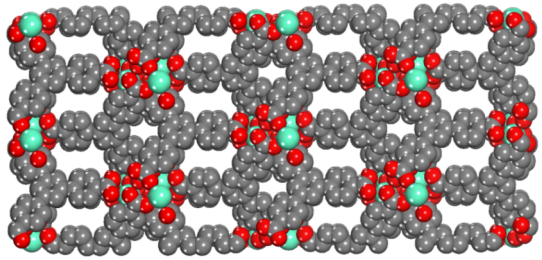
Predictive molecular modeling designed to *measure the binding energy for O_2 and N_2* on coordinatively unsaturated metal sites in MOFs



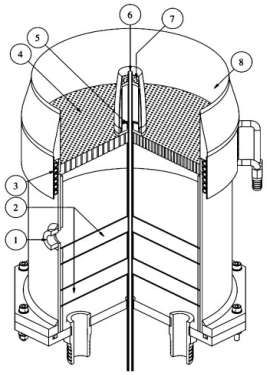
Materials development

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



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

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

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

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DFT Simulations Provide Molecular-level Details
Metal-O_2 and Metal-N_2 Binding Energies and Geometries

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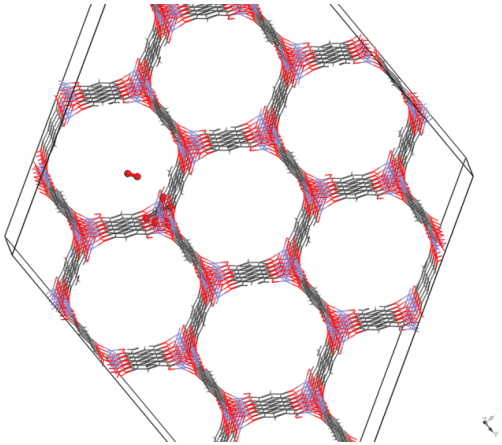
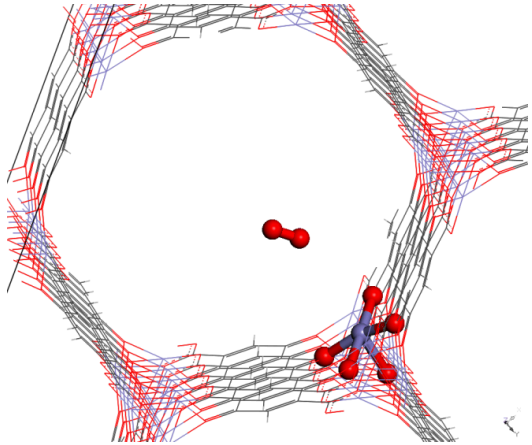
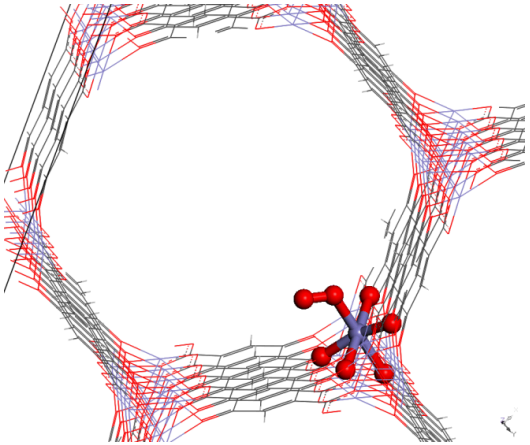
- MOFs with coordinatively unsaturated metal centers are promising materials for O_2/N_2 separations
- Two prototypical MOFs from this category, $Cr_2(BTC)_3$ (*J. Am. Chem. Soc.* **2010**, *132*, 7856–7857) and $Fe_2(DOBDC)$ (*J. Am. Chem. Soc.* **2011,** *133*, 14814-14822) both show preferential adsorption of O_2 over N_2
- 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_2 and bent and linear geometries for N_2 were evaluated
- Static binding energies for O_2 and N_2 at 0 K



MOF with O_2 in pore



O_2 ready to bind to metal



O_2 bound to metal

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

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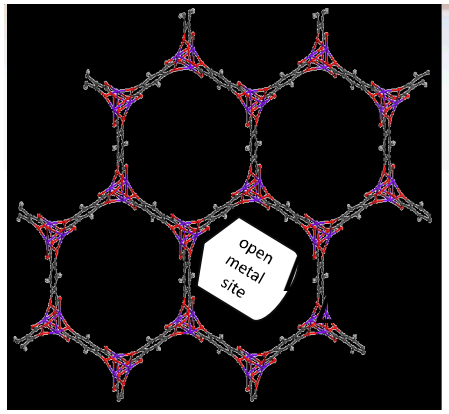
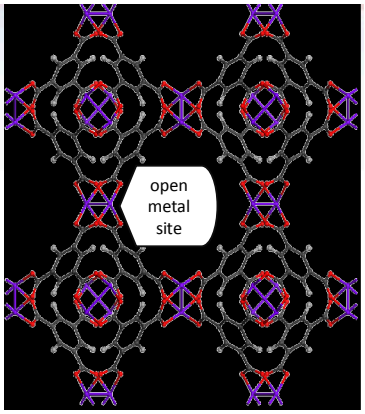


M_2(dobdc)



M_3(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 (ΔE_{O2}, ΔE_{N2})** were calculated by

$$\Delta E_{O2} = E_{MOF+O2} - E_{MOF} - E_{O2}$$

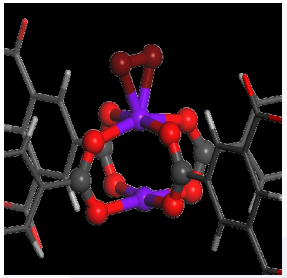
The **differences in binding energies ($\Delta\Delta$ E)** for oxygen and nitrogen were calculated by

$$\Delta\Delta E = - (\Delta E_{O2} - dE_{N2})$$

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

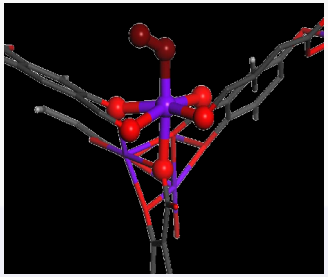
Attention Paid to Bonding Geometries

Side-on bonding
∡M-X-X 67° - 71°



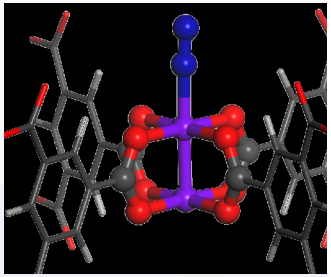
$Cr_3(btc)_2(O_2)$

Bent bonding
∡M-X-X 116° - 159°



$Mn_2(dobdc)(O_2)$

Linear bonding
∡M-X-X 165° - 179°



$Fe_3(btc)_2(N_2)$

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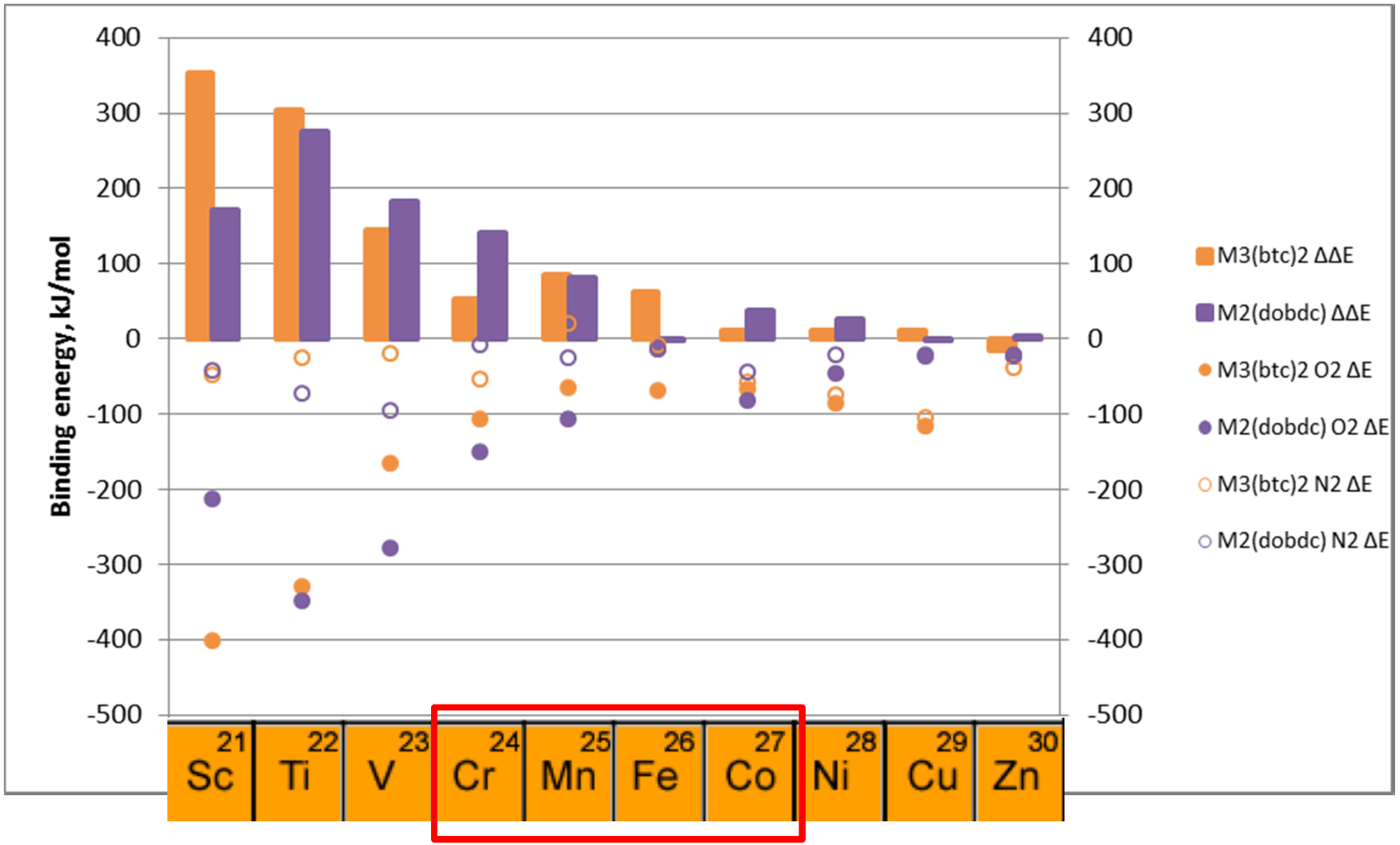
O_2 and N_2 binding energies trends across the first row transition metal series



Parkes, M.; Sava Gallis, D. F.; Greathouse, J.A.; Nenoff, T.M. *J. Phys Chem C*, **2015**, *119*, 6556.

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

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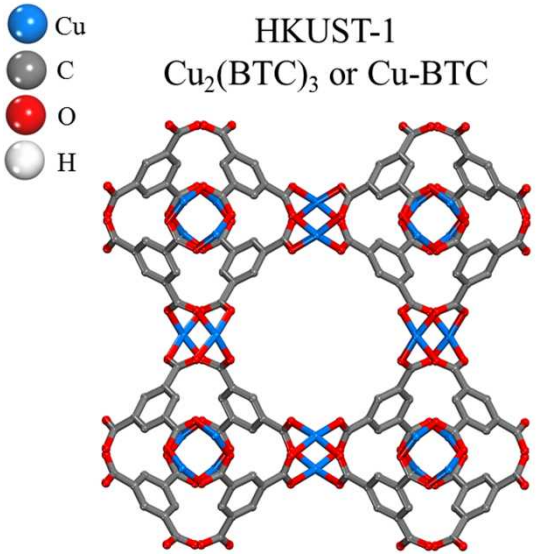
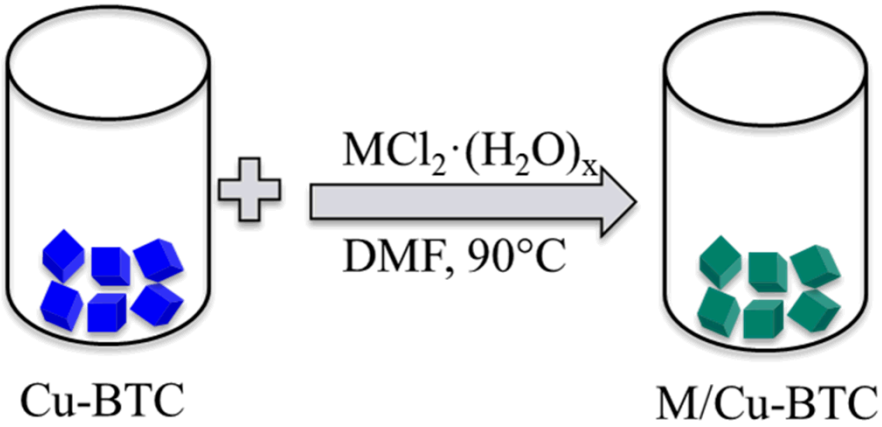
Need/Desire To Retain Porosity of MOF For Studies of Metal-O_2 Bonding Effects

- 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^2/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**

Sava Gallis, D. F.; Parkes, M.; Greathouse, J.A.; Nenoff, T.M. *Chem. Mater.*, **2015**, *27*(6), 2018.

