SAND2014-16323C

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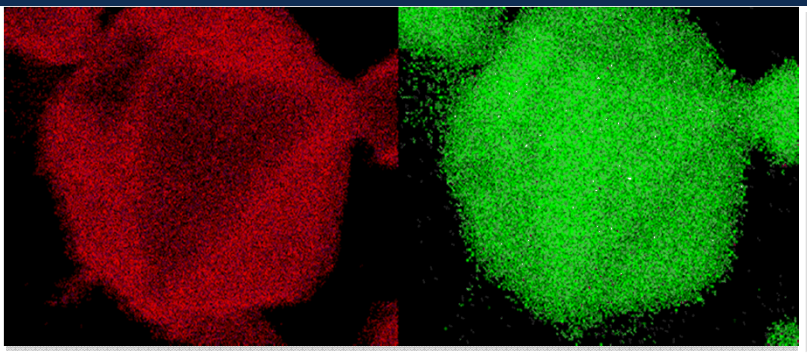

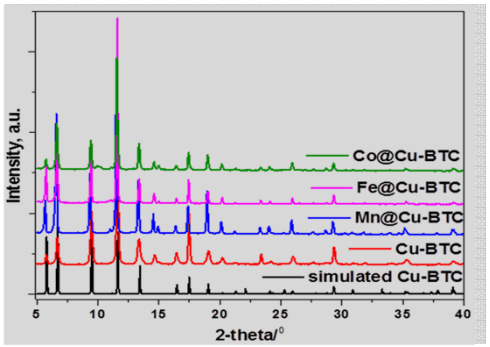

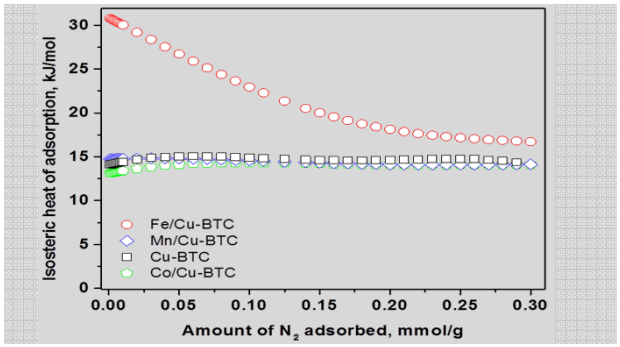

Efficient Light Gas Separations with MOFs via Predictive Modeling and Tuned Synthesis

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

2014 ACS Fall Meeting, ENFL, San Francisco
August 11, 2014

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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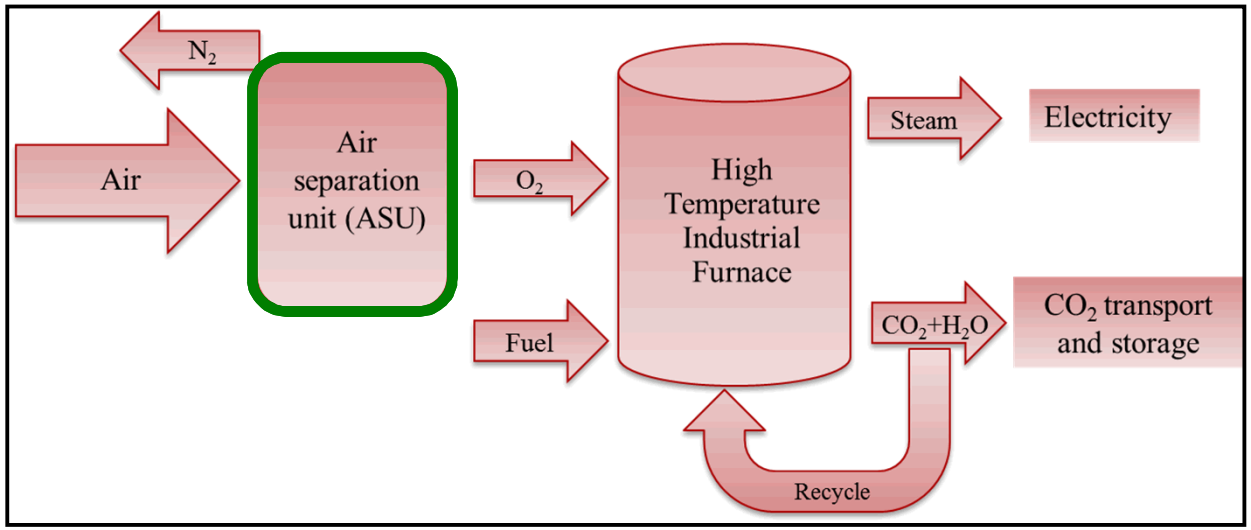
O_2/N_2 air separations with MOFs to increase efficiency of ASU



- 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 modeling, materials development, combustion testing, and systems analysis for improved energy efficiency

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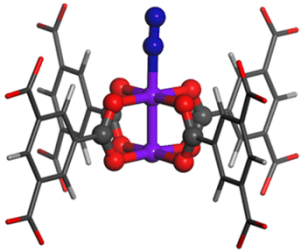
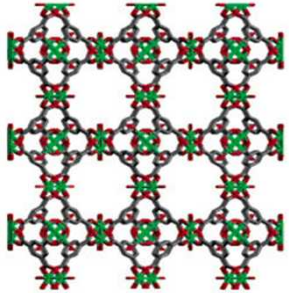
Predictive molecular modeling

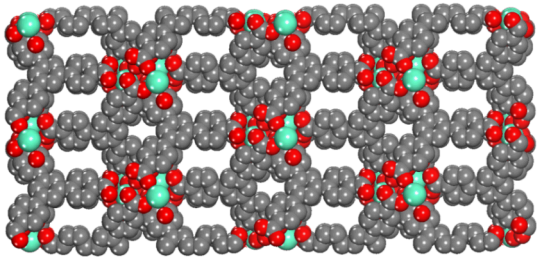
Predictive molecular modeling designed to *measure the binding energy for O_2 and N_2* on coordinatively unsaturated metal sites in MOFs



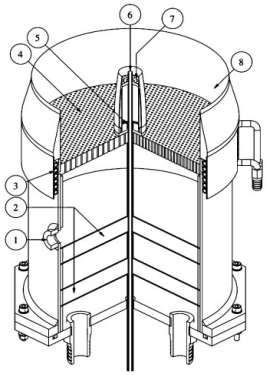
Materials development

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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MOFs Platforms: Known/Literature and SNL

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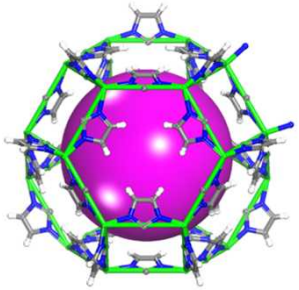
O_2: 3.46Å ; N_2: 3.64Å

ZIF's successful on single gas Syngas separations: Size Selectivity

Al-MIL-53

Open Metal Centers

ZIF-8

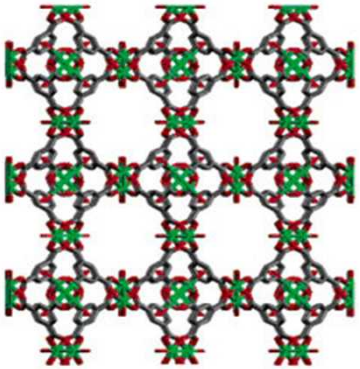


11.6 x 14.6Å pore diameter
3.4 Å pore opening
1100 m^2/g

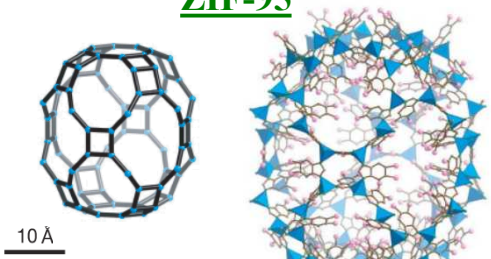
Fe-HKUST

Fe-BTC

Cu-BTC



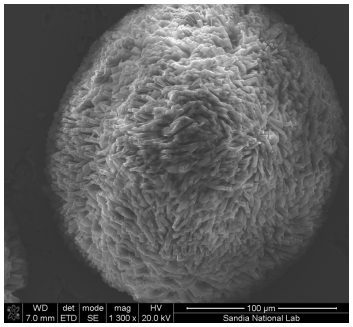
ZIF-95

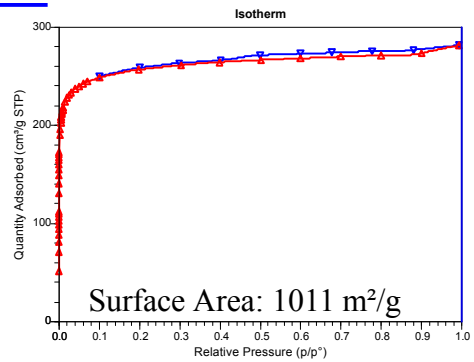


24 Å pore diameter
3.65 Å pore opening
1240 m^2/g

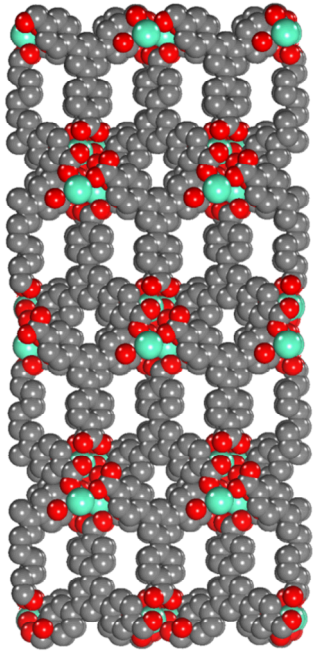
Underlined = synthesized in house

SMOF-3





Type I isotherm, steep rise indicates strong adsorbent-adsorbate interactions



SMOF-7

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

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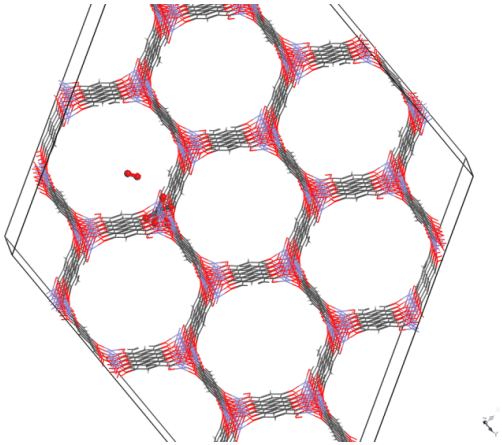
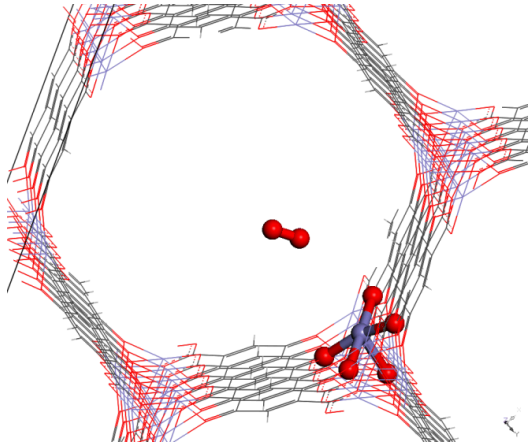
DFT simulations provide molecular-level details of the metal-O_2 and metal-N_2 binding energies and geometries

