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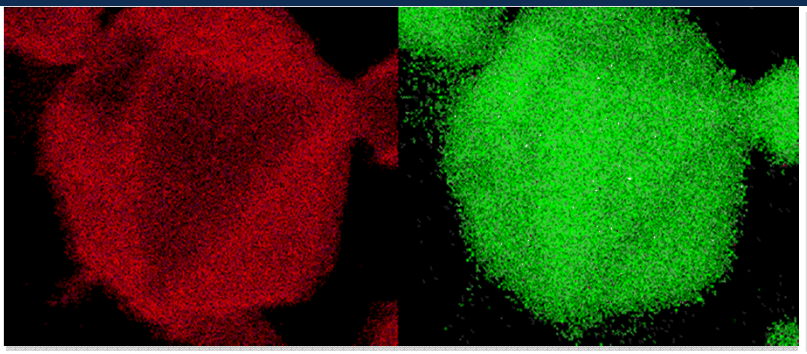

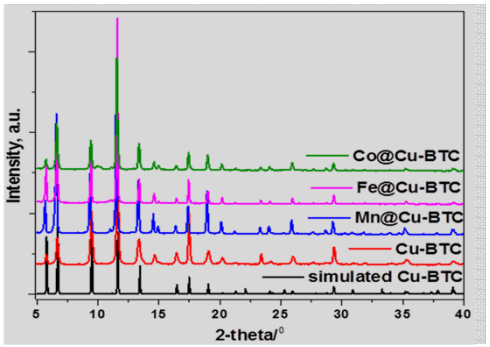

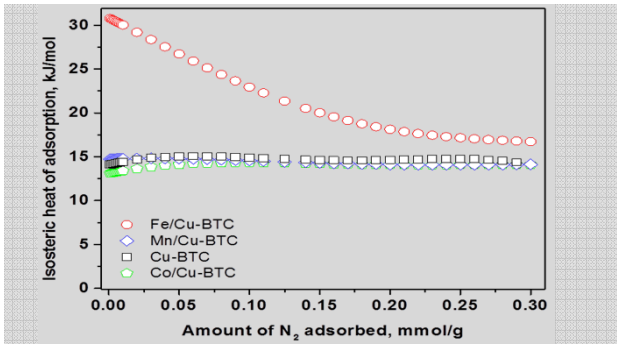

Oxygen Separations with MOFs via Predictive Modeling and Tuned Synthesis

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

November 13, 2014

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Outline

I. Nenoff Research Portfolio
II. Metal-organic Frameworks (MOFs) for Separations
III. O_2 separations for Oxyfuel Combustion
    a. Introduction
    b. Modeling
    c. Metal-substituted MOFs
    d. SMOF-7
    e. Oxyfuel, combustion and technoeconomic analysis
IV. Conclusions and Future Work

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I. Nenoff Portfolio

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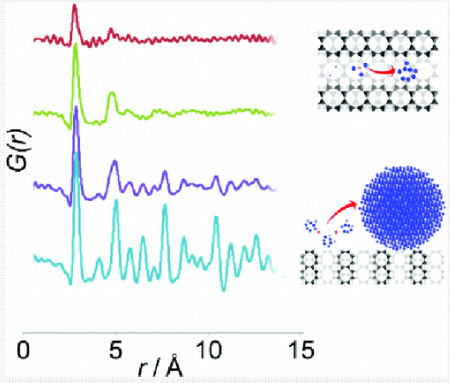
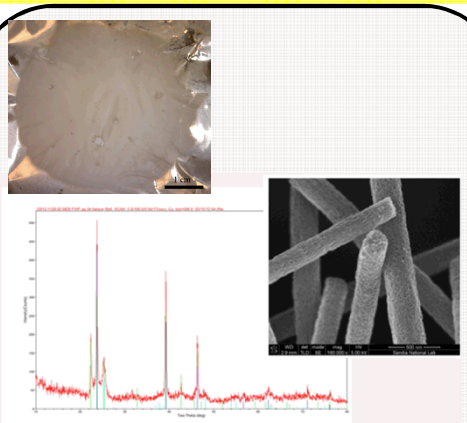
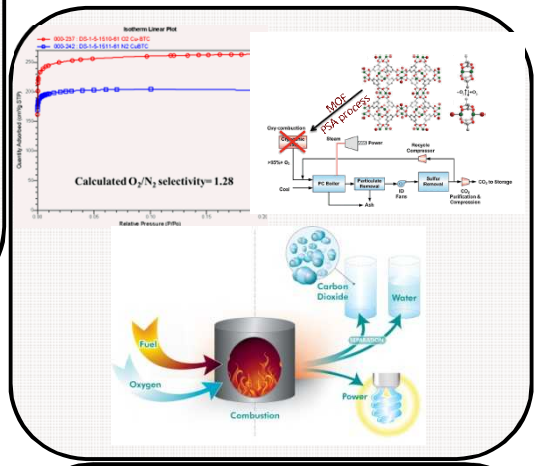
Nanoparticle Occluded Zeolites: Catalysis and Separations