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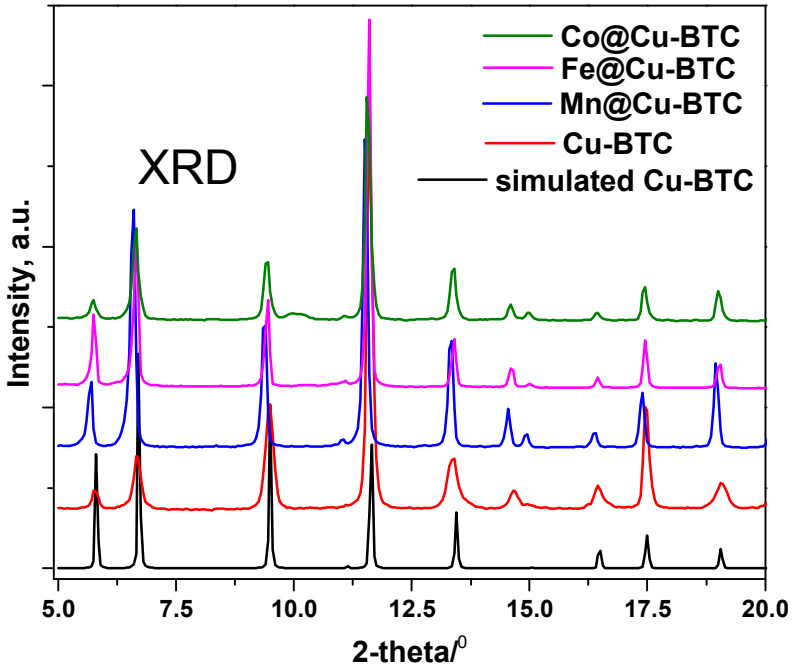
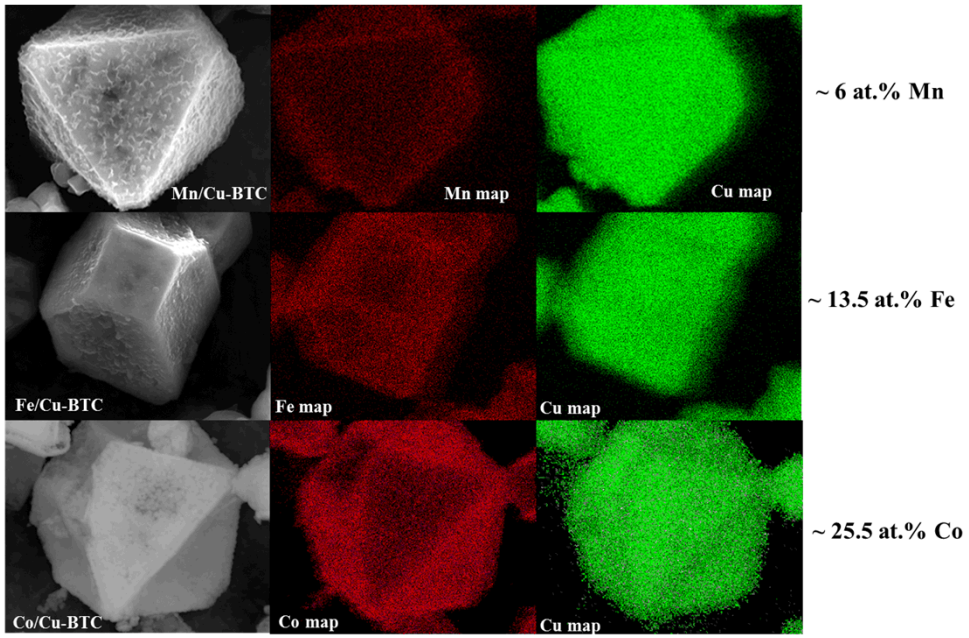
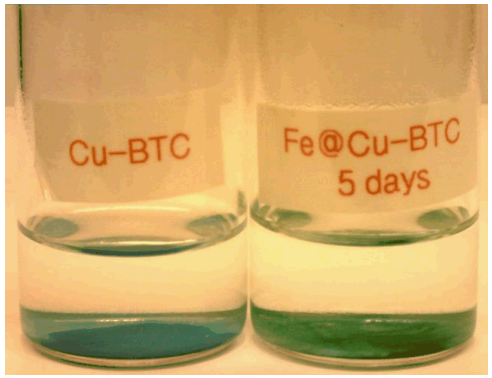
Confirmation of In-Framework Metal Substitution – Unit Cell Expansion & Elemental Mapping



SEM-EDS



	Expansion (Å)	M-O average bond length (Å)
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



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Excellent DFT and Experiment Correlation at Low Temperature and Low Pressure

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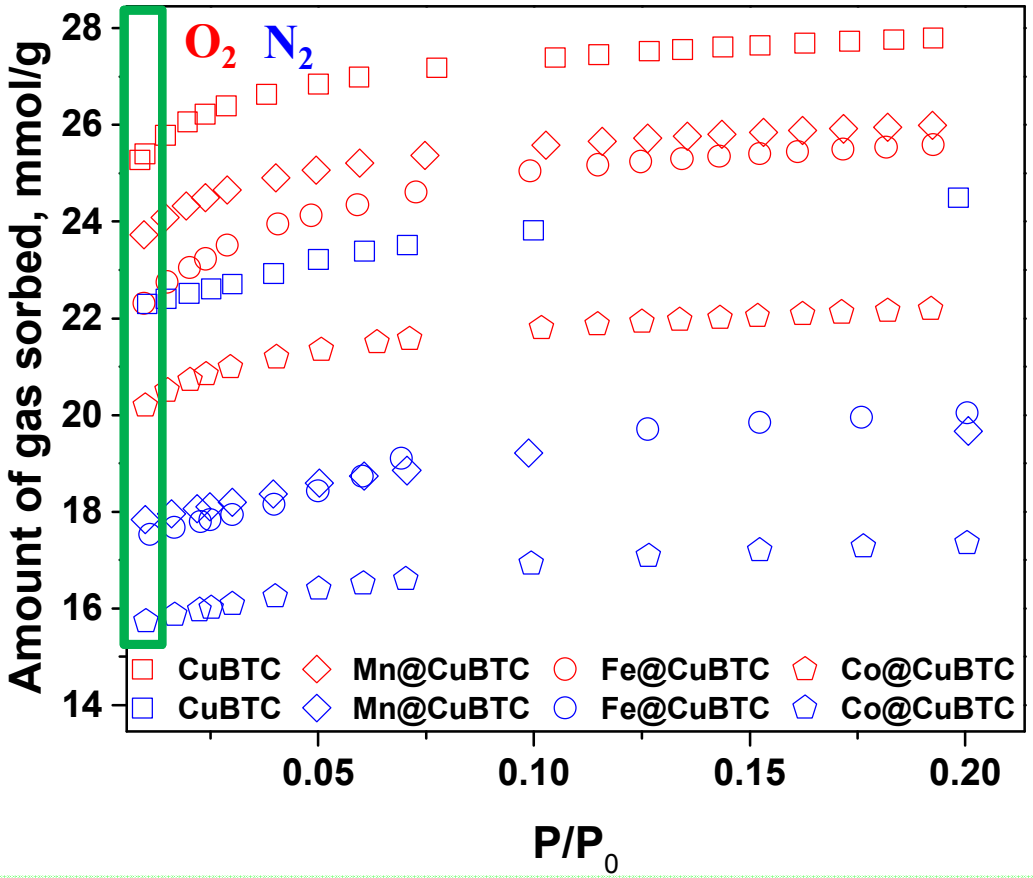
Cu>Mn>Fe>Co (DFT)
Cu>Mn>Fe>Co (exp)

	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 (~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

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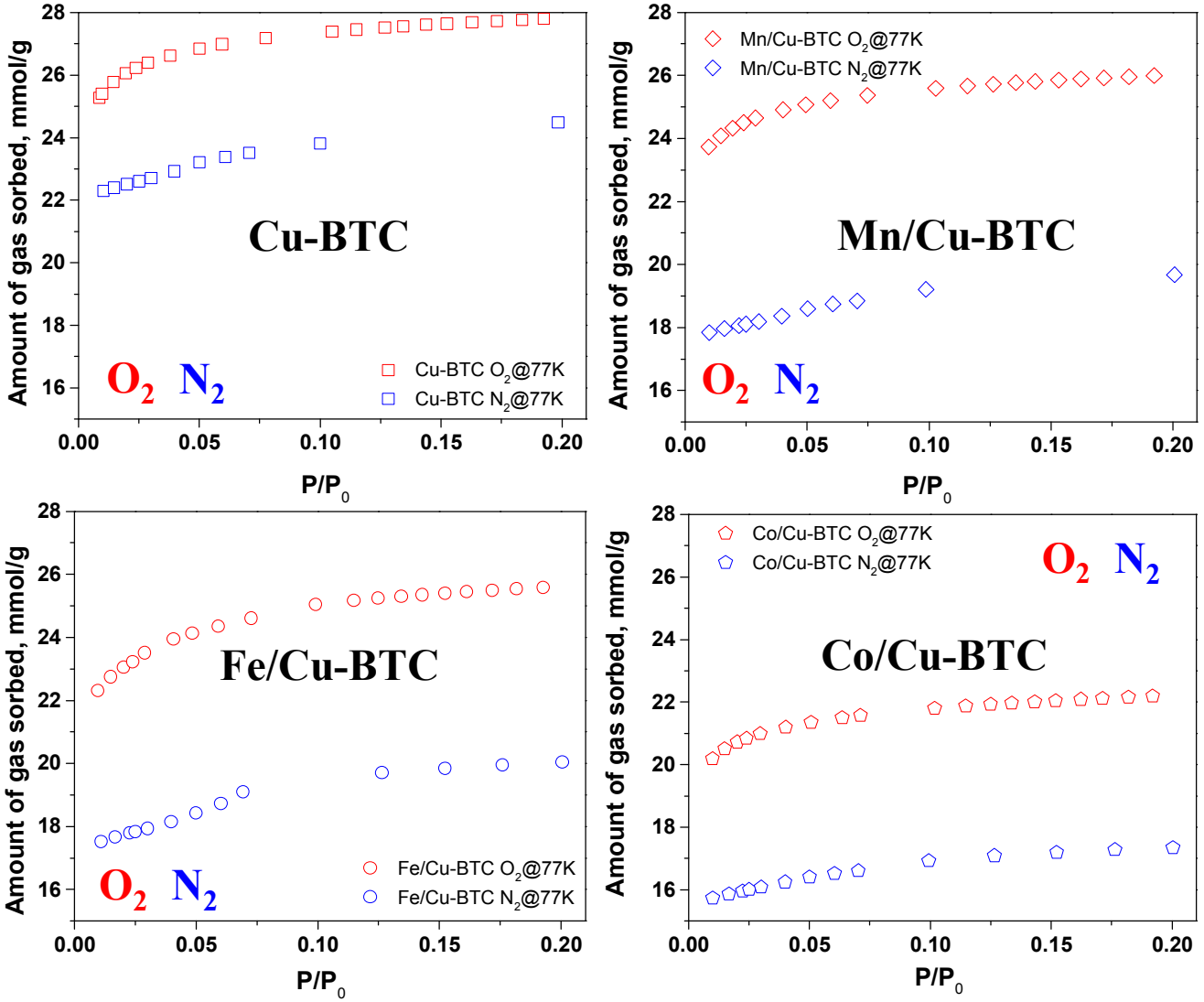
77 K: All Samples have ***Higher*** O_2 Loadings over N_2



The highest O_2/N_2 selectivity is observed for the Mn/Cu-BTC sample

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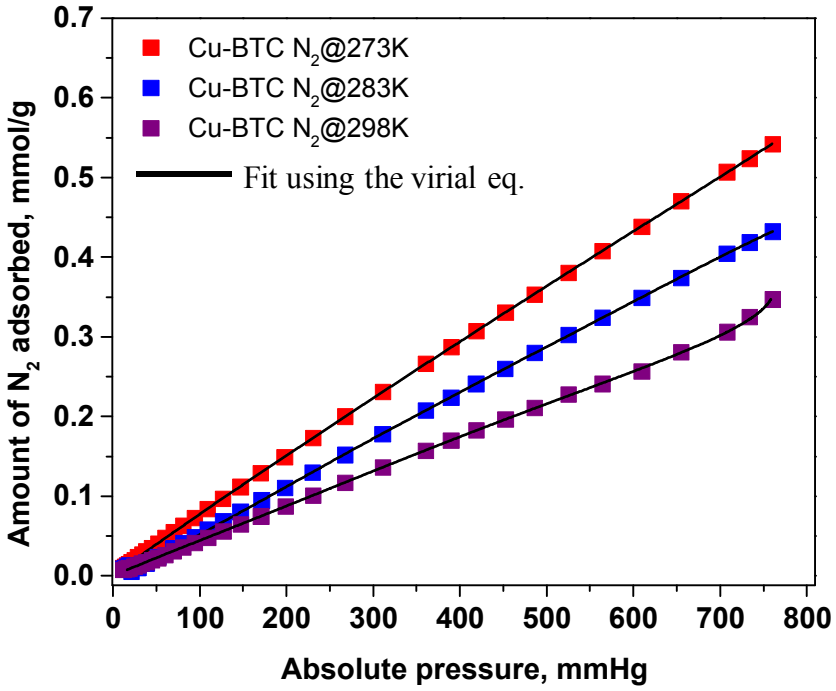
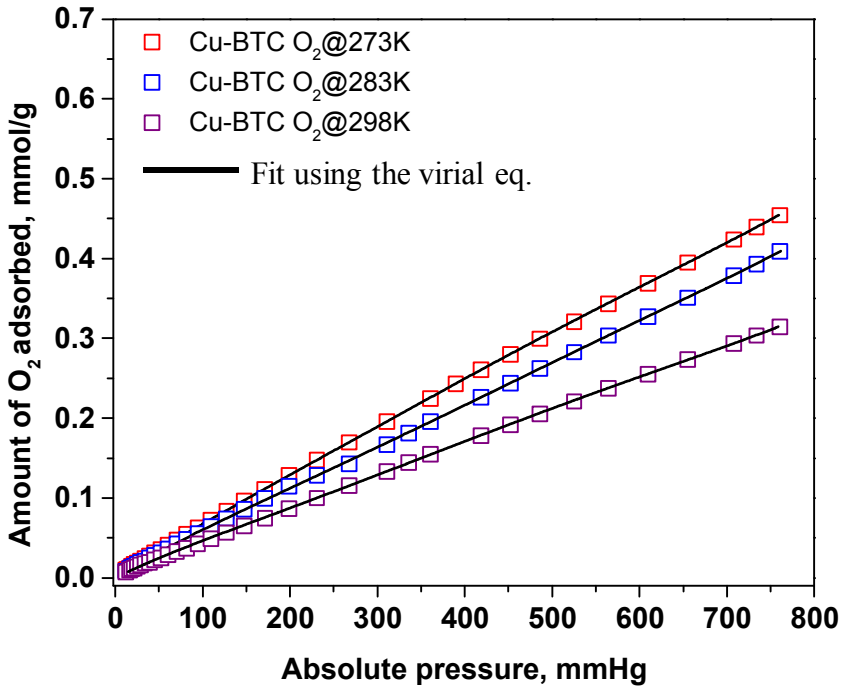
273-298 K: As Temperature Increases, O_2 Loadings Decrease Relative to N_2