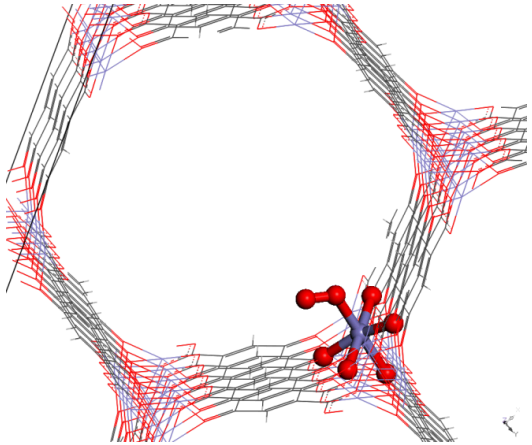
- MOFs with coordinatively unsaturated metal centers are promising materials for O_2/N_2 separations
- Two prototypical MOFs from this category, $Cr_2(BTC)_3$ (*J. Am. Chem. Soc.* **2010**, *132*, 7856–7857) and Fe_2(DOBDC)(*J. Am. Chem. Soc.* **2011,** *133*, 14814-14822) both show preferential adsorption 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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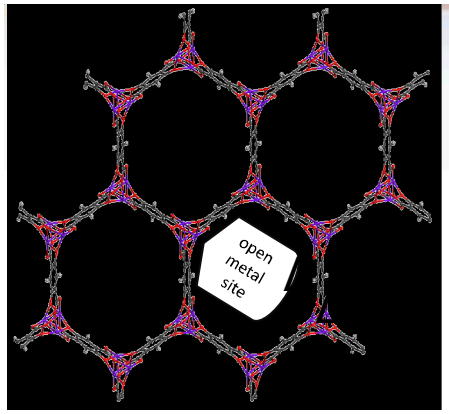
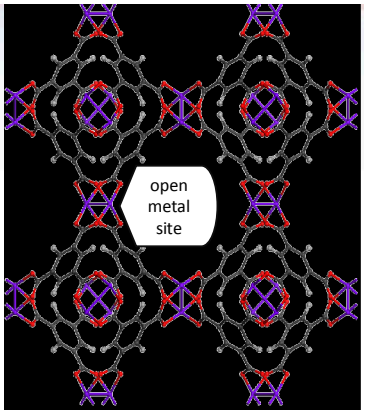


M_2(dobdc)



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

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

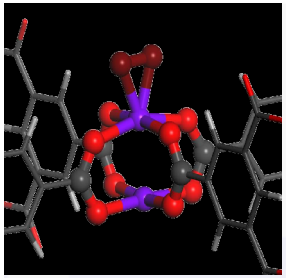
The **differences in binding energies ($\Delta\Delta$ E)** for oxygen and nitrogen were calculated by

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

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

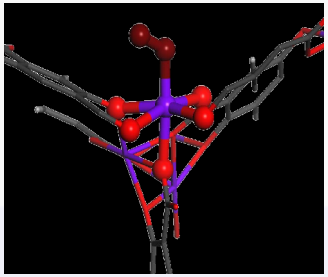
Attention Paid to Bonding Geometries

Side-on bonding
∡M-X-X 67° - 71°



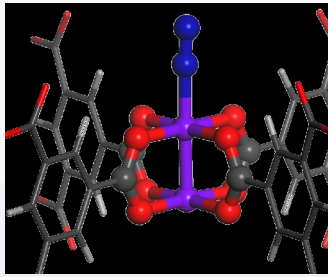
$Cr_3(btc)_2(O_2)$

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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Transition to Quantum Calculations to Estimate Metal-Oxygen Binding Energy

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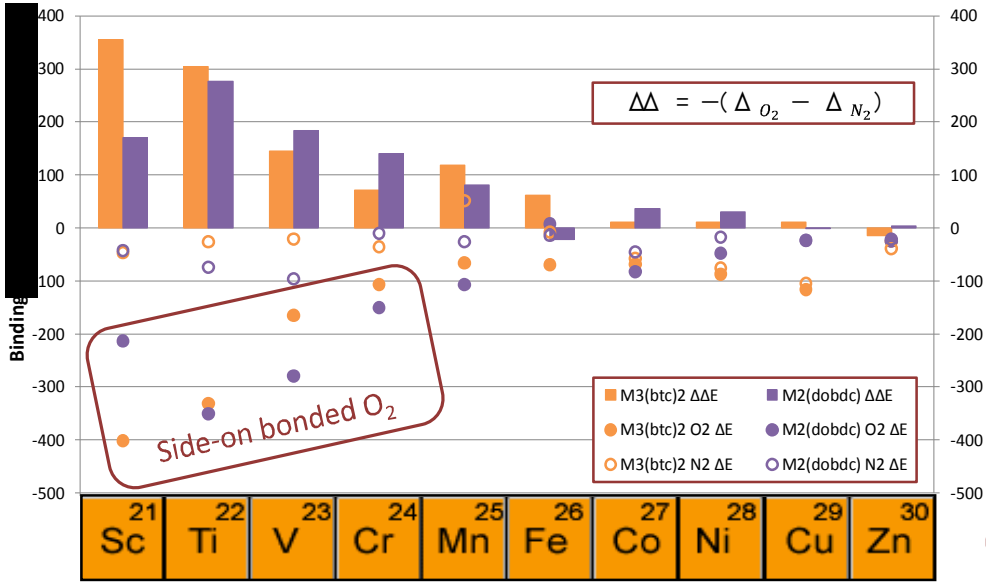
Binding Energy Calculated as a Function of Metal Site

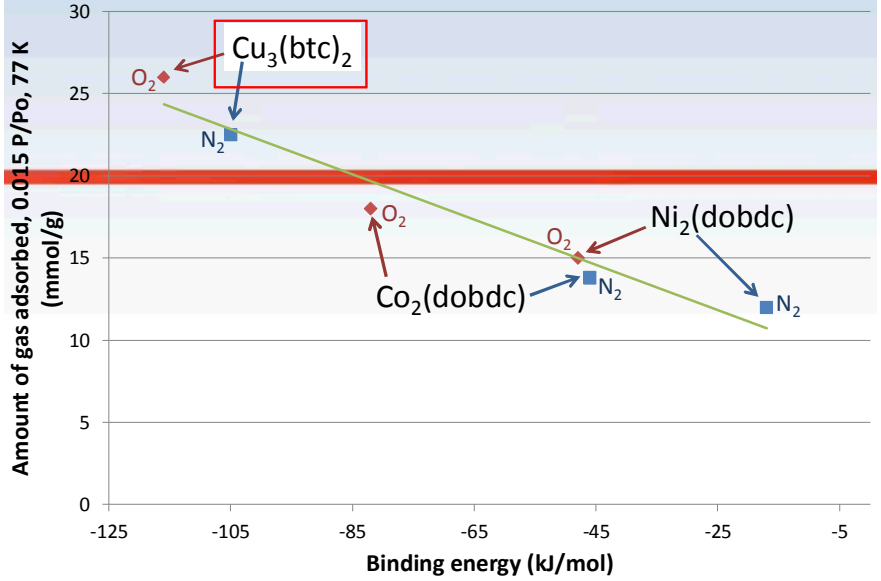


Parkes, M.; Sava Gallis, D. F.; Greathouse, J.A.; Nenoff, T.M. "Screening MOFs for O_2/N_2 Separations: Role of MOF Metal Center", **2014**, in preparation.

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

Experimental Confirmation

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.

Targeted synthesis of porous Mn-, Fe- and Co- analogues of Cu-BTC

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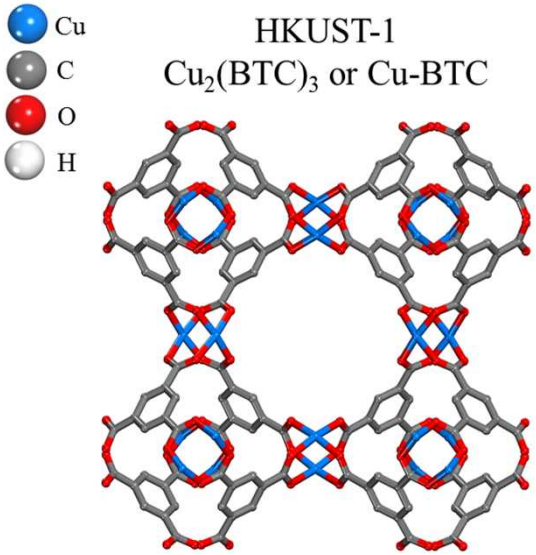
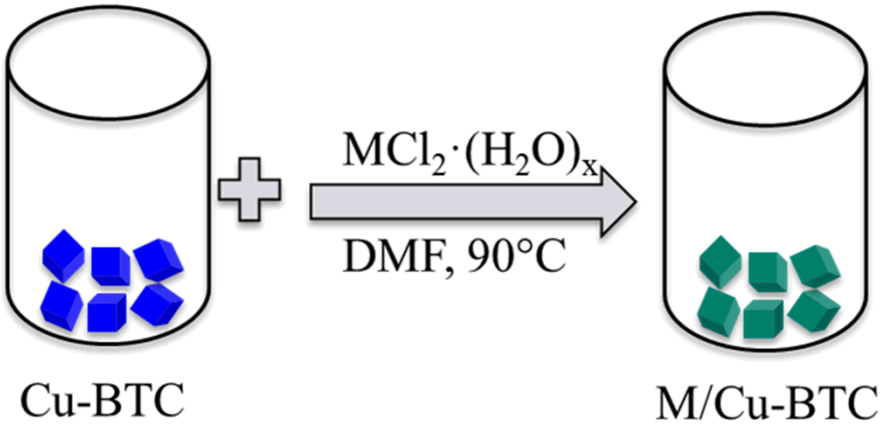
- Porous analogues of Cu-BTC include: Cr, Mo, Ru, Ni (the Ru and Ni have much lower than expected surface areas, 1000-1100 m^2/g)

- 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. "O_2/N_2 separations with Metal substituted MOFs", **2014**, in preparation.