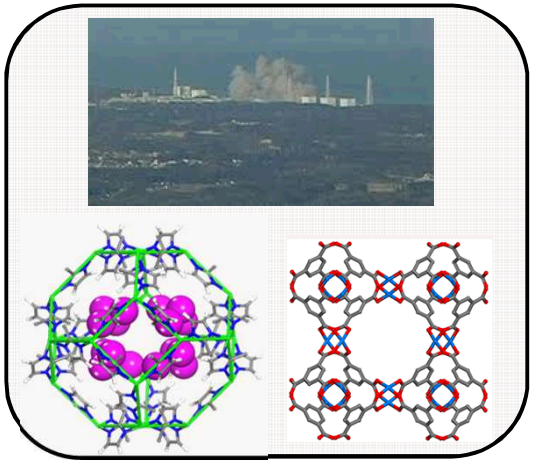
High Temperature Membranes for Gas Separations: Nanoporous Nanofibers



MOFs for Gas Separations & Use in Oxyfuel Combustion

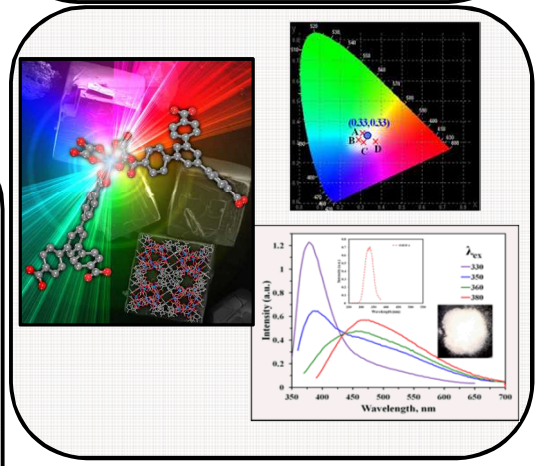


Materials design, synthesis, characterization, and testing



Volatile Radionuclides Capture

Nuclear Waste Glass & Ceramics



Solid-State Lighting

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Nanoparticle Occluded Zeolites: Catalysis and Separations