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

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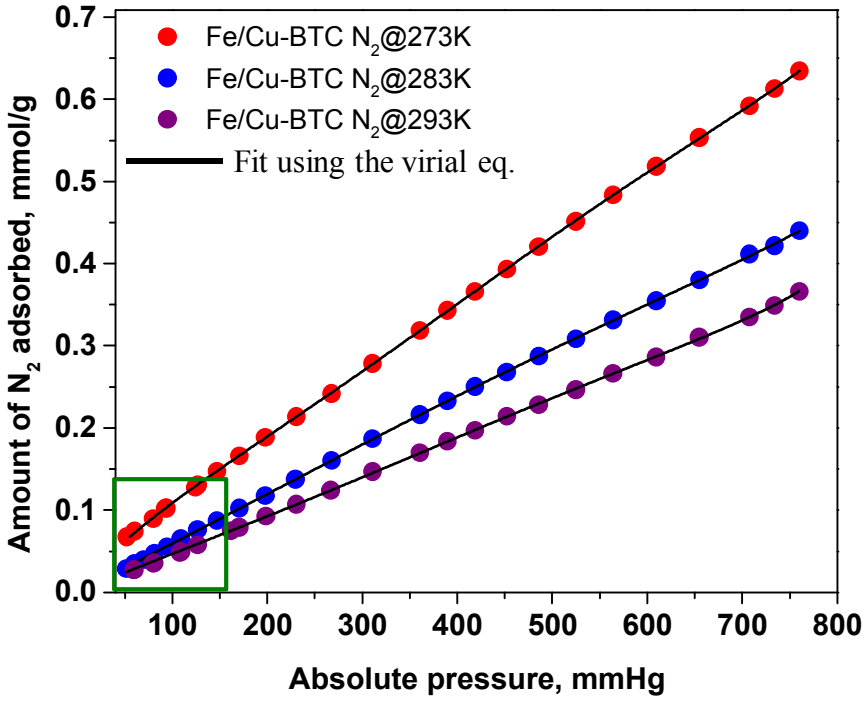
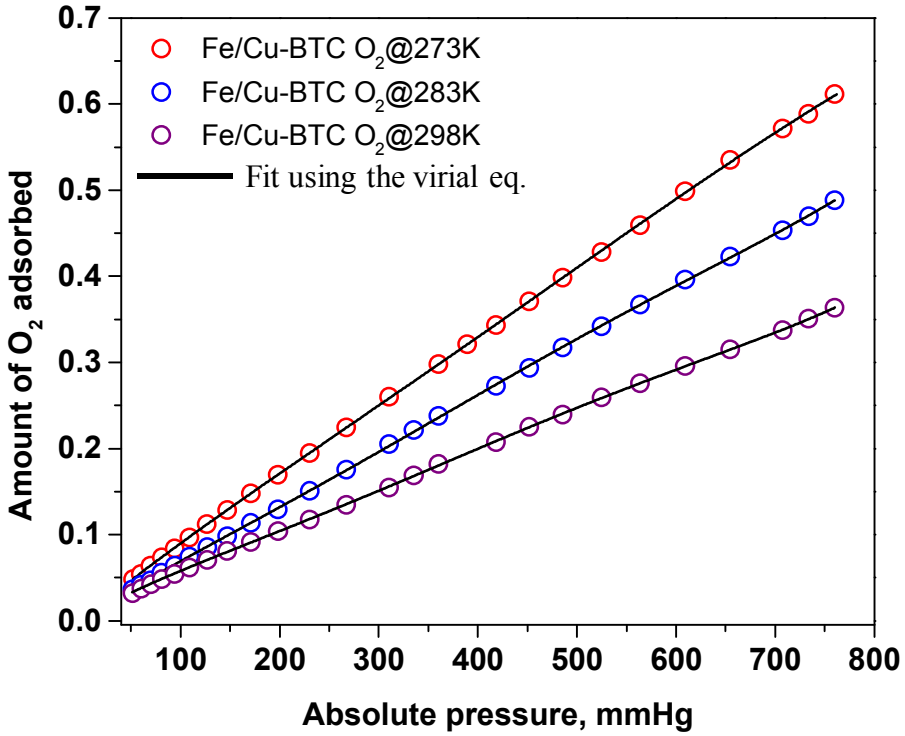
N_2@273 K in Fe/Cu-BTC Trend Deviation: Slightly Higher N_2 Uptake at Lowest Loading Levels (at lowest pressures)





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

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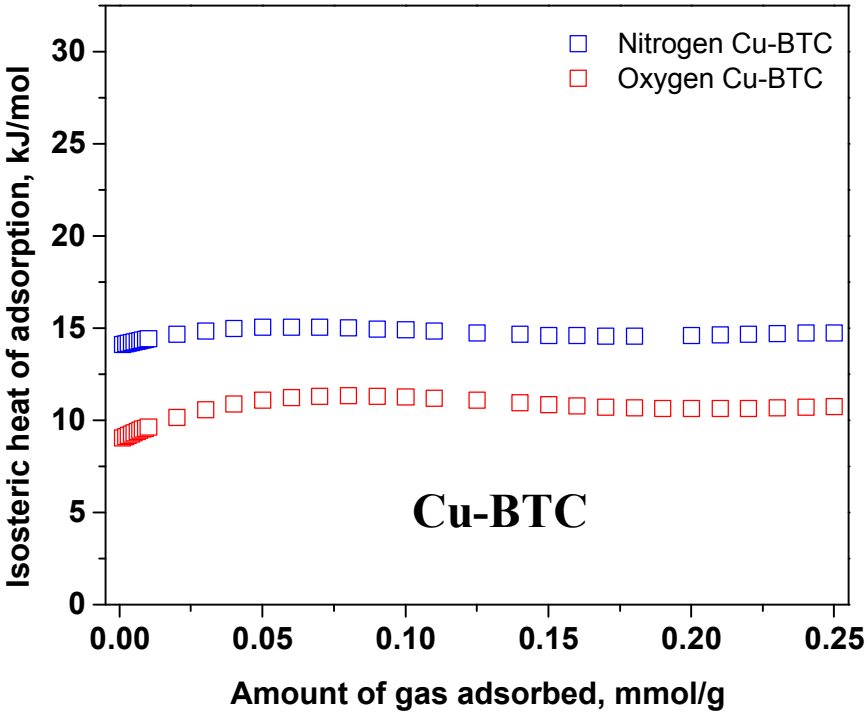
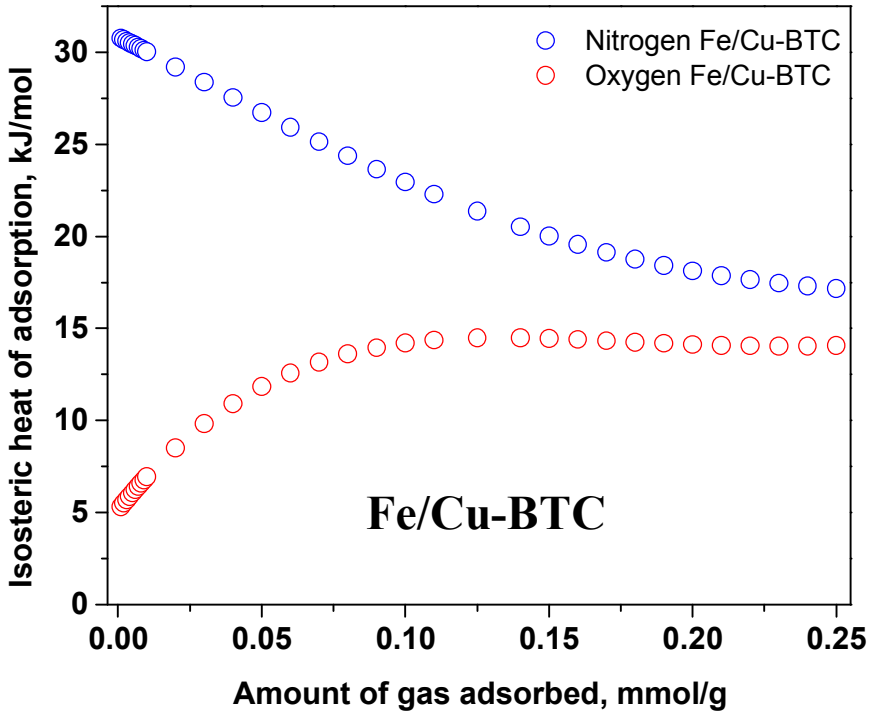
Isosteric Heats of Adsorption for O_2 (red) and N_2 (blue) Comparison of Cu-BTC vs Fe/Cu-BTC Data





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?

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Transition to Quantum Calculations to Estimate Metal-Oxygen Binding Energy

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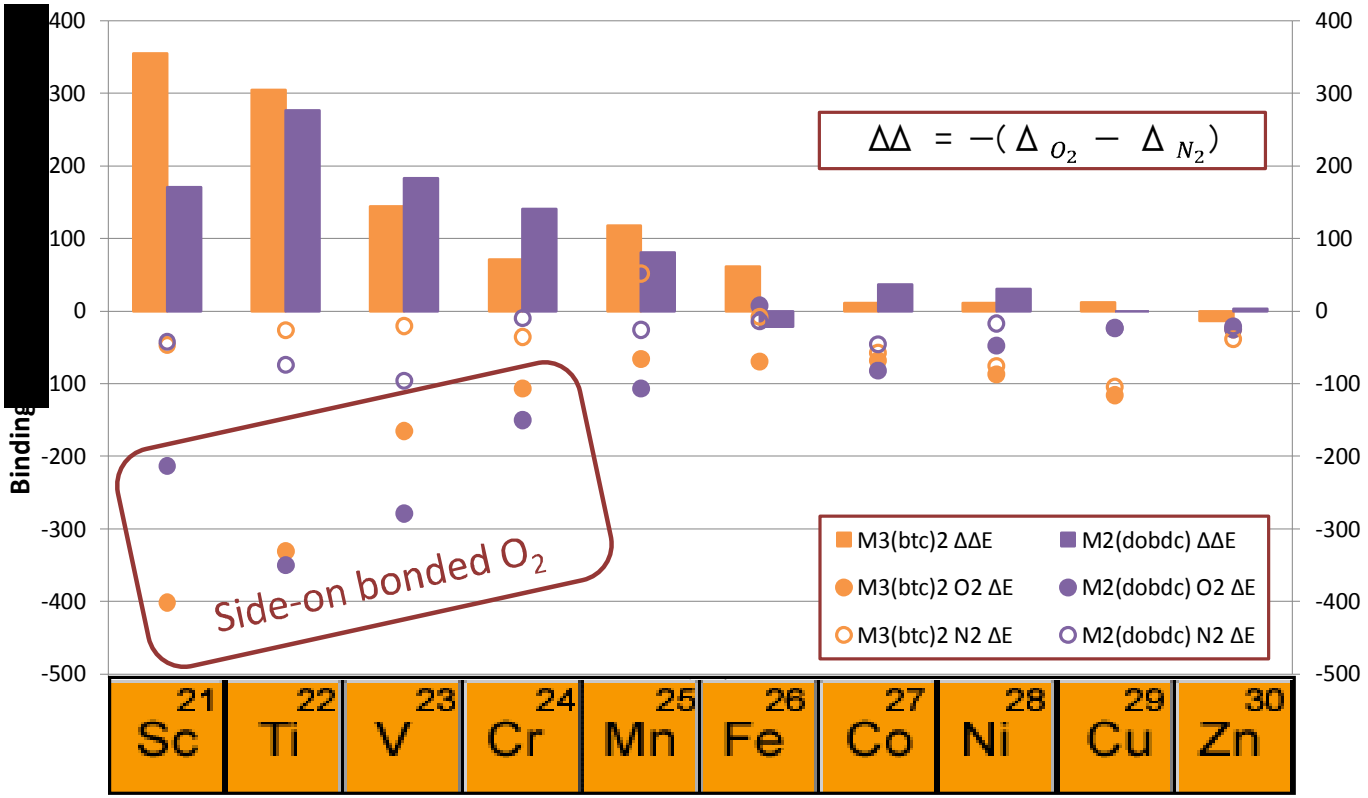
Binding Energy Calculated as a Function of Metal Site



Parkes, M.; Sava Gallis, D. F.; Greathouse, J.A.; Nenoff, T.M.
"Screening MOFs for O_2/N_2 Separations: Role of MOF Metal Center",
J. Phys Chem C, **2015**, *119*, 6556.

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

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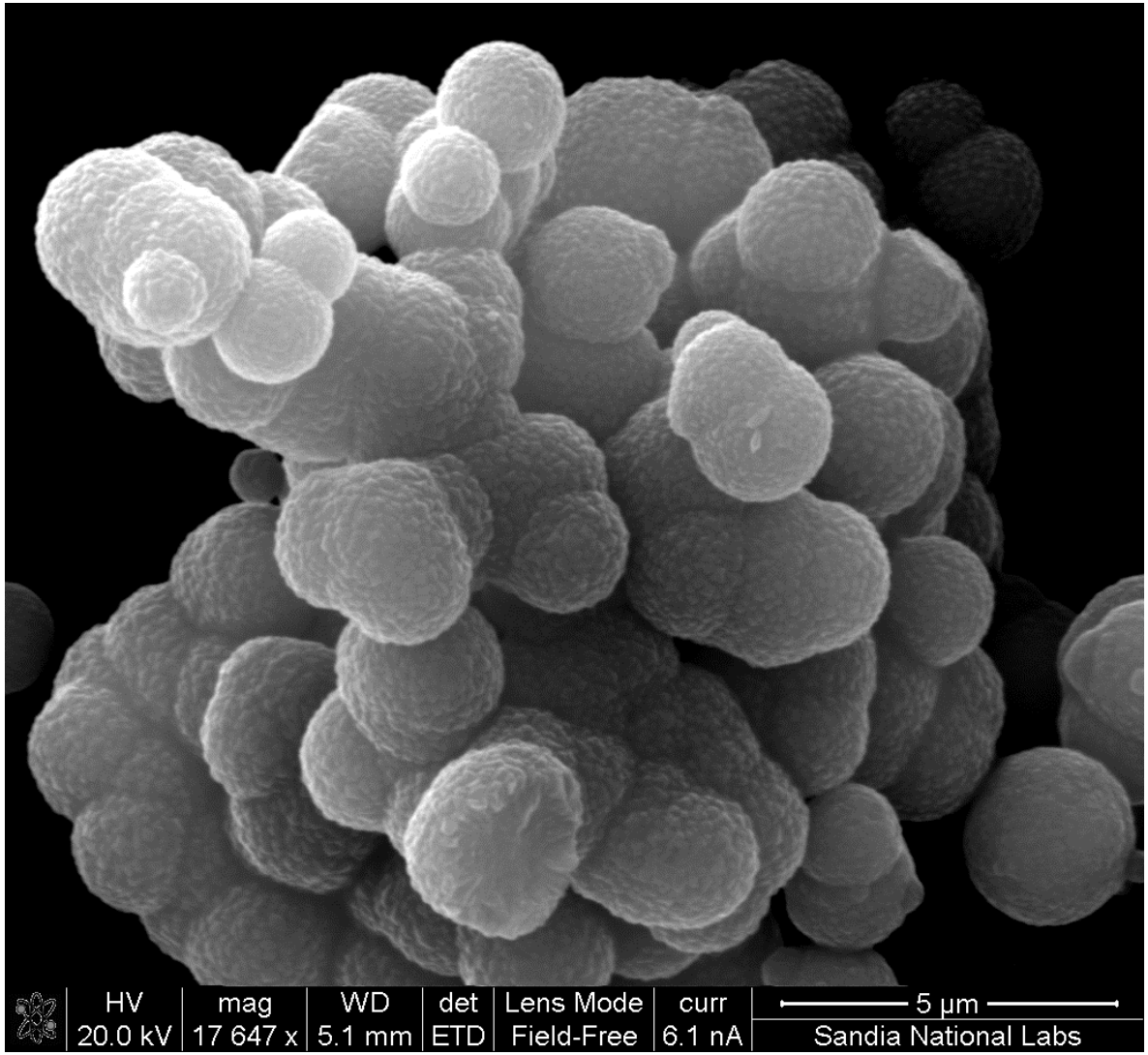
Modeling Designed / Inspired MOF Synthesis