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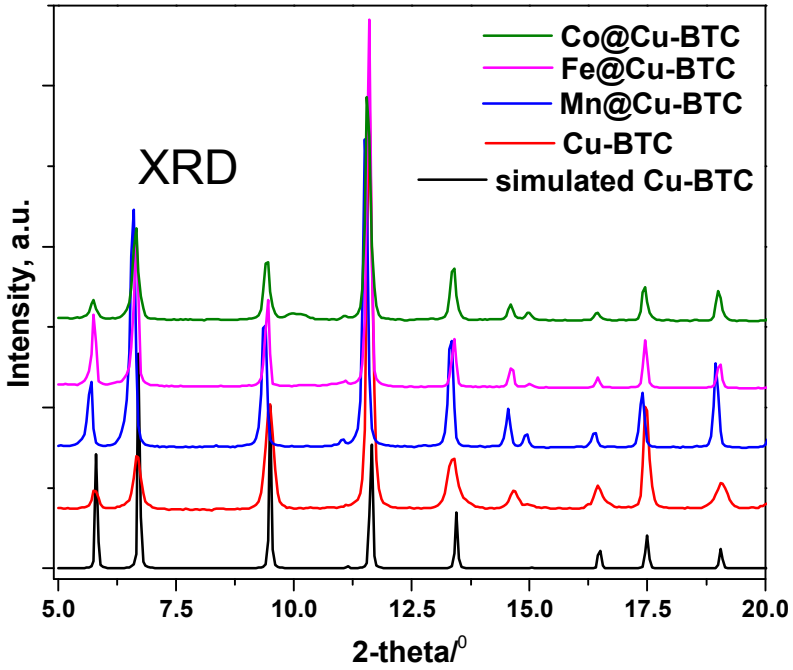
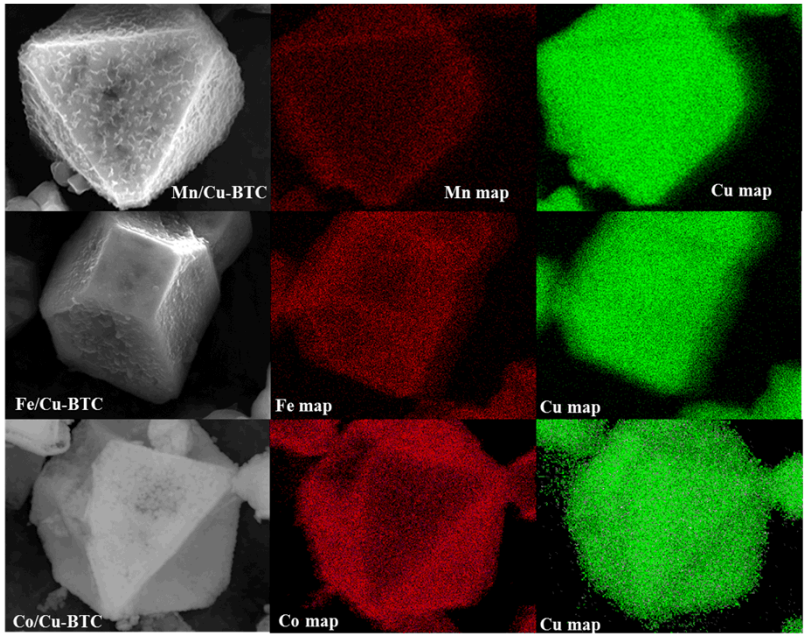
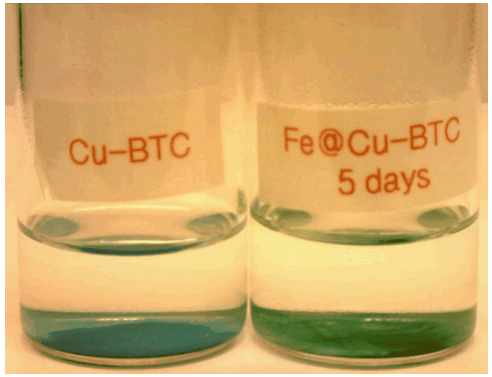
Confirmation of in-framework metal substitution – unit cell expansion & elemental mapping



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

SEM-EDS





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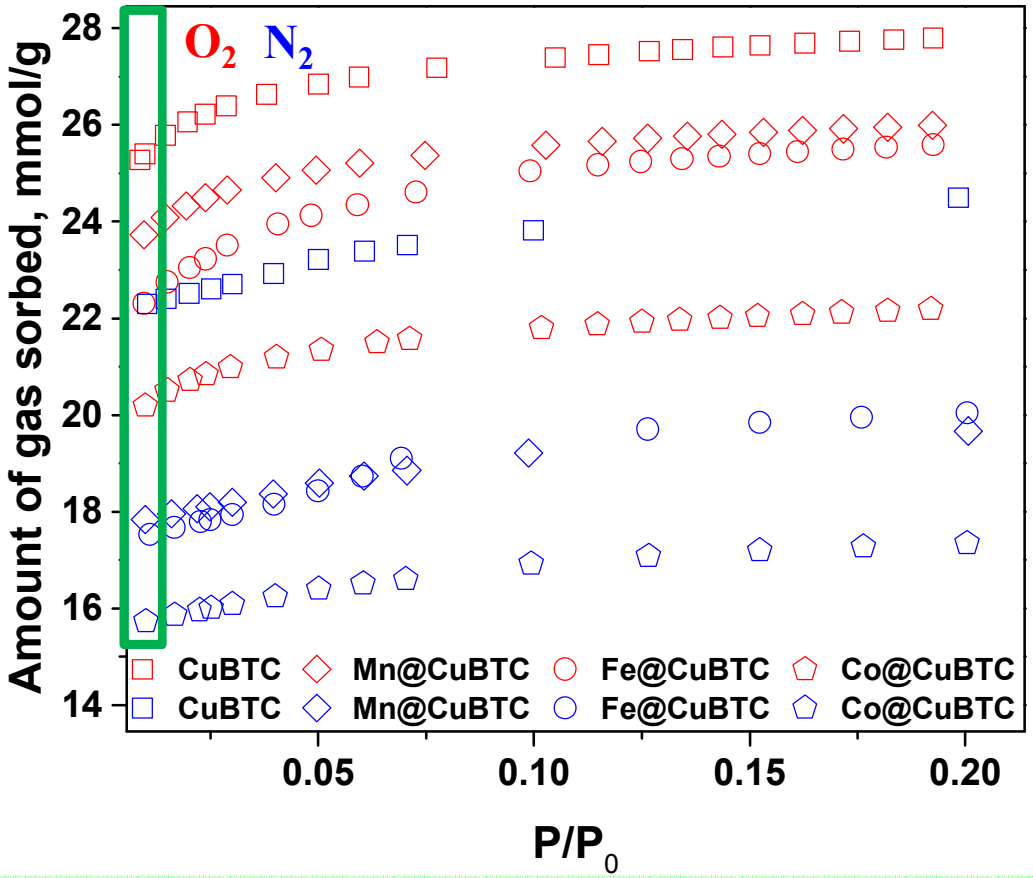
Excellent DFT and experiment correlation at low temperature and low pressure

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 (~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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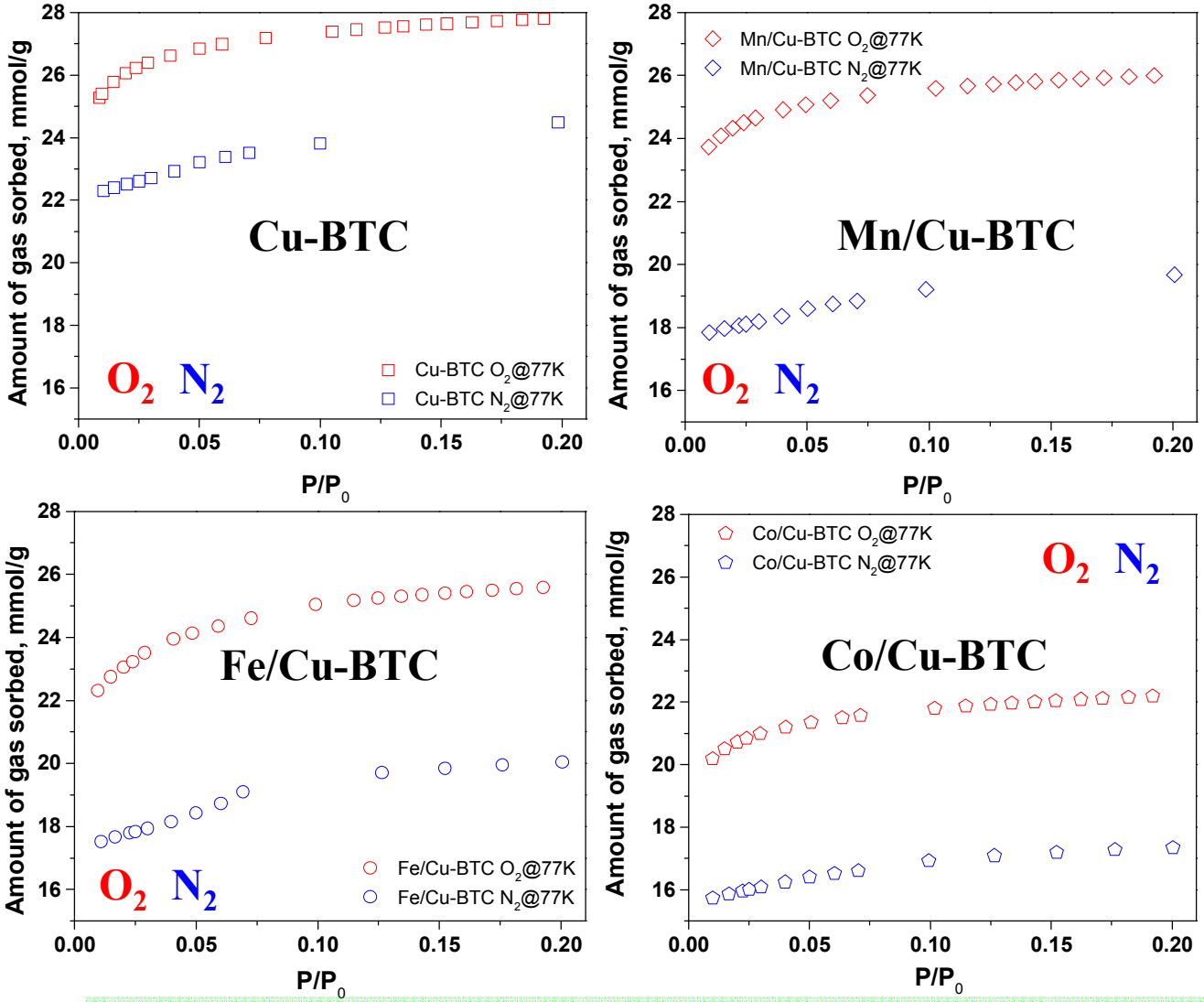
77 K: all samples have higher O_2 loadings over N_2