SMOF-8



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

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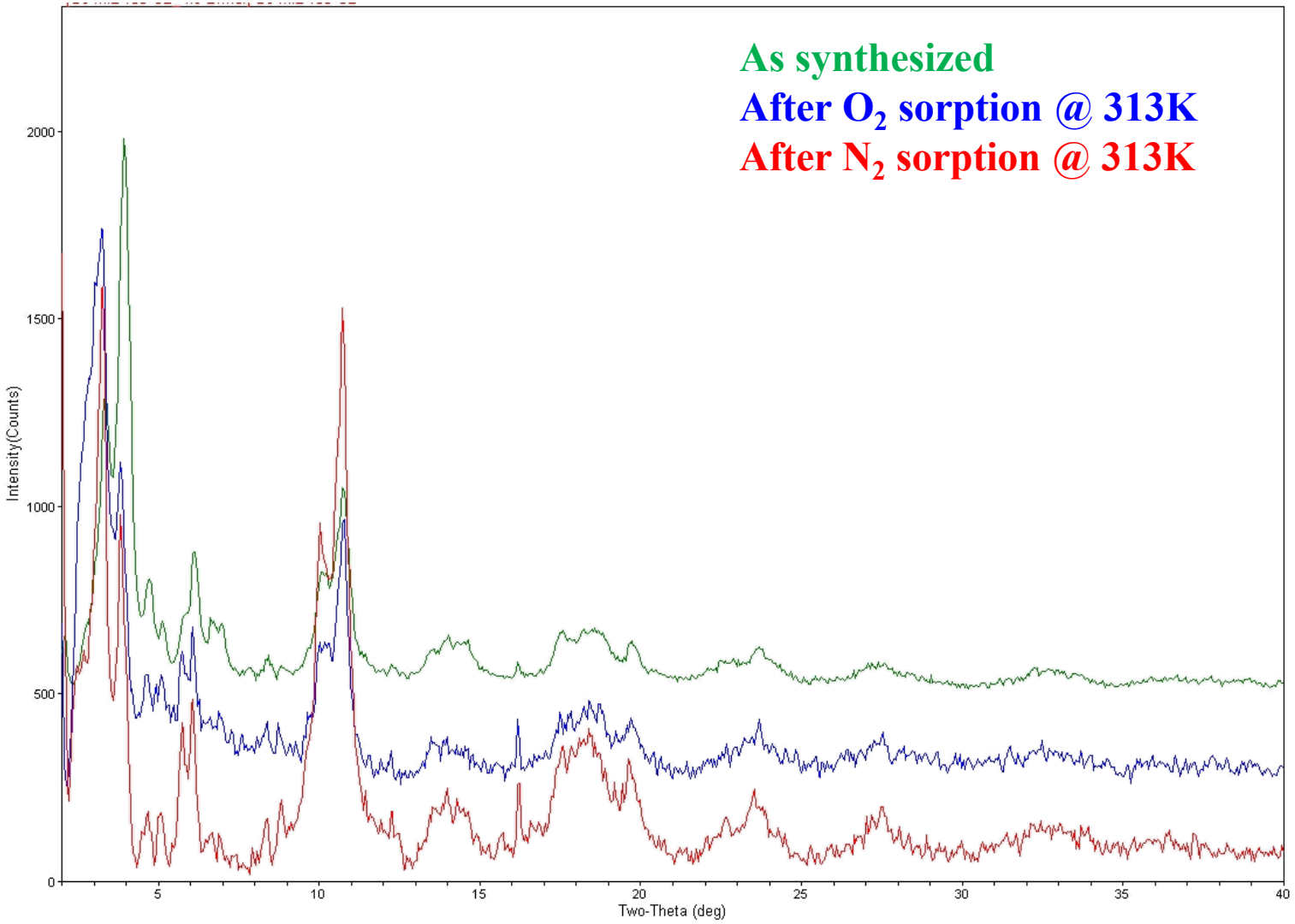

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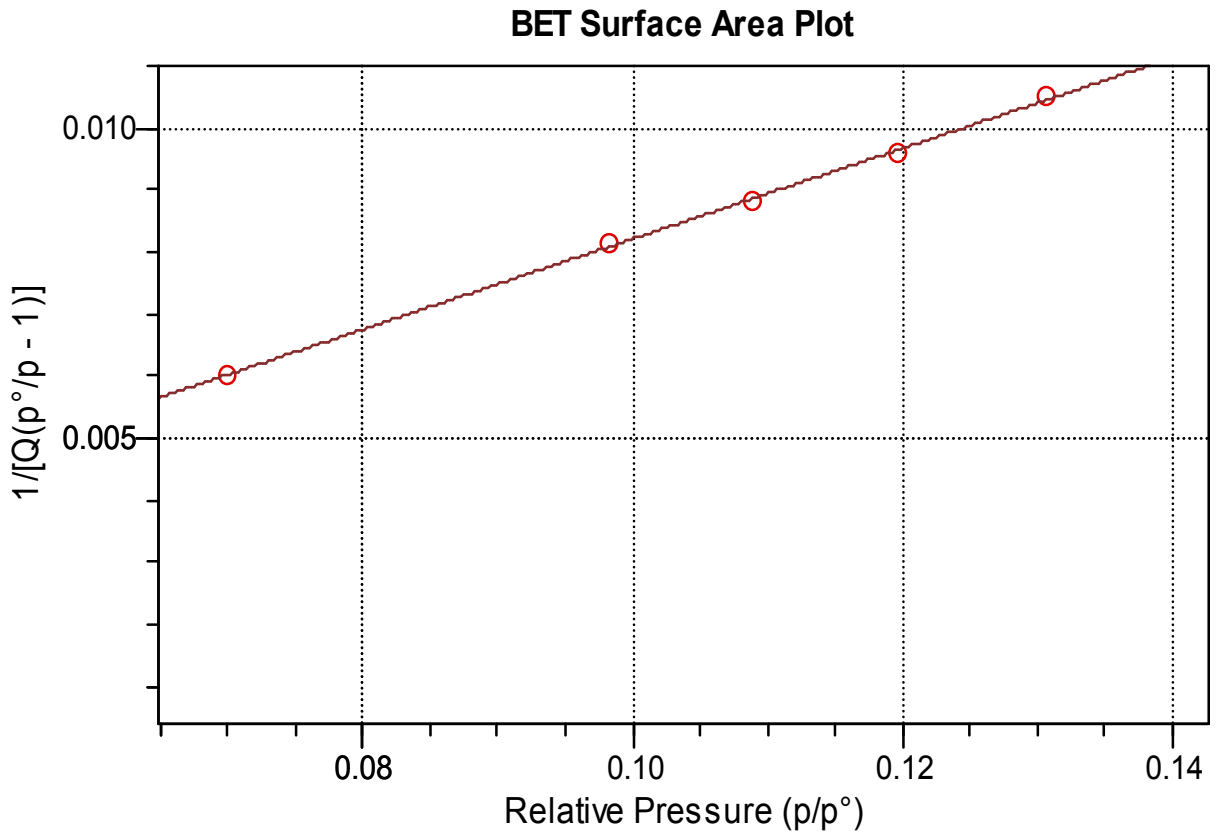
SMOF-8: High Surface Area with Accessible Metal Centers



BET surface area: 1321.7194 ± 24.4623 m²/g

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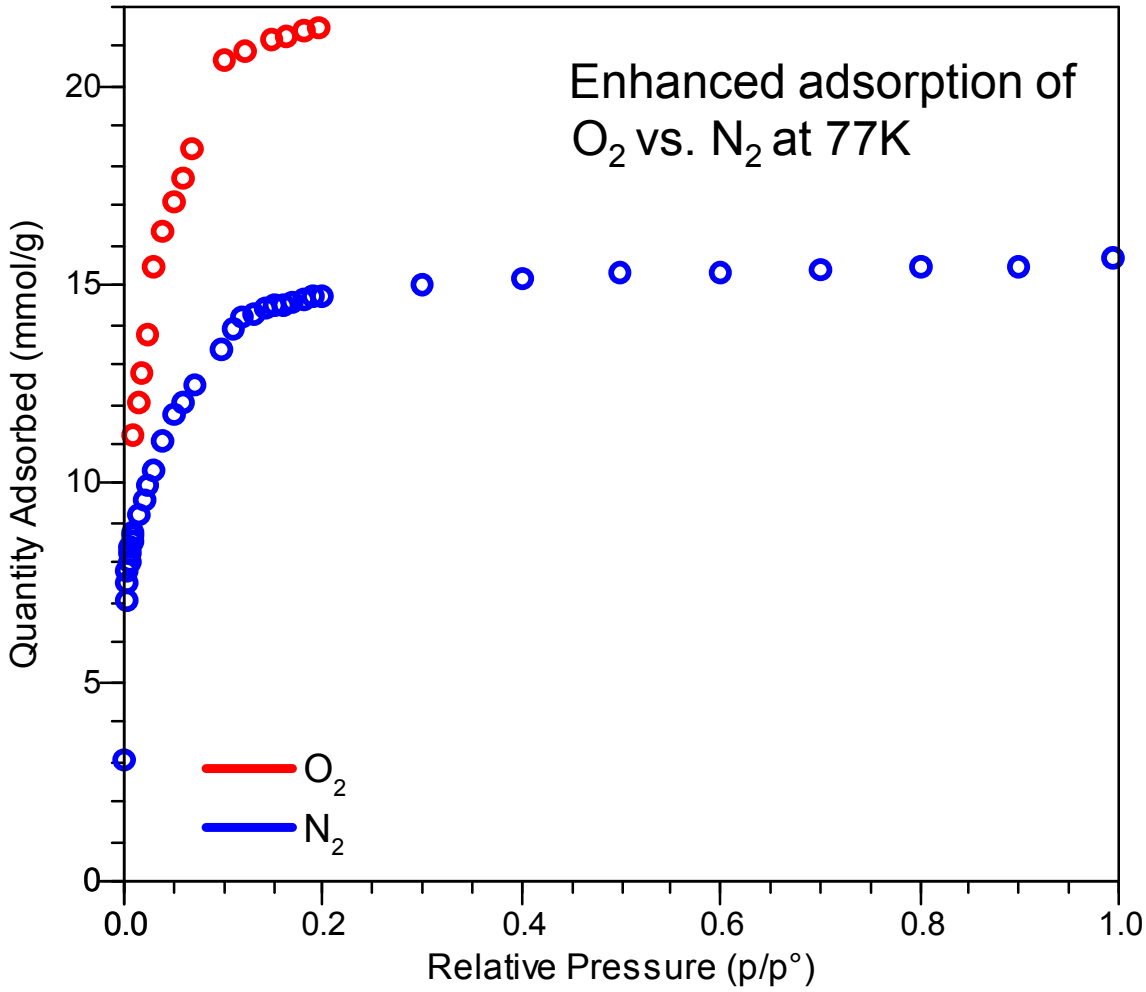
SMOF-8: Metal-Center has a role at 77K



How does SMOF-8 behave at more realistic operational temperatures?

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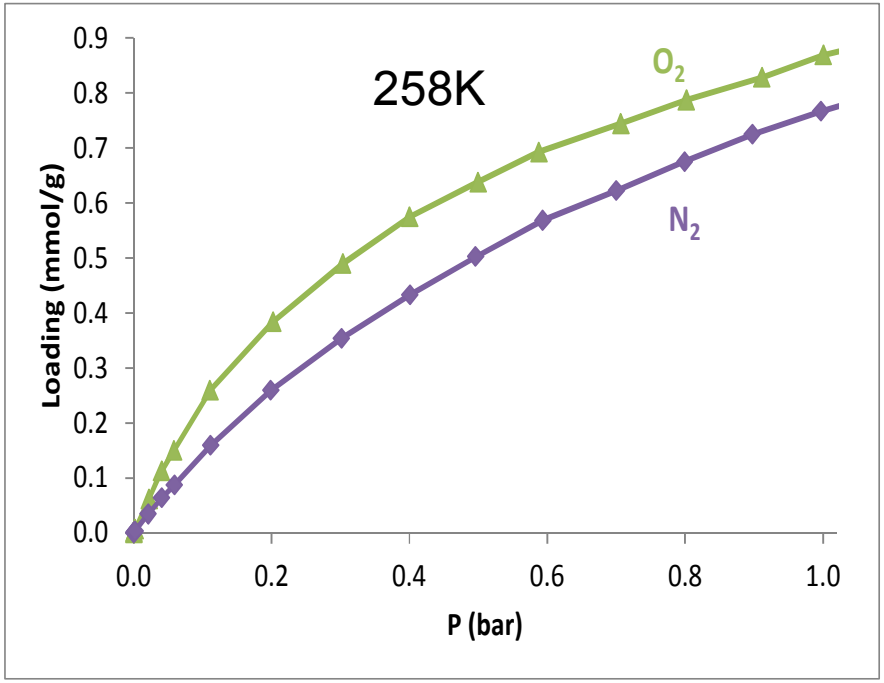
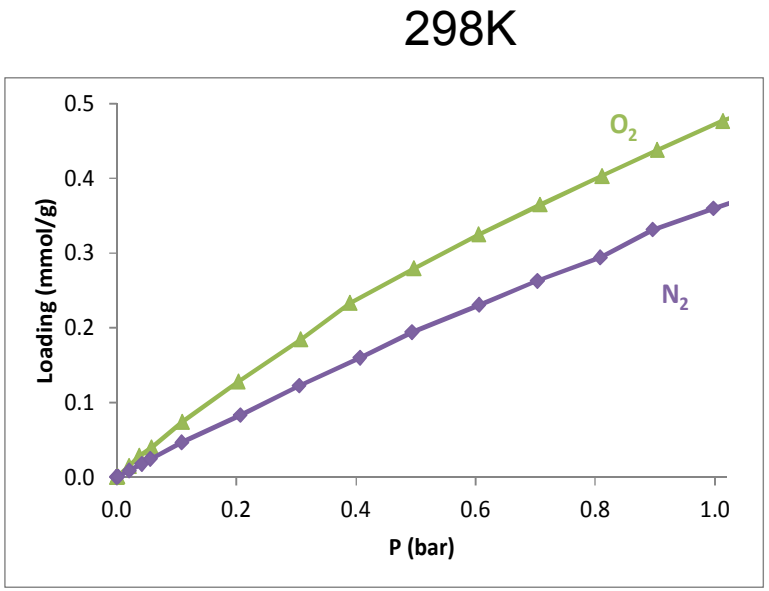
SMOF-8: GCMC Isotherm Calculations at 258K and 298K

- **Grand Canonical Monte Carlo (GCMC) Simulations**
- Pure gas (N_2 or O_2) adsorption over pressure range 0 - 1 bar.
- Temperature range matched with experiment: 258 K, 298 K, 313 K.
- Grand canonical ensemble (constant chemical potential, temperature, volume) using the Towhee code (Martin, *Mol. Sim*. **2013**, 39, 1212).
- Gas-gas and MOF-gas interaction energies include van der Waals and electrostatic interactions.
- Framework atoms kept at their crystallographic coordinates.





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

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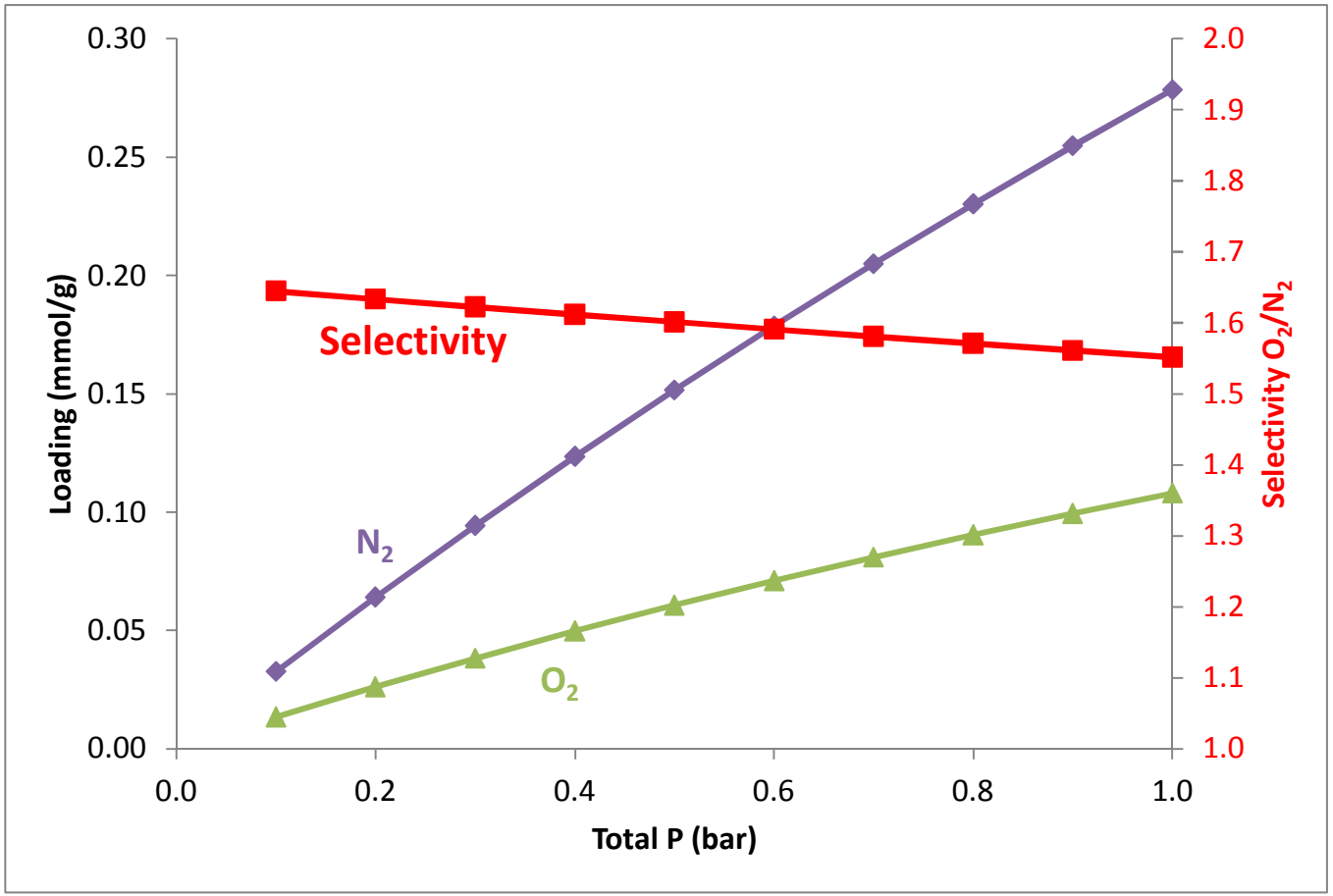
Simulations of Competitive Gas Adsorption: based on GCMC data, 298K



Ideal Adsorbed Solution Theory (IAST) used to calculate mixture adsorption and O_2/N_2 selectivity for **20:80 mixture (O_2:N_2)**.

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SMOF-8: Enhanced Quantity of O_2 vs N_2 Adsorbed over Wide Temperature Range (at least to 313K)

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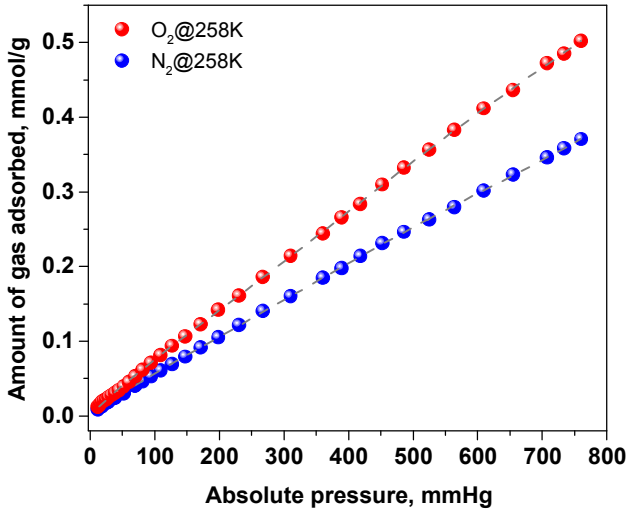
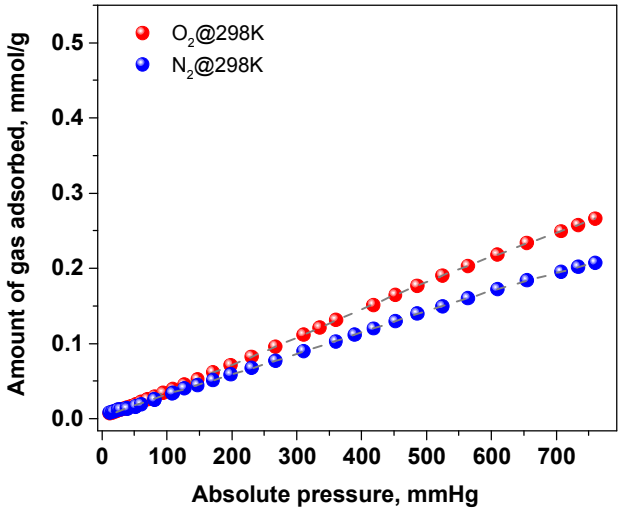
Fit using the virial eq.

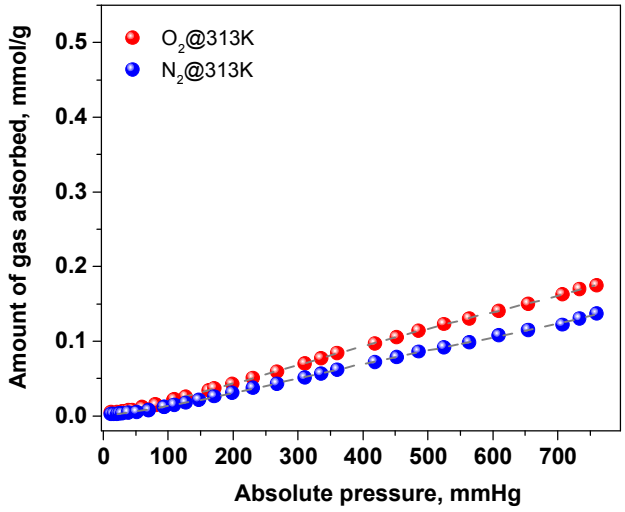
SMOF-8
O_2 vs. N_2 @**258K**



SMOF-8
O_2 vs. N_2 @**298K**



SMOF-8
O_2 vs. N_2 @**313K**



Isotherm trends mimic those predicted by GCMC

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SMOF-8: Enhanced Quantity of O_2 vs N_2 Adsorbed over Wide Temperature Range (at least to 313K)

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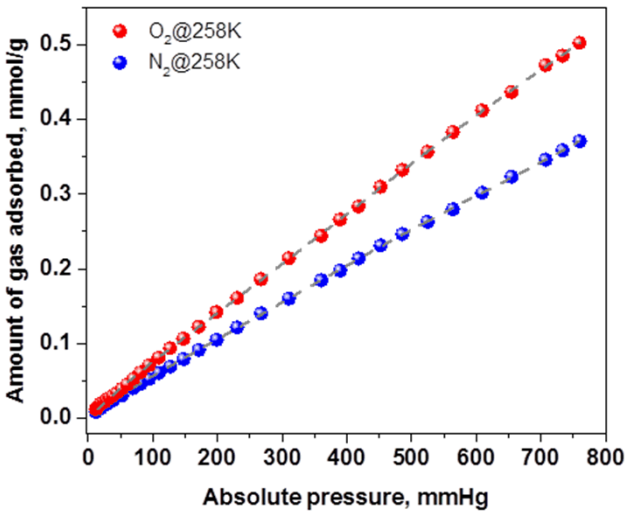
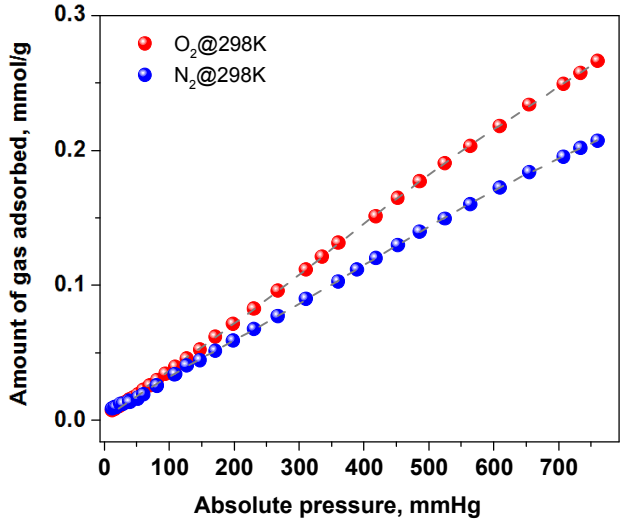
Fit using the virial eq.

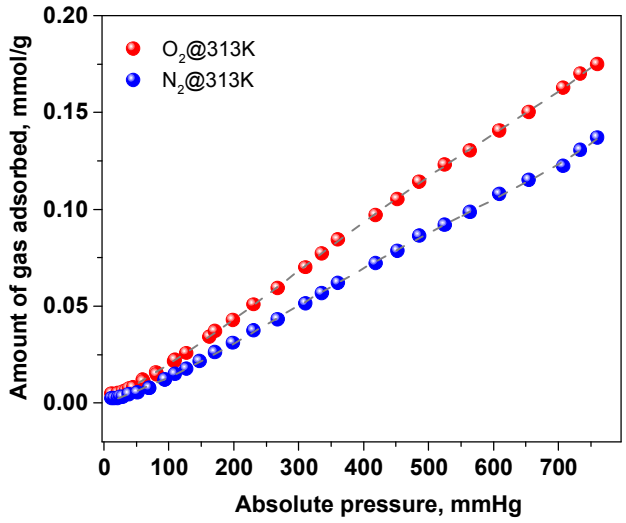
SMOF-8
O_2 vs. N_2 @**258K**



SMOF-8
O_2 vs. N_2 @**298K**



SMOF-8
O_2 vs. N_2 @**313K**



Isotherm trends mimic those predicted by GCMC

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SMOF-8: Isosteric Heat of Adsorption (kJ/mol)
Higher Binding Energy in SMOF-8 for O_2 vs N_2

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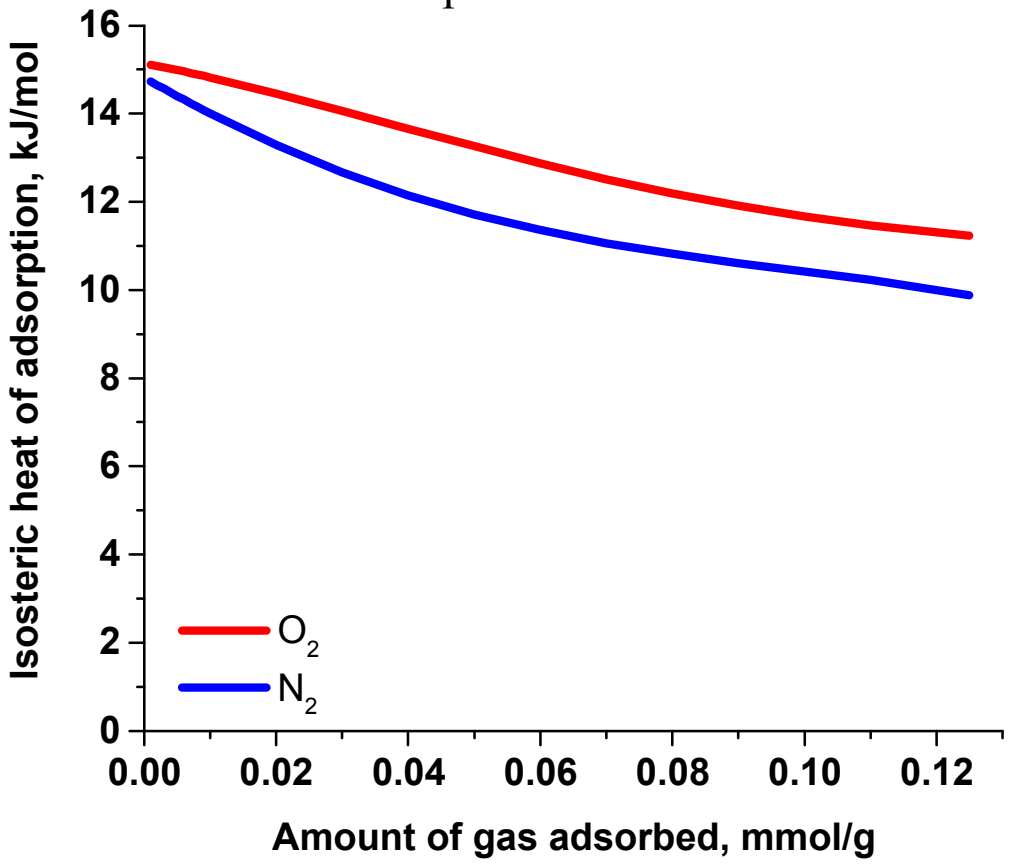
Qst derived from 258K, 298K and 313 K
Independent Virial Fit HOA