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

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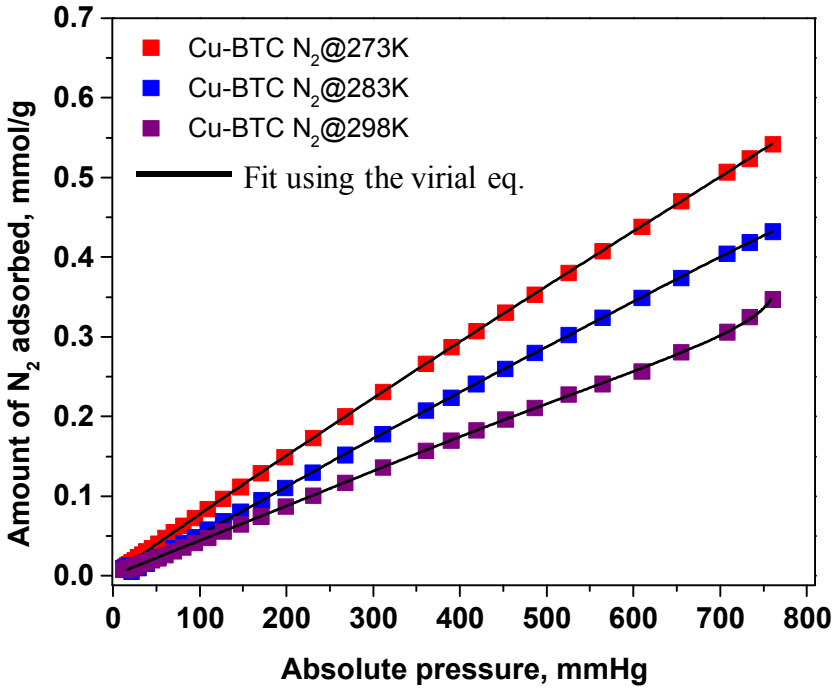
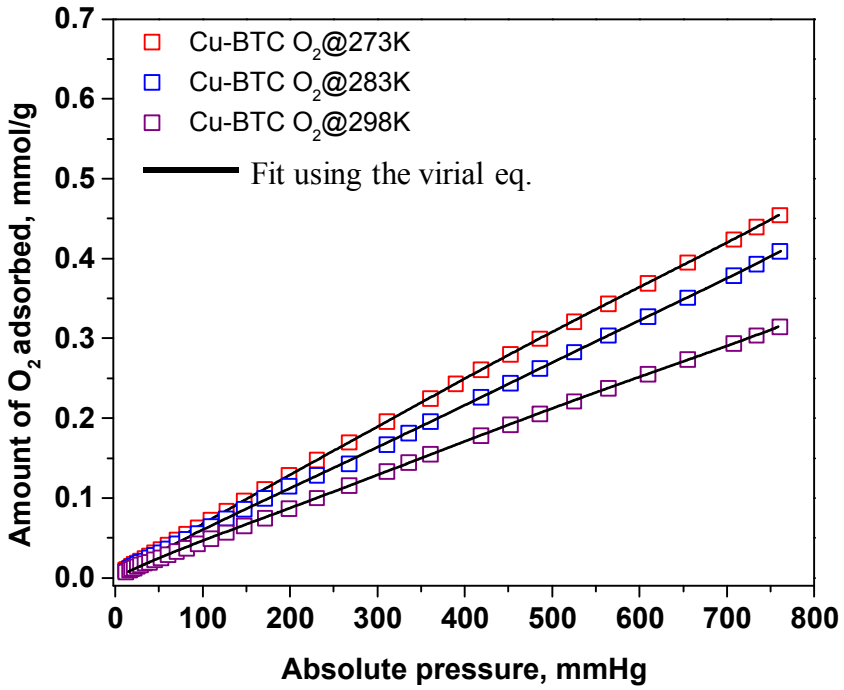
273-298 K: as temperature increases, O_2 loadings decrease with respect to N_2

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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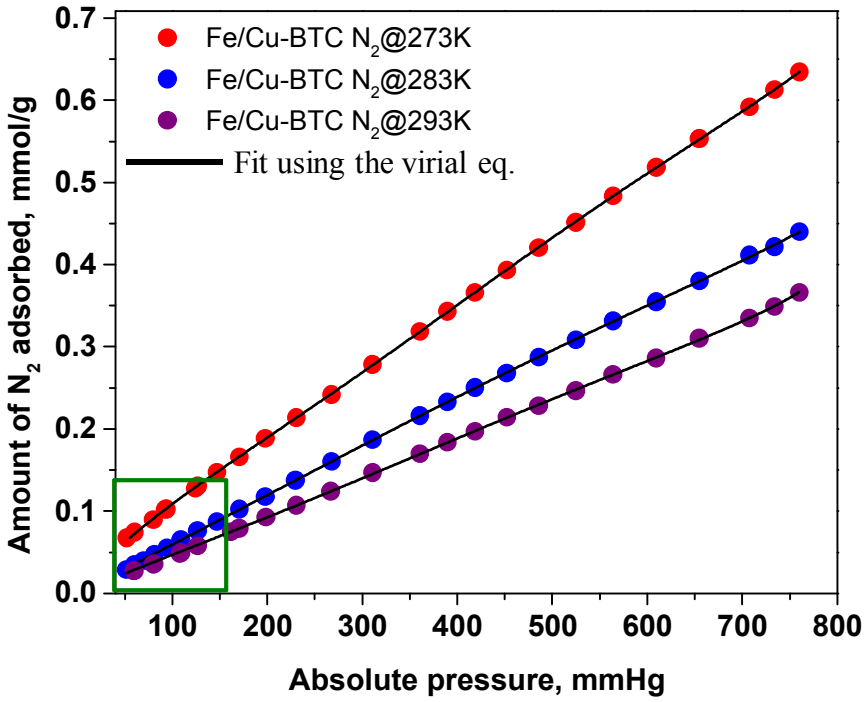
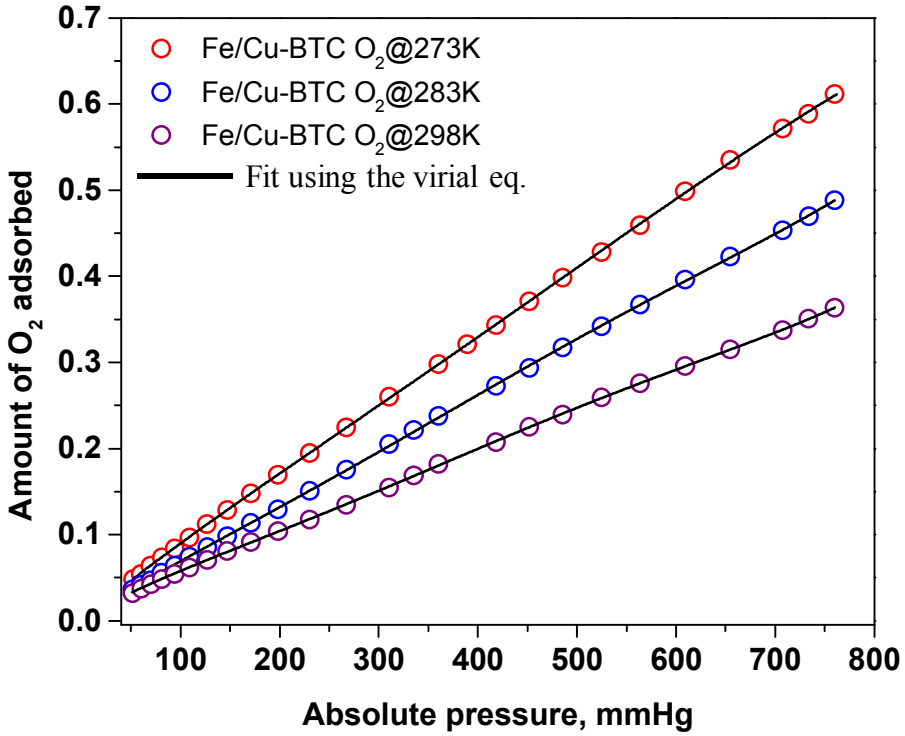
N_2@273 K in Fe/Cu-BTC : slightly higher N_2 uptake at lowest loading