Conclusions and future work

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- Successfully synthesized partially substituted
  Co-, Fe- and Mn- analogues of Cu-BTC
- Assessed the effect on metal substitution on the O_2 and N_2 adsorption capacity at both cryogenic and close to room temperature ranges
- For the Co-, Mn- and original Cu-BTC, O_2 preferentially adsorbs over N_2 at 77K. ***However,*** the trend is reversed at 298K, where N_2 preferentially adsorbs over O_2
- Based on predictive modeling, we studied early transition metal metal-center MOFs for enhanced O_2 sorption.
- **SMOF-8**: Early transition metal MOFs show preference for O_2 vs N_2 over wide temperature range (up to at least 313K), as confirmed by isosteric heats of adsorption.
- Next Steps: Data transfer to *Technoeconomic Analysis* and *Burner Design* for Oxyfuel combustion applications

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Thank You

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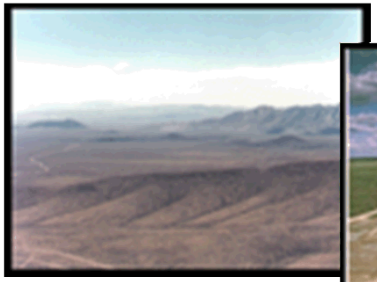
Sandia National Laboratories' Sites

Albuquerque, New Mexico

Kauai Test Facility
Hawaii

Tonopah Test
Range,
Nevada

Livermore,California



Yucca Mountain
Nevada

WIPP,
New Mexico

Pantex, Texas

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Extra slides

Transition to Quantum Calculations to Estimate Metal-Oxygen Binding Energy

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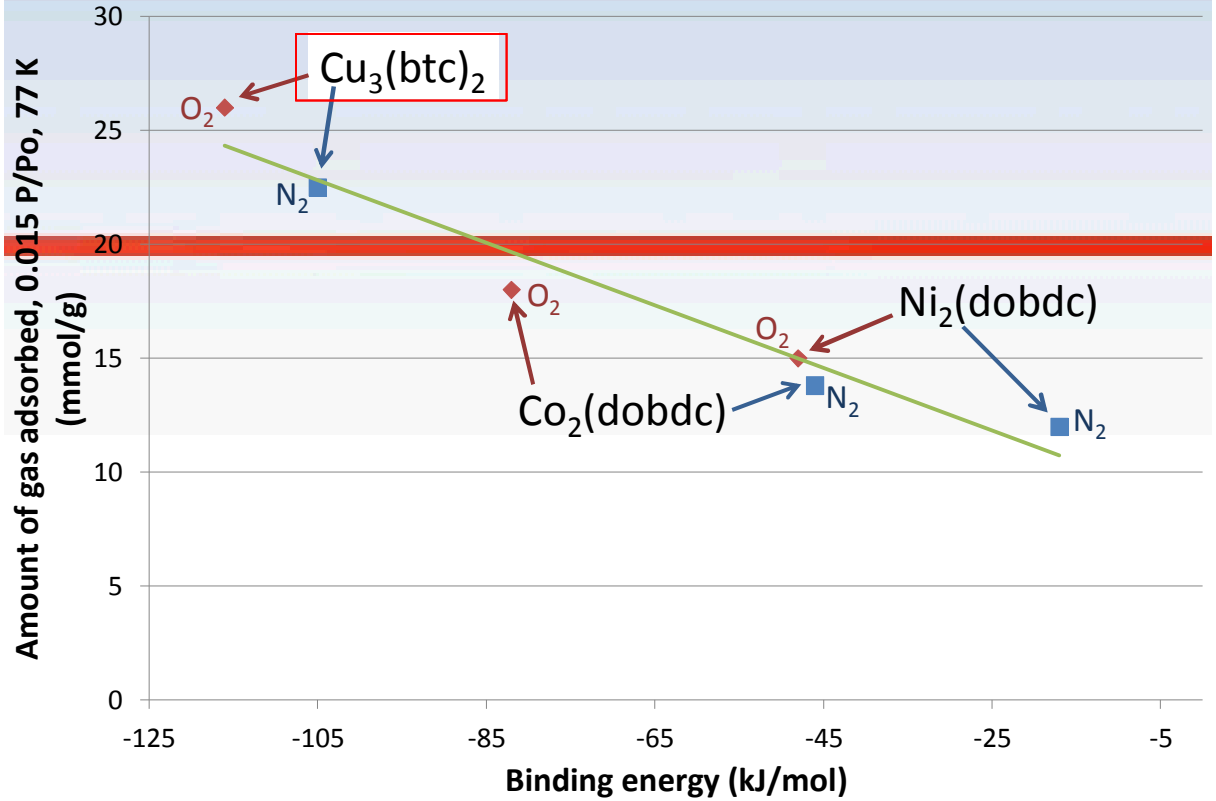
Low-temperature, low-pressure O_2 and N_2 adsorption measurements were done for three MOFs: $Cu_3(btc)_2$, $Co_2(dobdc)$, and $Ni_2(dobdc)$.



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

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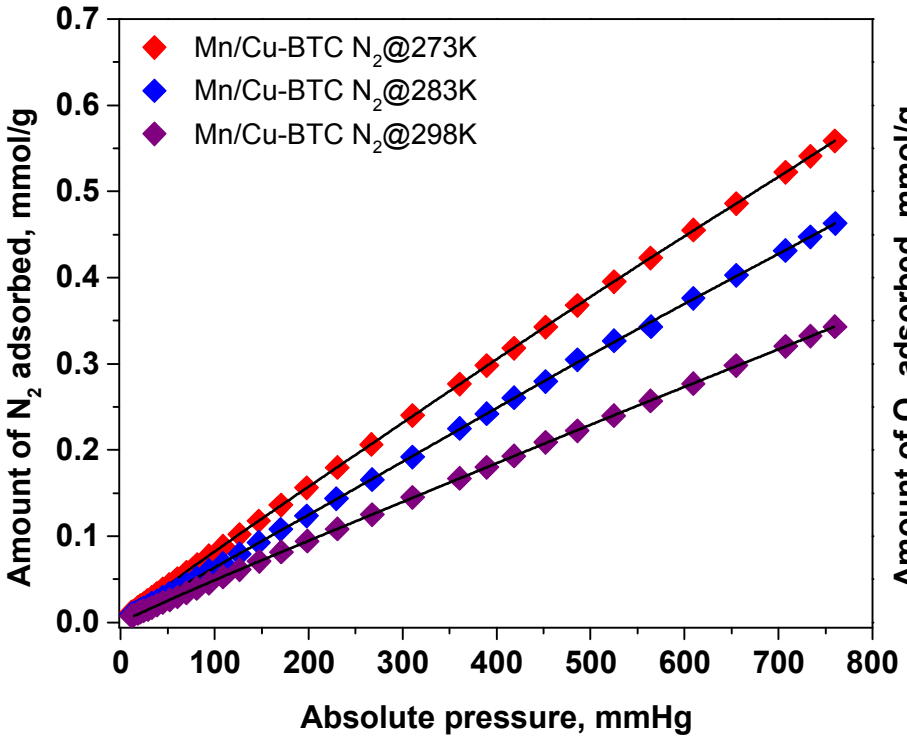
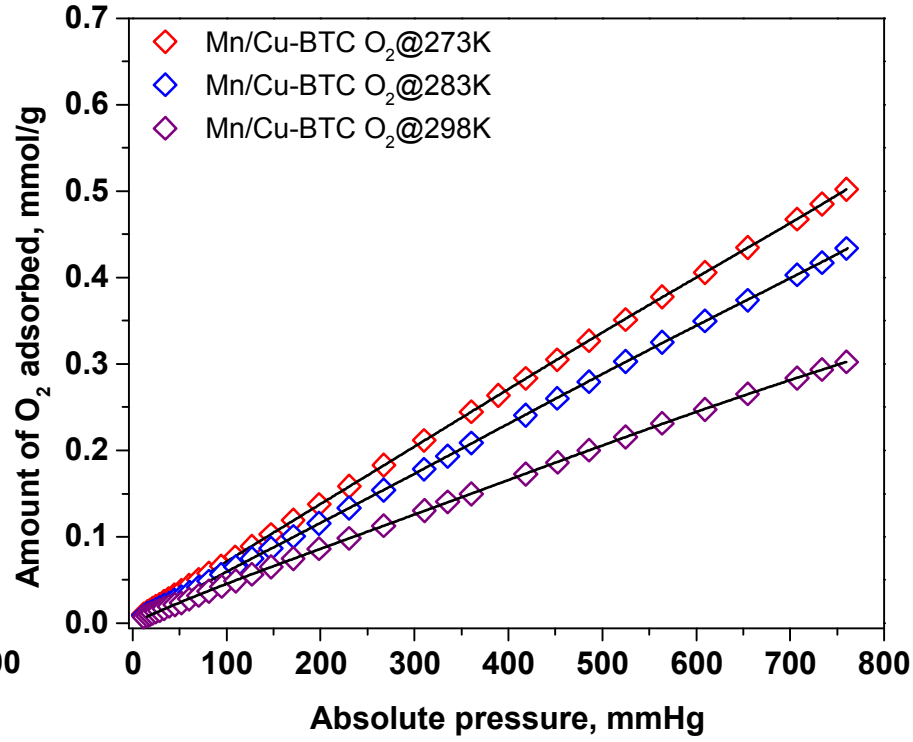
N_2 and O_2 adsorption isotherms measured at 273, 283, and 298K on pristine Mn/Cu-BTC





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

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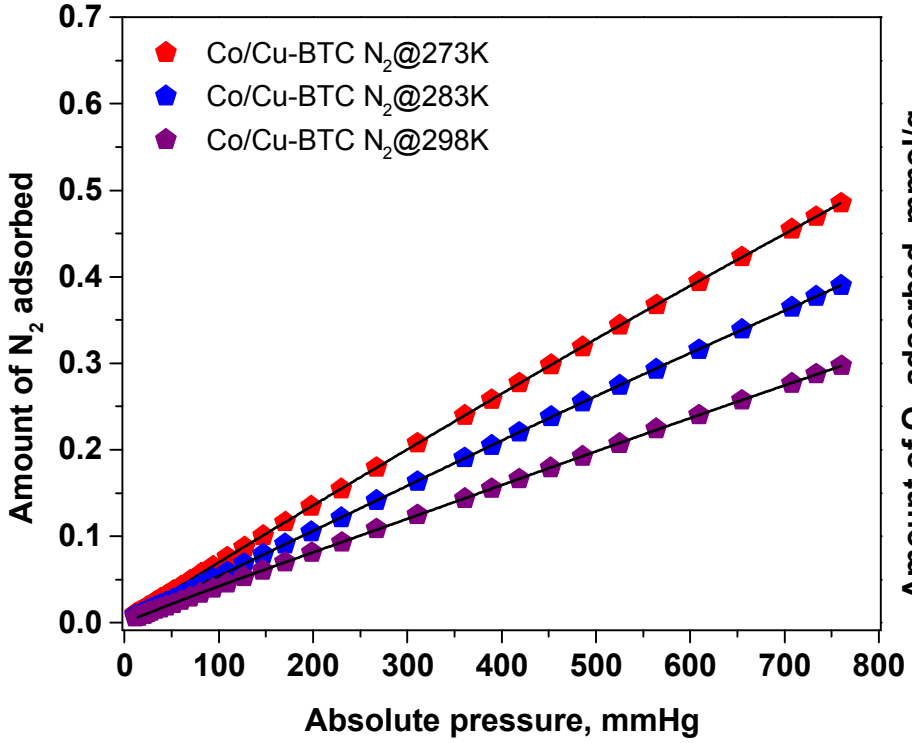
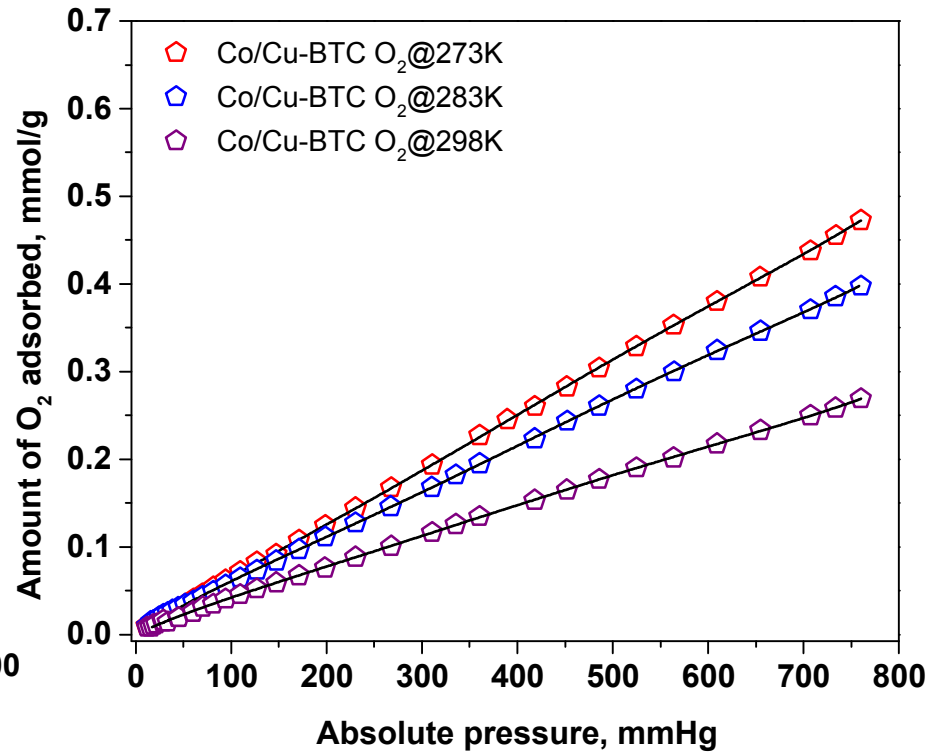
N_2 and O_2 adsorption isotherms measured at 273, 283, and 298K on pristine Co/Cu-BTC