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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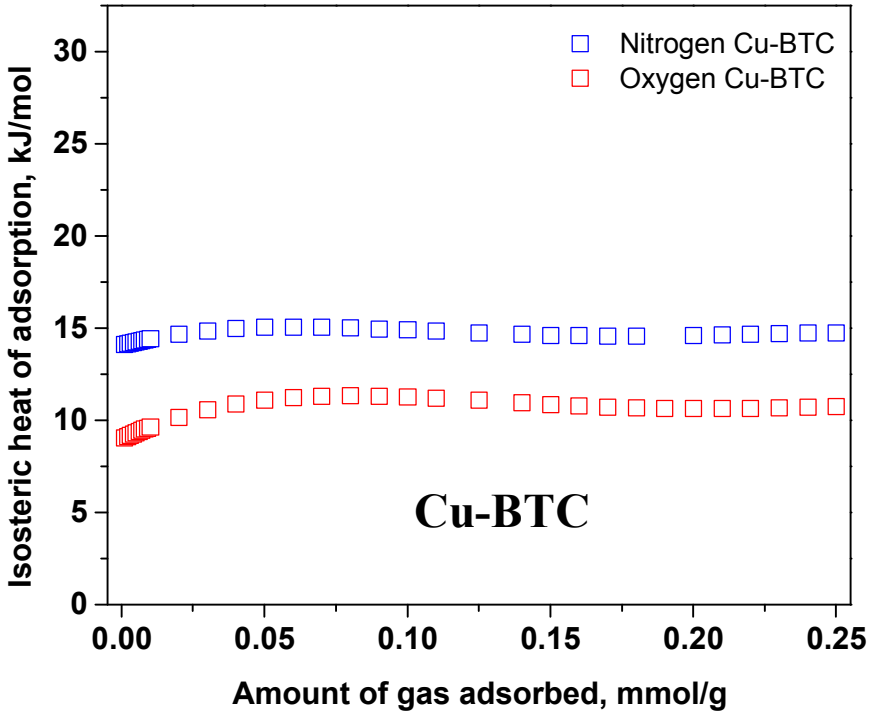
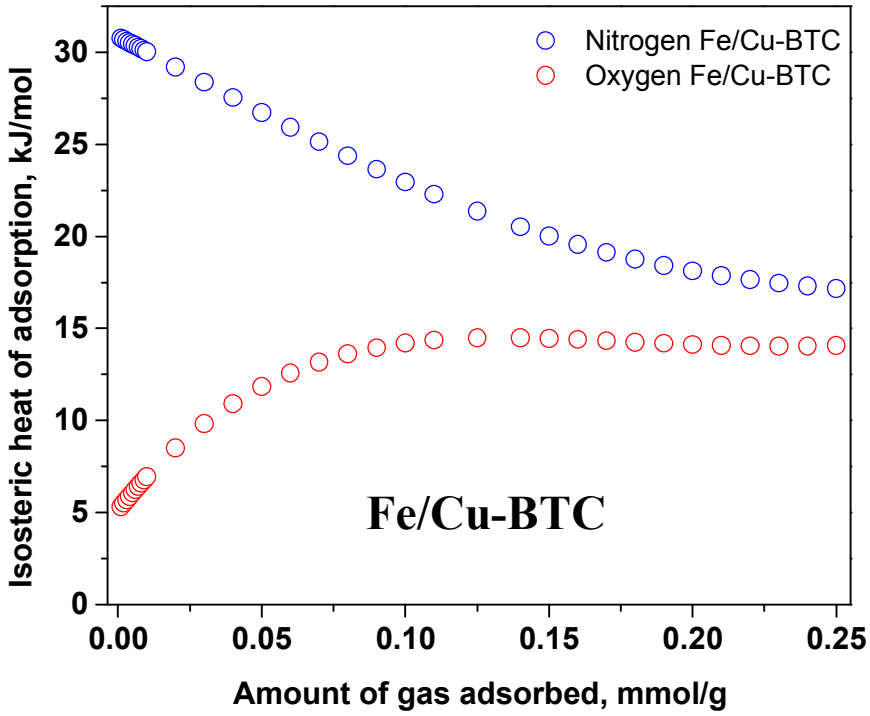
Isosteric heats of adsorption for O_2 (red) and N_2 (blue)





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

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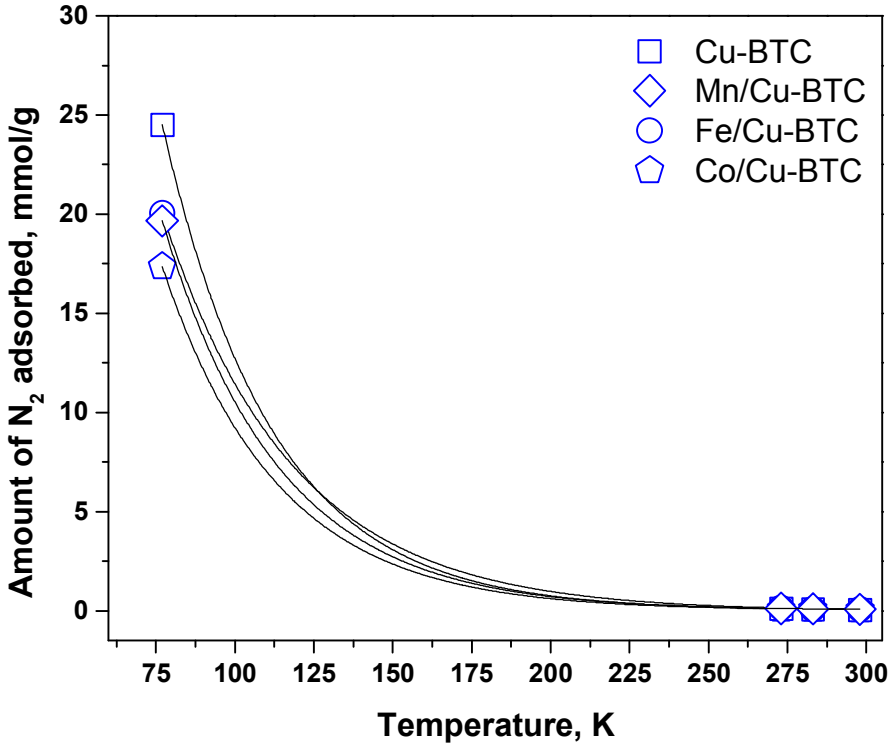
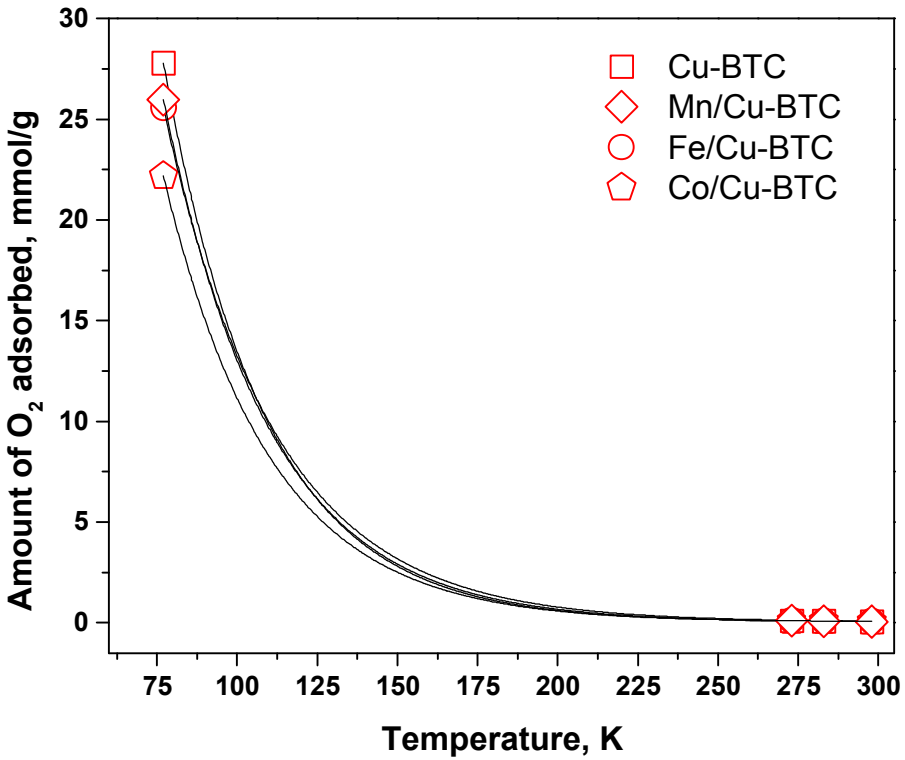
At 77K the metal sites play an important role, while at 273-298 K have a less pronounced effect

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

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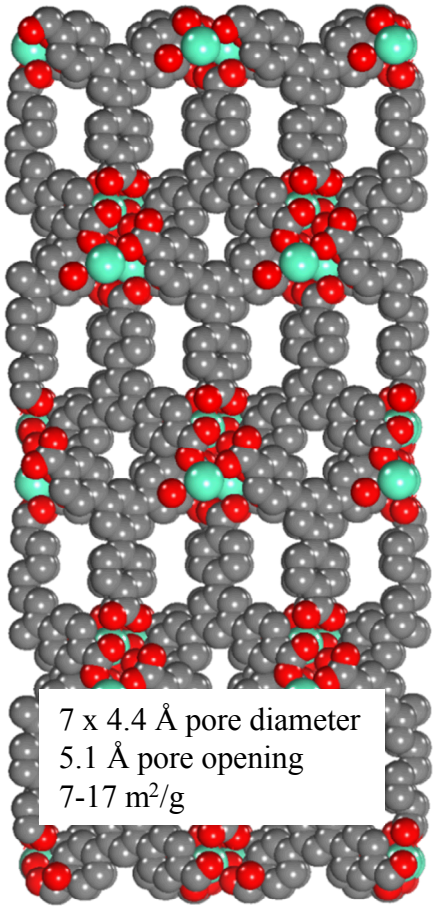
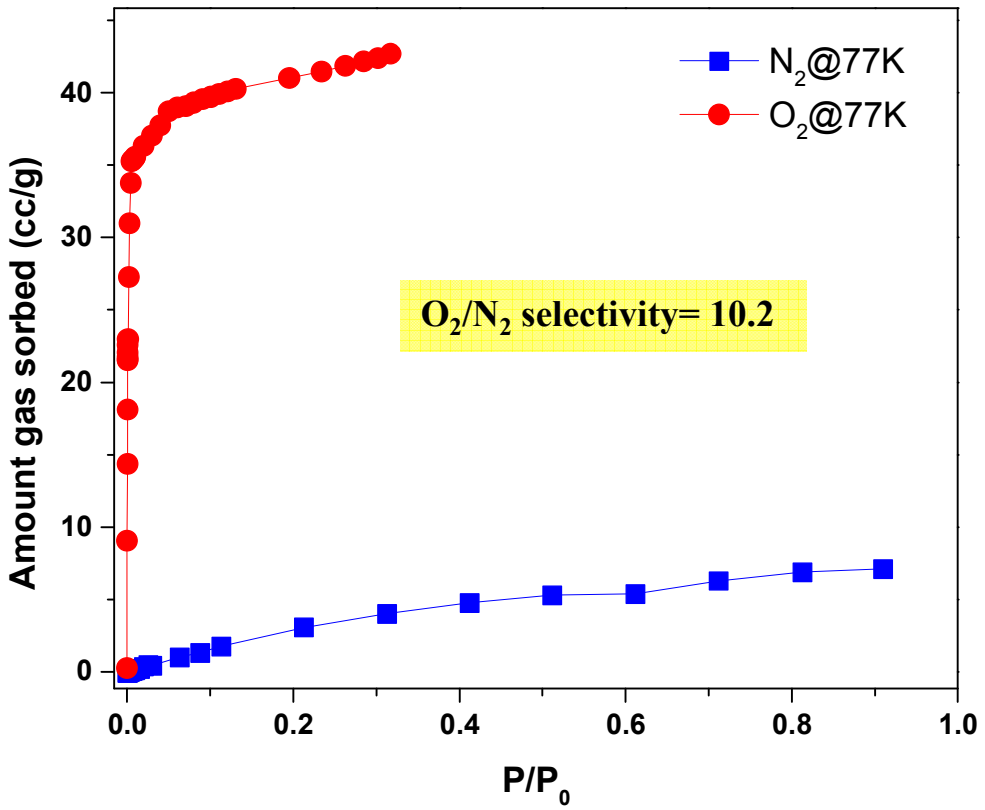
SMOF-7: O_2 vs. N_2 Single Gas Sorption Isotherm, at 77K

Sandia National Laboratories

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

SMOF-7





HIGH Selectivity, LOW Capacity

Estimated BET SA (only two runs), mostly associated with external surface area
On ASAP 2020 = 7.7174 ± 0.4221 m²/g; On Quantachrome = 17.045 m²/g

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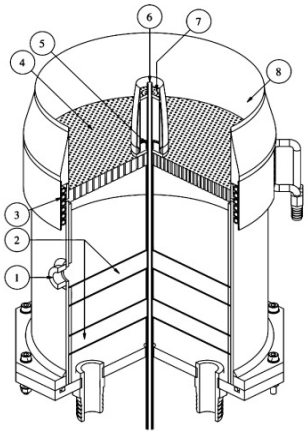
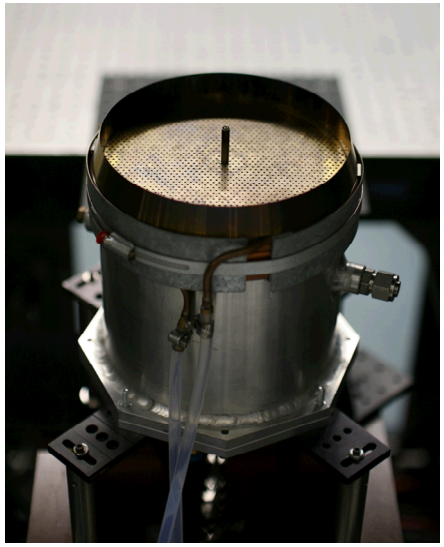
Coupling of Burner design and Oxy-fuel Combustion to Radiant Heat Transfer



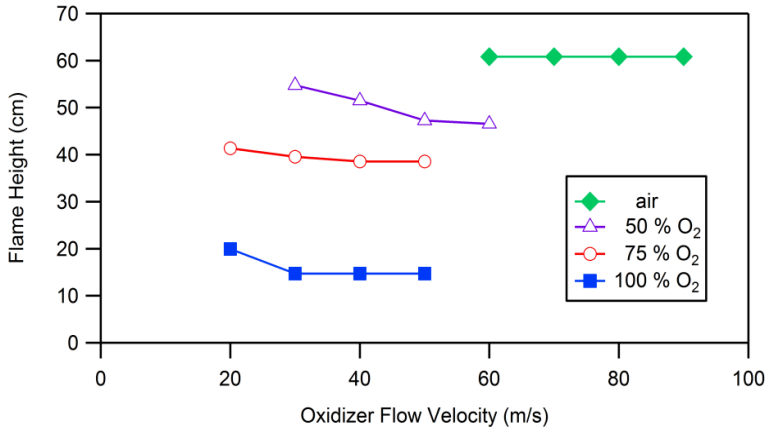
Balloon number	Description
1	Flashback over-pressure sensing port
2	Glass bead filled cavities
3	Cooling water coil
4	Coflow perforated baseplate
5	Pilot mixture feed exit
6	Central jet exit
7	Pilot perforated baseplate
8	Coflow collar



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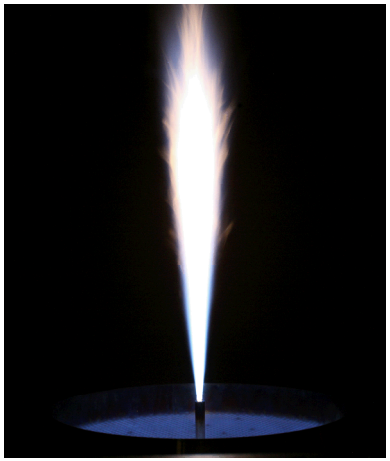
Performed preliminary testing performed with oxidizers of pure oxygen and with 50% O_2 in N_2, using an overall equivalence ratio of 1, with a constant methane flow

- 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)

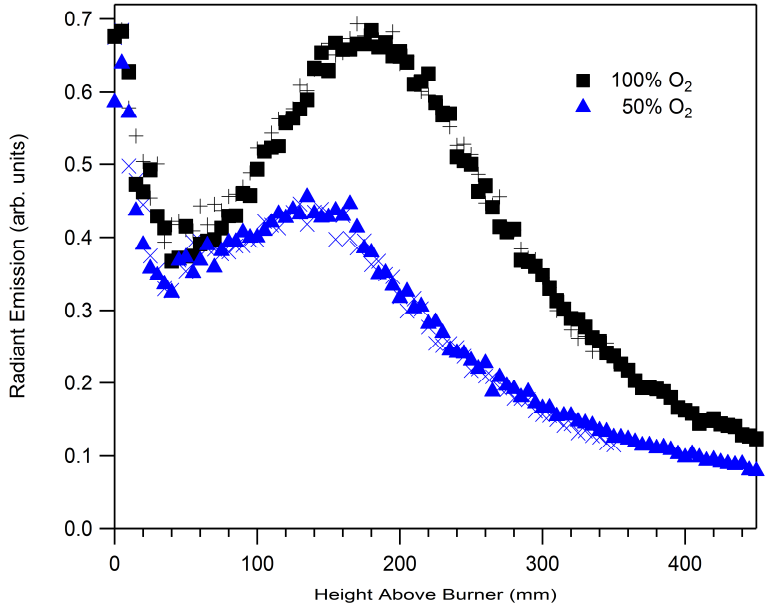
50% O_2 in N_2



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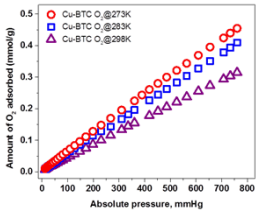
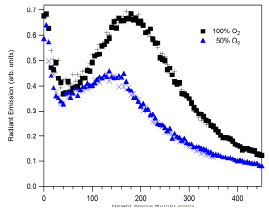
MOF adsorption isotherms (N_2 & O_2) (from MOF team)



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



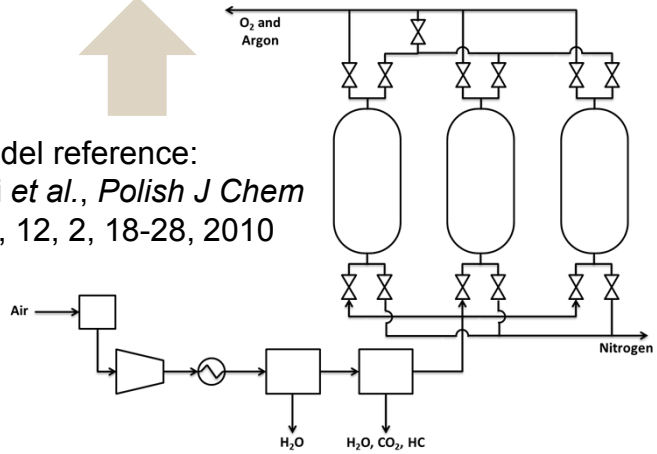
Can MOF-based PSA reduce energy consumption by 5% vs. conventional PSA air separation?

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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Conclusions and future work

- 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
- O_2 preferentially adsorbs over N_2 at 77K
- The trend is reversed at 298K, where N_2 preferentially adsorbs over O_2
- The Fe/Cu-BTC sample is an unique case in the room temperature range, with very significantly higher N_2 binding energy over O_2 at lowest loadings
- Future studies will focus on the synthesis of the most promising candidates identified by the DFT calculations

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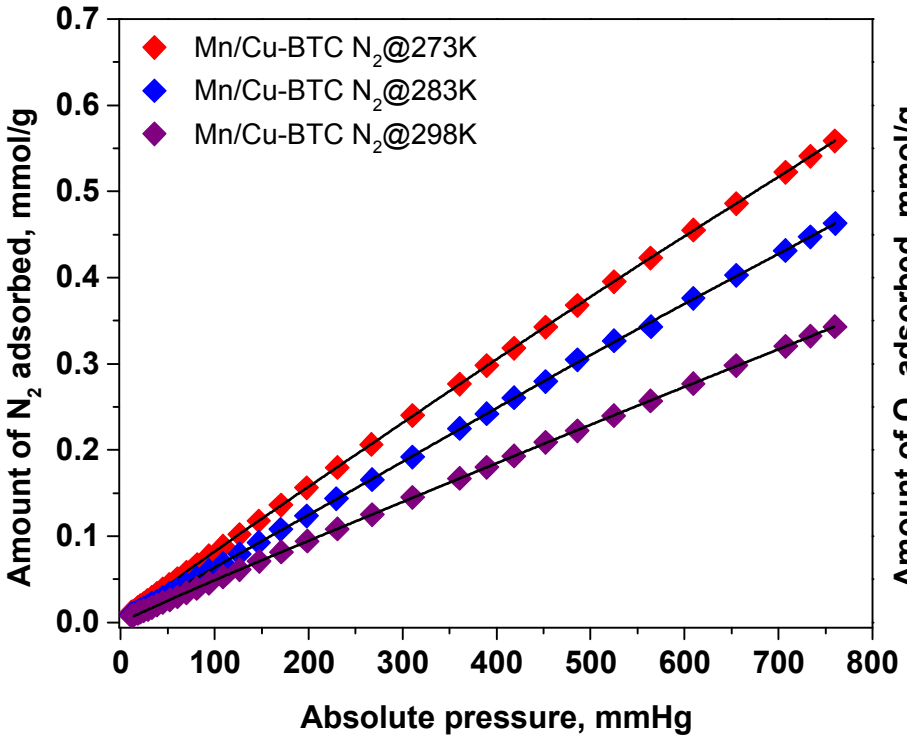
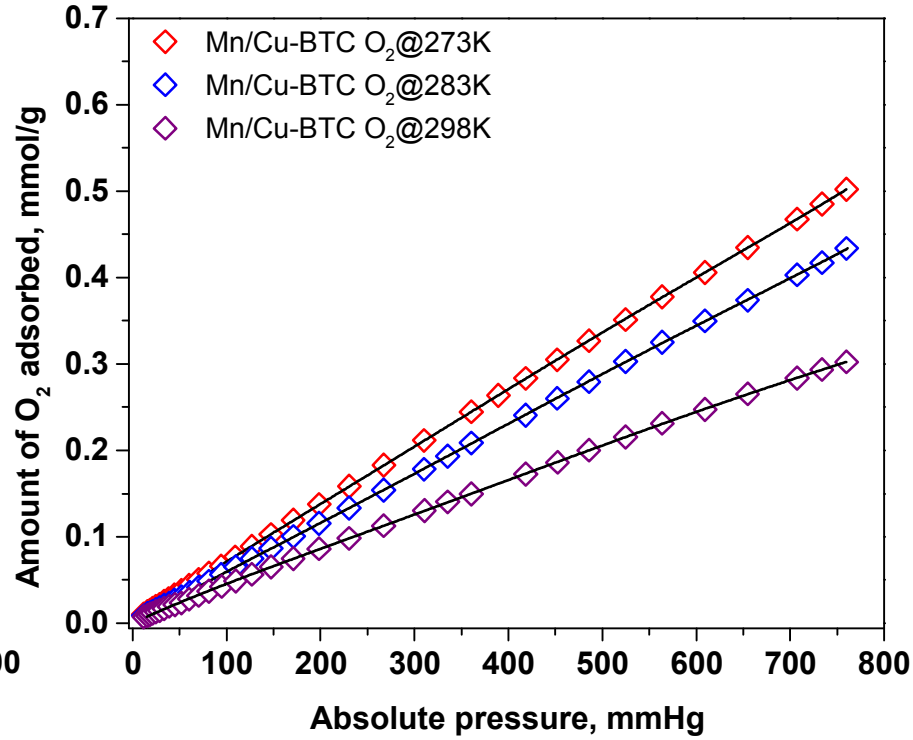
N_2 and O_2 adsorption isotherms measured at 273, 283, and 298K on pristine Mn/Cu-BTC