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

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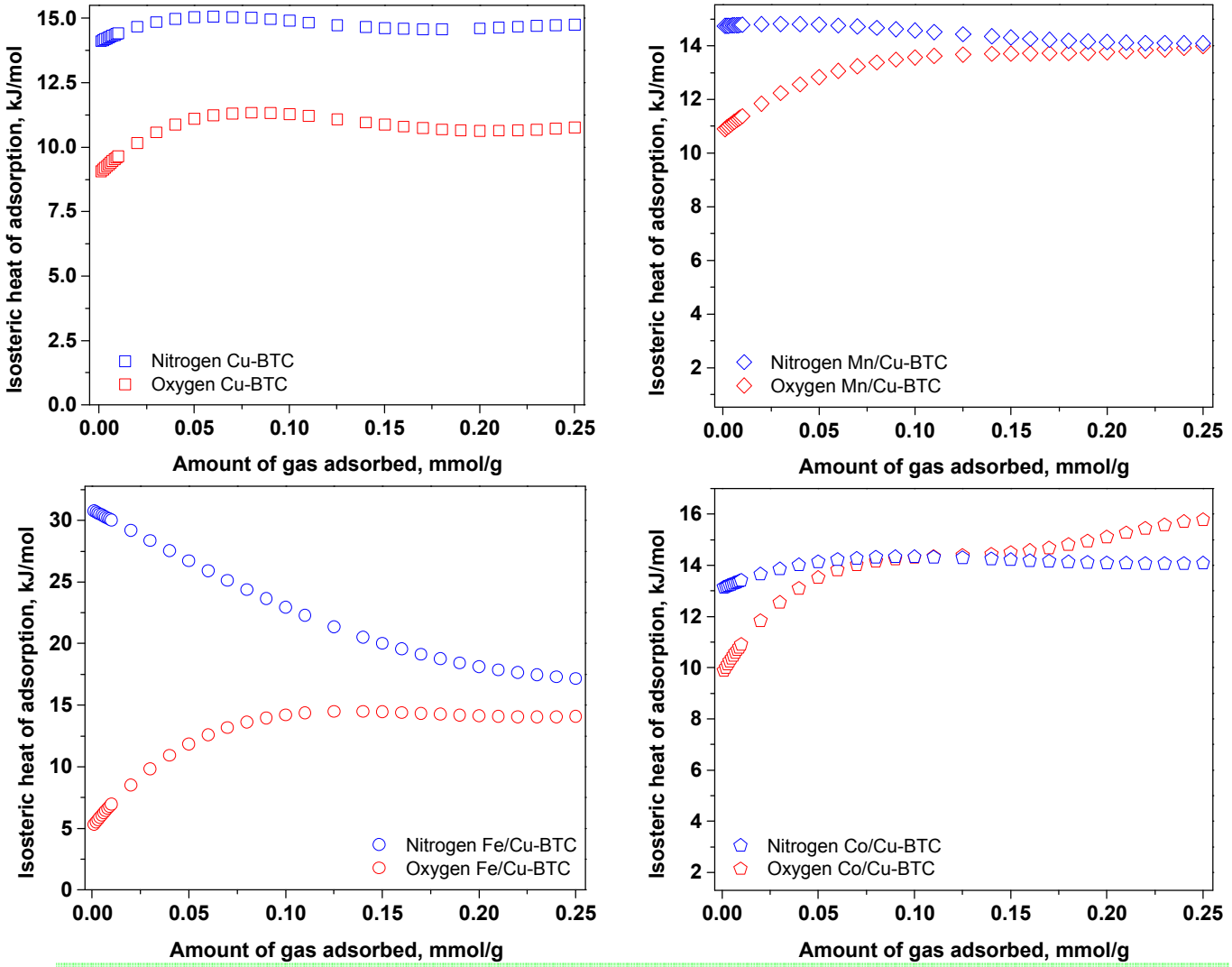
Significantly higher binding energy of N_2 over O_2 is noted for the Fe/Cu-BTC sample



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

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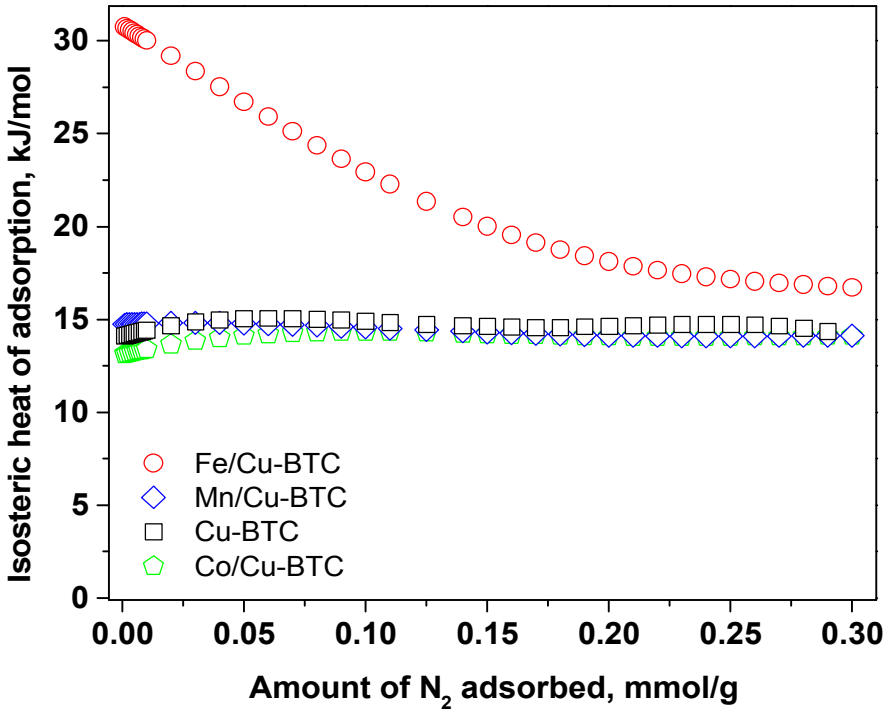

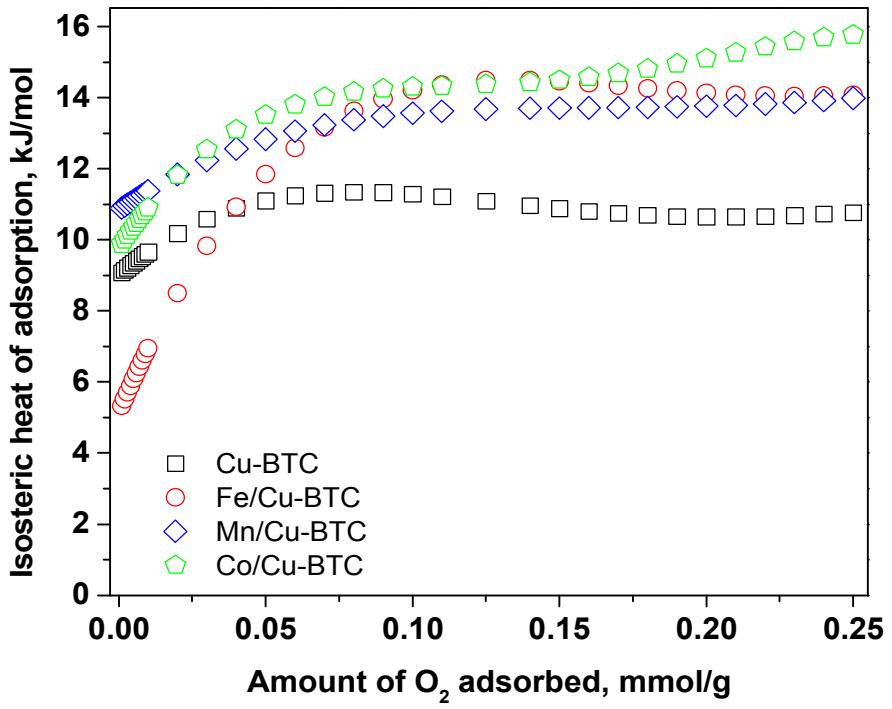

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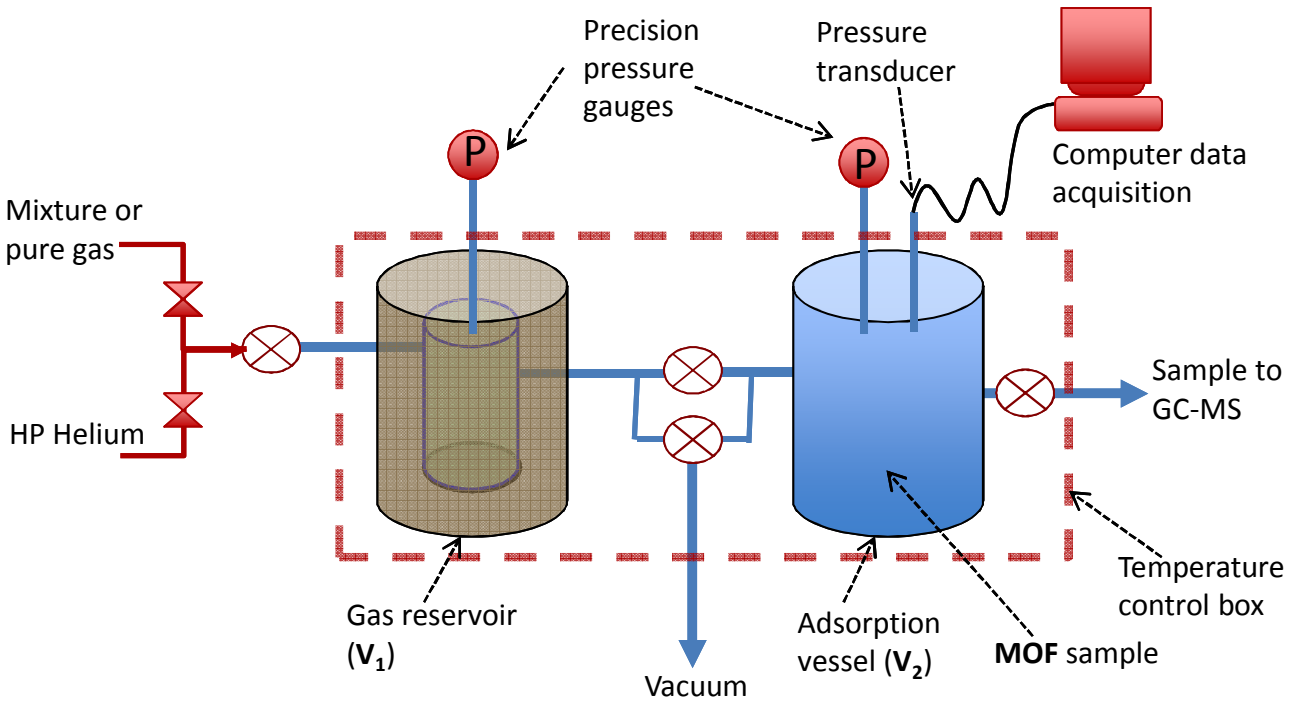
O_2/N_2 Gas mixture adsorption measurements containing 20% O_2 and 80% N_2



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

Samples tested for adsorption of O_2/N_2 mixture containing 20% O_2 and 80% N_2 at 21, 35, and 48.5°C, respectively.

P_{eq}, bar	Amount adsorbed., cm^3 (STP).g^{-1}.bar^{-1}		aO_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

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Combustion Studies plus MOF O_2 Separations for Improved Combustion Process Efficiency

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

5% improved efficiency ← heat/radiation improvement w/oxyfuel ← enhanced O_2/N_2 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

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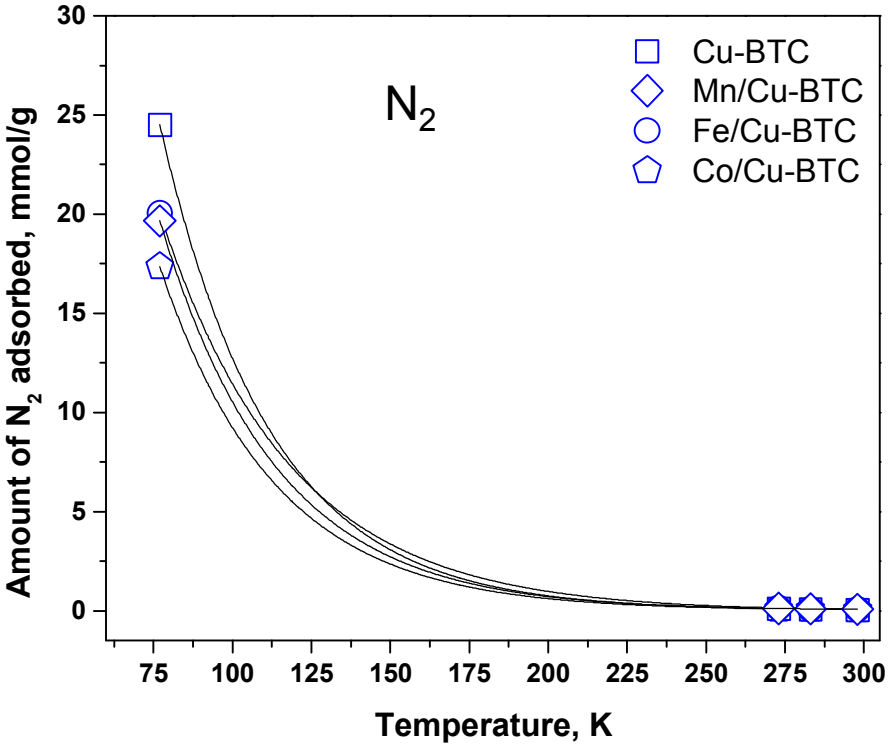
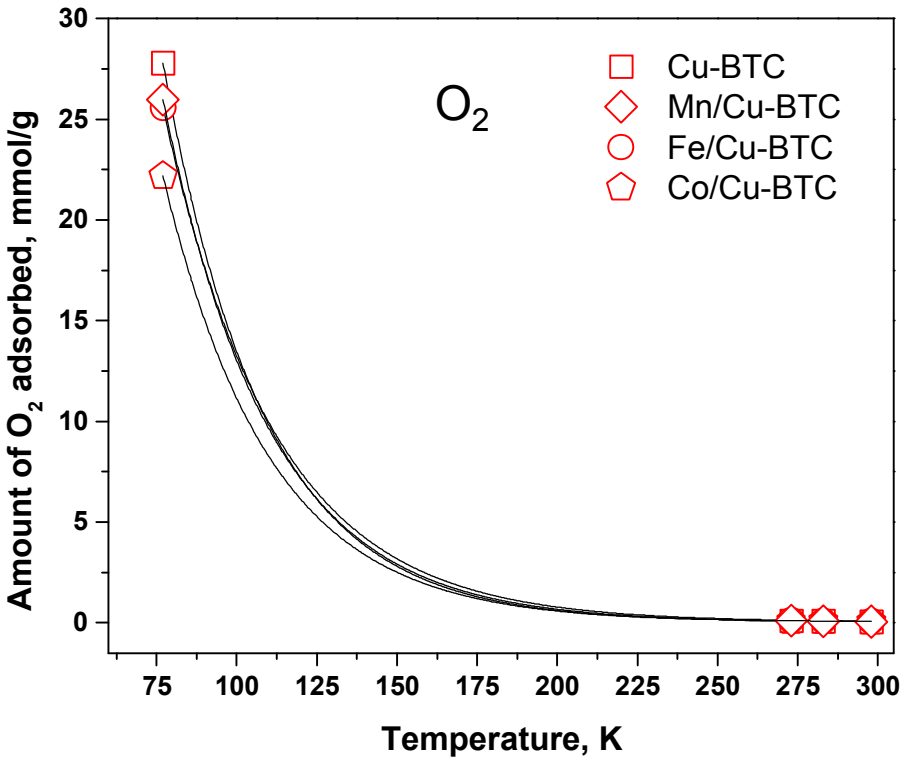
At 77K, Metal Sites Play an Important Role, while at *273 - 298 K* Metal Sites have a *Smaller Effect*