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

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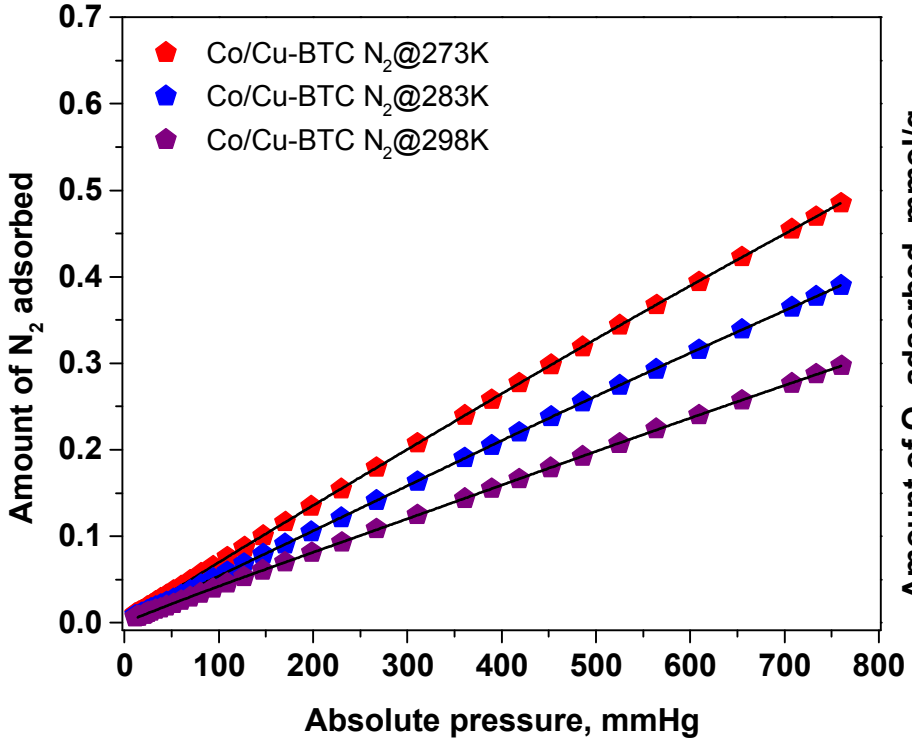
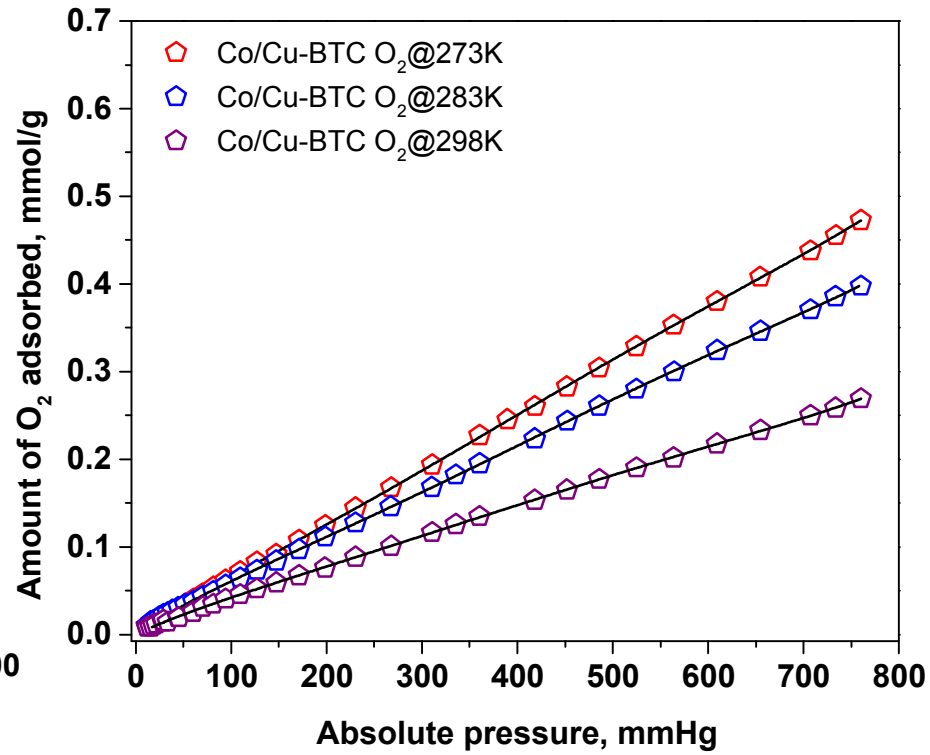
N_2 and O_2 adsorption isotherms measured at 273, 283, and 298K on pristine Co/Cu-BTC





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

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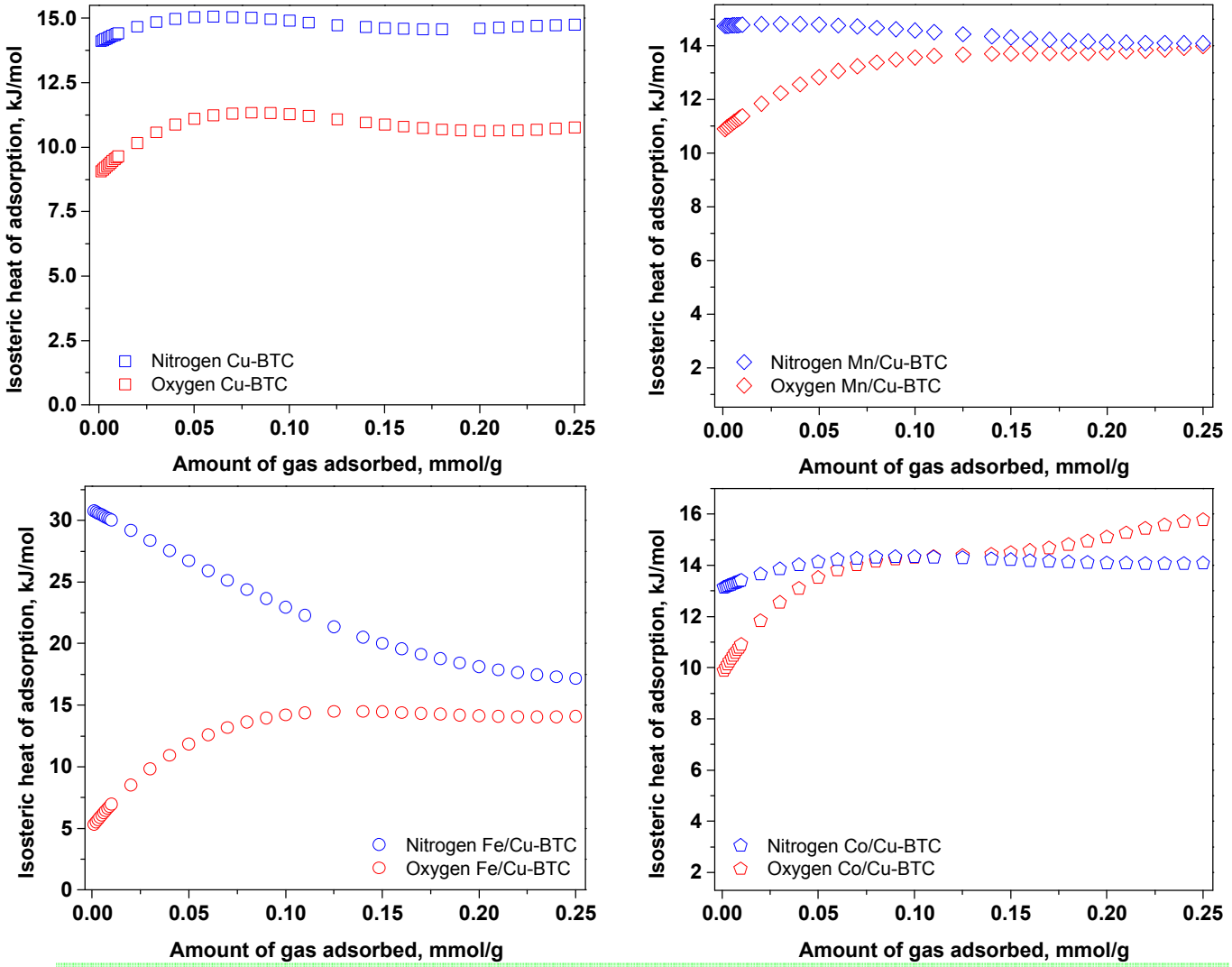
Significantly higher binding energy of N_2 over O_2 is noted for the Fe/Cu-BTC sample



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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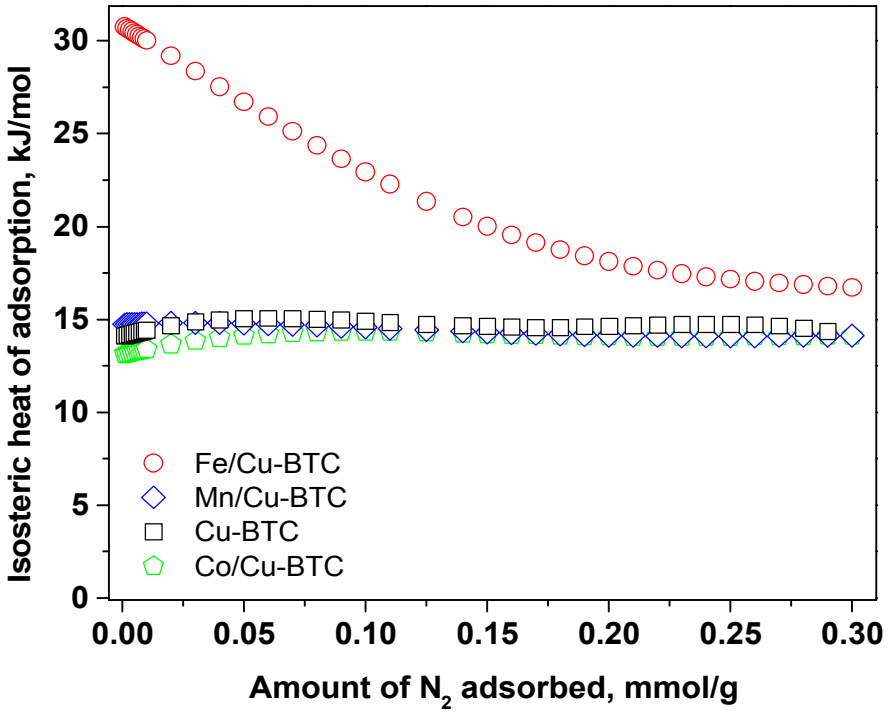

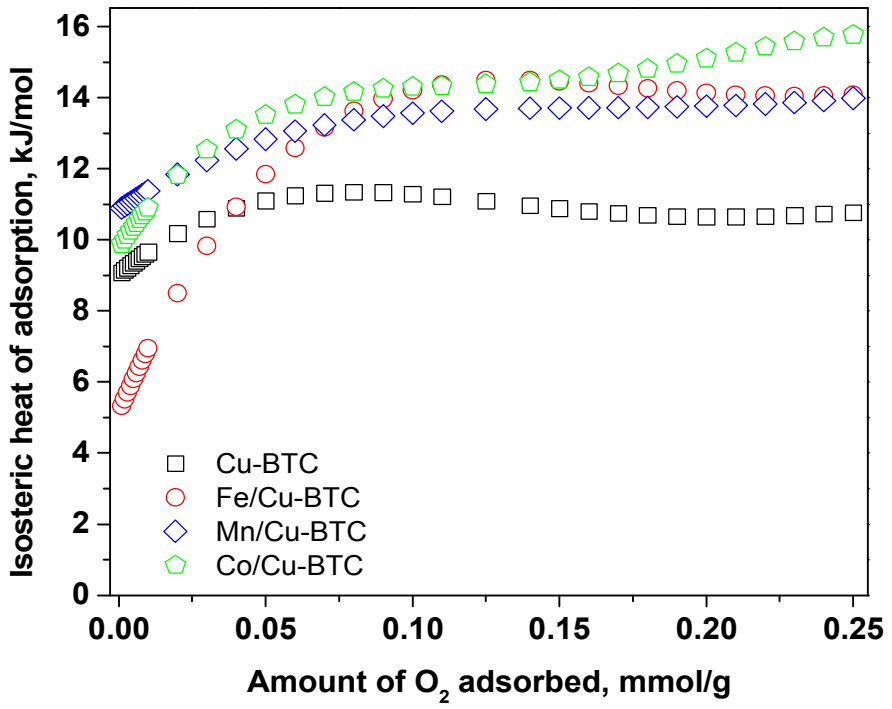

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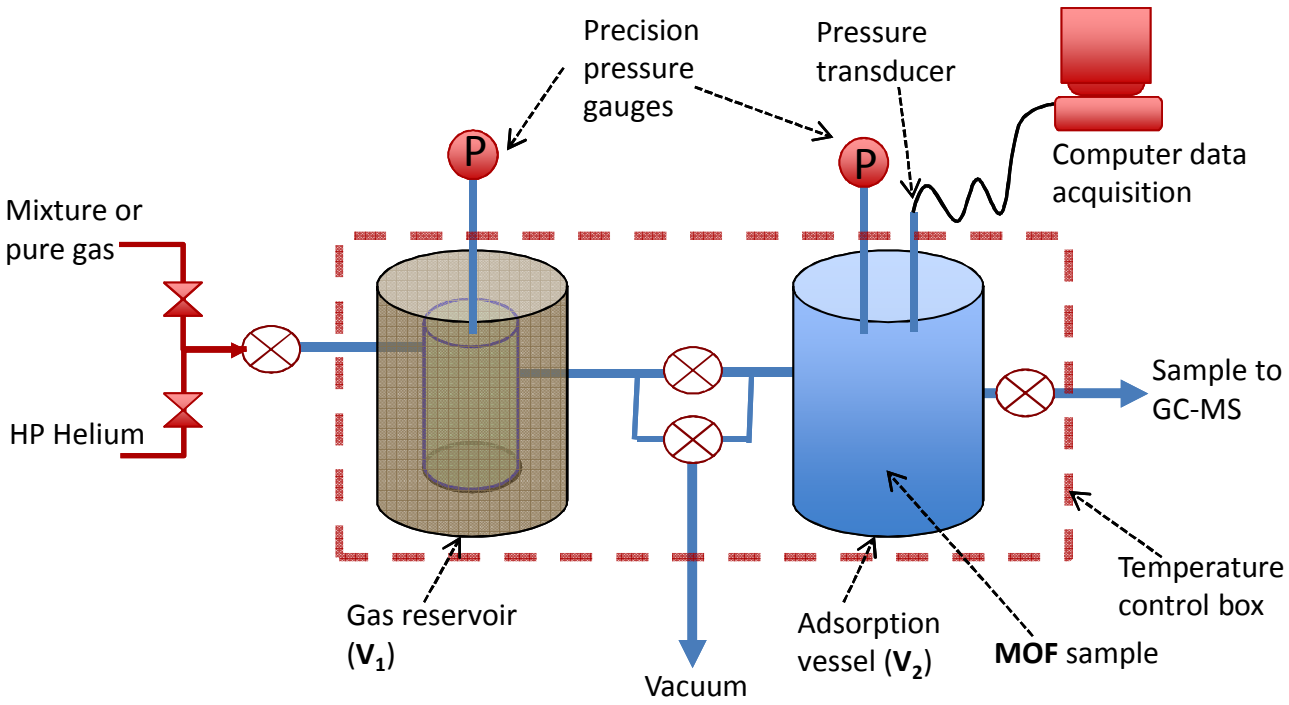
O_2/N_2 Gas mixture adsorption measurements containing 20% O_2 and 80% N_2

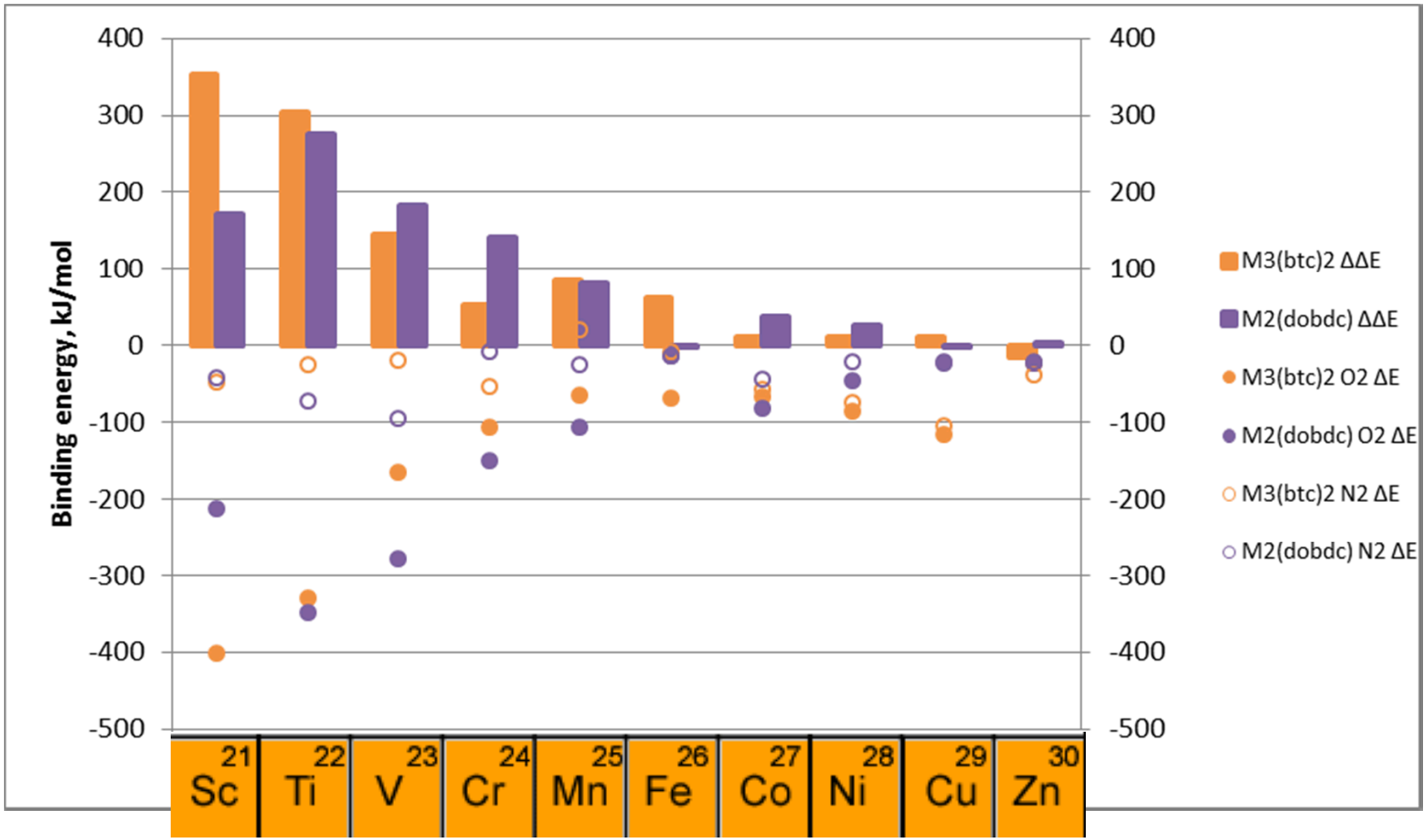


Room temperature (294K) in pressure range of 1.77 to 5.2 bars.

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

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



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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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