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

Chem. Mater. **2015**, *27*(6), 2018

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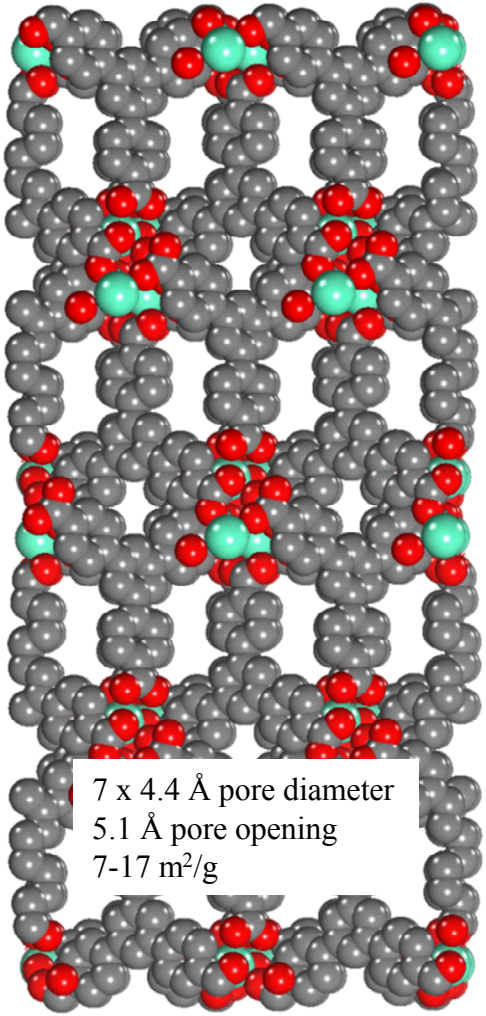
SMOF-7: O_2 vs. N_2 Single Gas Sorption Isotherm, at 77K

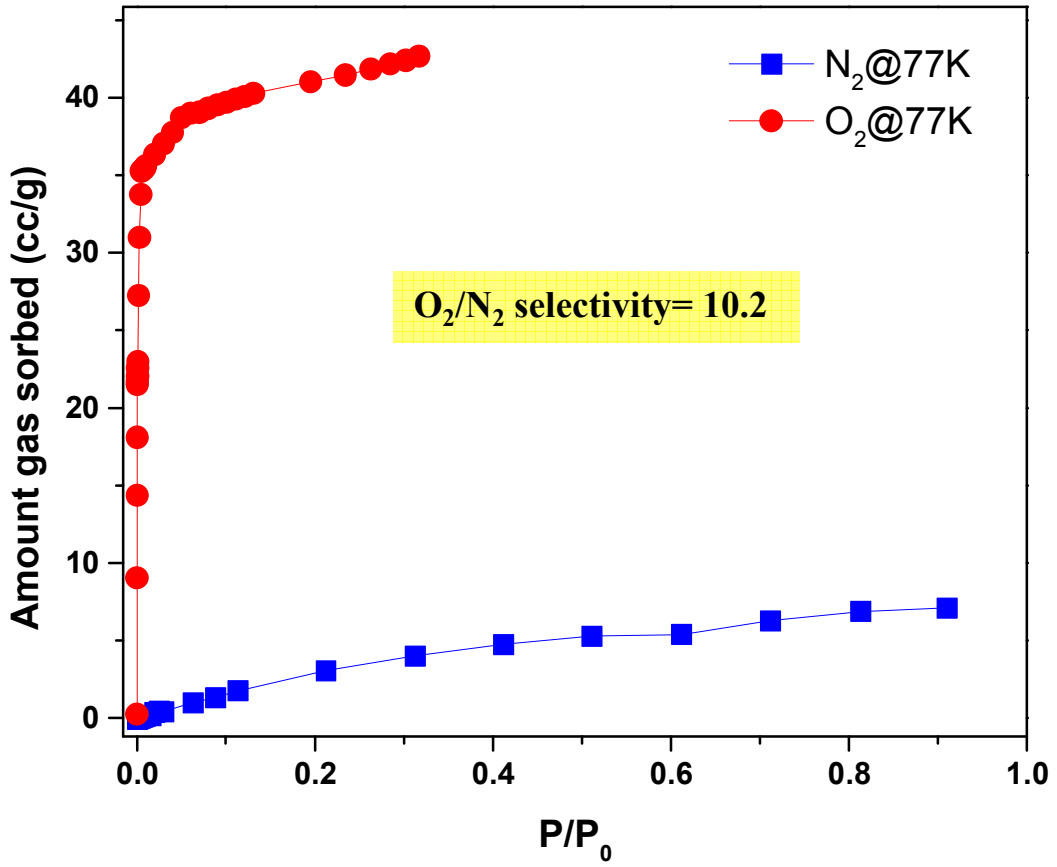
Sandia National Laboratories

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

SMOF-7



7 x 4.4 Å pore diameter
5.1 Å pore opening
7-17 m^2/g



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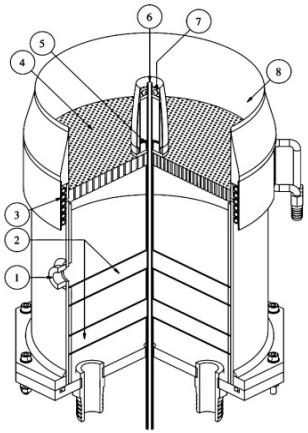
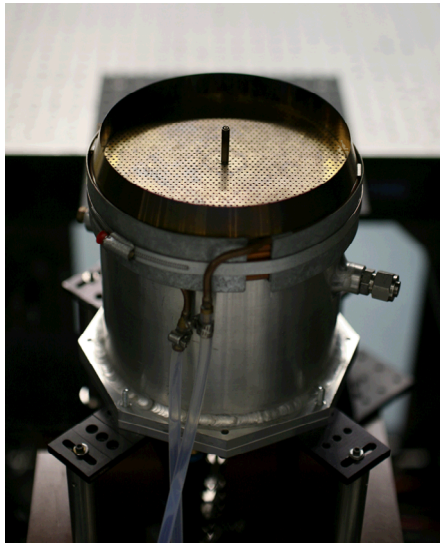
Coupling of Burner design and Oxy-fuel Combustion to Radiant Heat Transfer



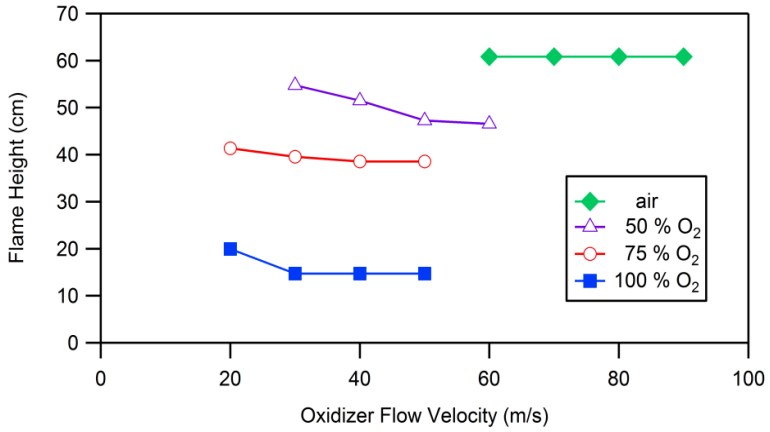
Balloon number	Description
1	Flashback over-pressure sensing port
2	Glass bead filled cavities
3	Cooling water coil
4	Coflow perforated baseplate
5	Pilot mixture feed exit
6	Central jet exit
7	Pilot perforated baseplate
8	Coflow collar



-Newly designed and constructed burner with smaller diameter inside tube for CH_4 into oxider jet flow

- Allows either premixed or non-premixed methane-air flame

- Designed specifically for pure O_2 and enriched 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 ½ the flow of oxygen, to maintain stoichiometric combustion conditions.

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Preliminary Investigation of Oxygen-Enriched NG Flames

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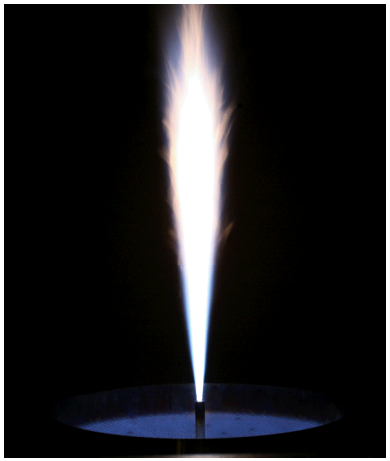
Performed preliminary testing performed with oxidizers of pure oxygen and with 50% O_2 in N_2, using an overall equivalence ratio of 1, with a constant methane flow

- Velocity (Re) of oxidizer flow is 50% lower when using pure O_2, making for taller flame (slower mixing)
- Soot formation is enhanced when using pure O_2 (higher temperatures, slower mixing)

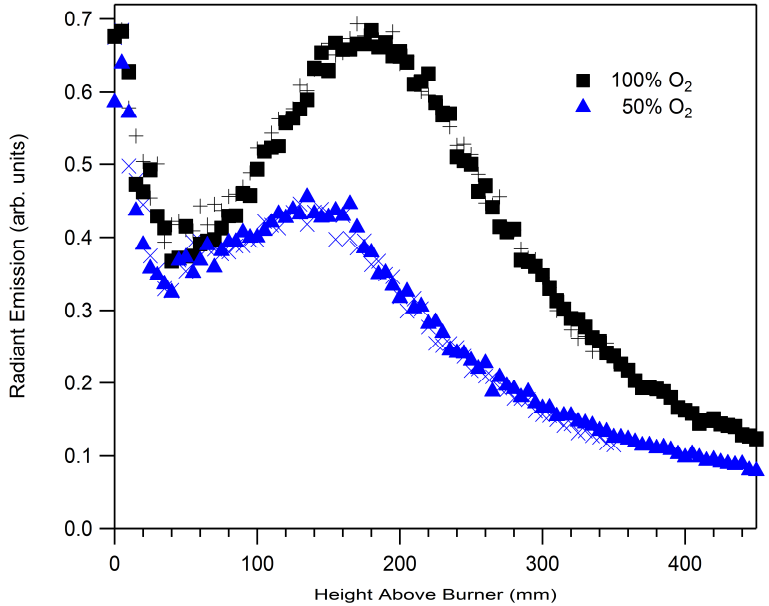
50% O_2 in N_2



100% O_2

Radiant emission measurements have been performed along the flame centerline

- Data for 100% O_2 shows significantly more thermal radiation
- Flame temperatures are higher when using pure O_2 (more radiation from flame products)
- Some soot is formed in the 100% O_2 flame



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Systems Analysis of MOF-based Air Separation

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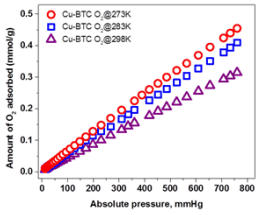
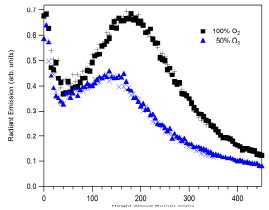
MOF adsorption isotherms (N_2 & O_2) (from MOF team)



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



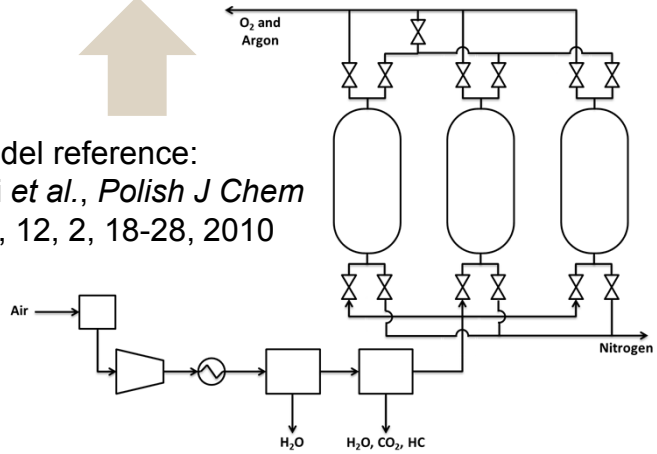
Can MOF-based PSA reduce energy consumption by 5% vs. conventional PSA air separation?

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

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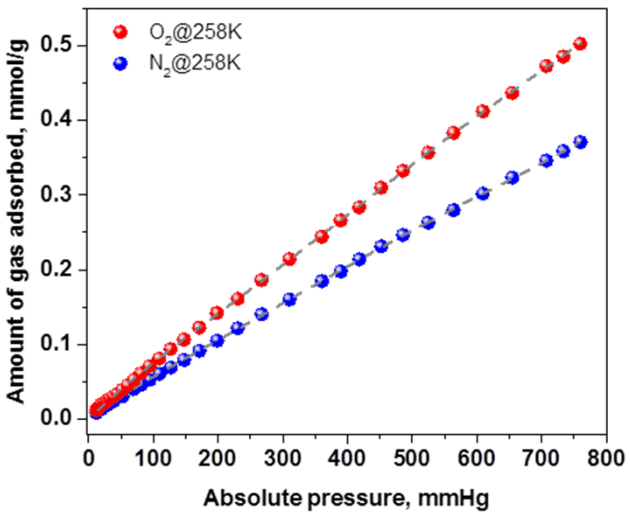
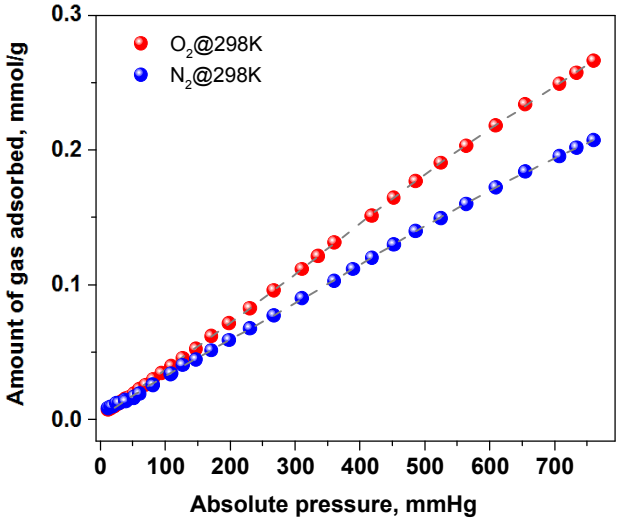
SMOF-8
O_2 vs. N_2@258K



SMOF-8
O_2 vs. N_2@298K



SMOF-8
O_2 vs. N_2@313K