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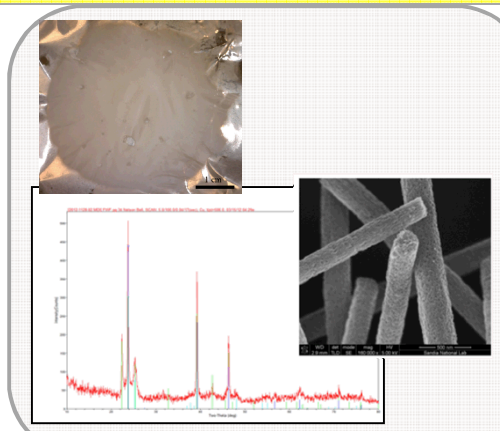
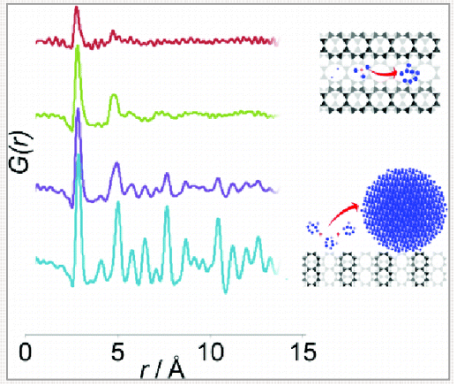
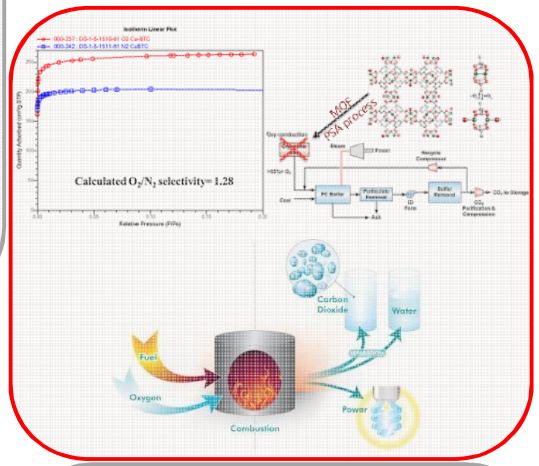
High Temperature Membranes for Gas Separations: Nanoporous Nanofibers





MOFs for Gas Separations & Use in Oxyfuel Combustion



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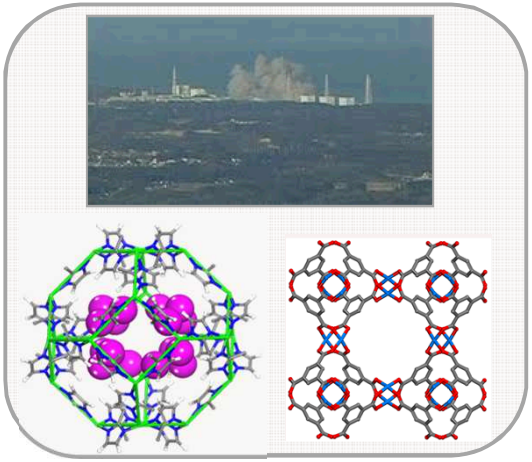

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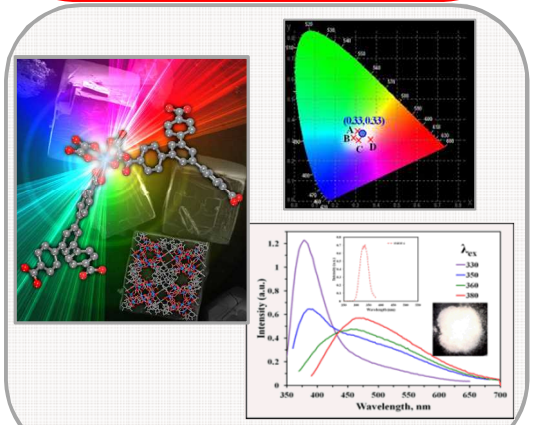

Solid-State Lighting

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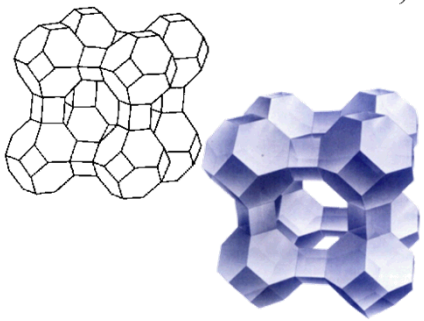
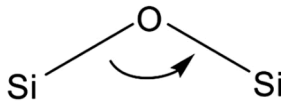
II. Metal-organic Frameworks (MOFs)

- Zeolite Structures are built from SiO_4 or $Si(Al)O_4$ tetrahedra linked through bridging oxygen atoms;
  >150 structures, SA ~ 100 m^2/g

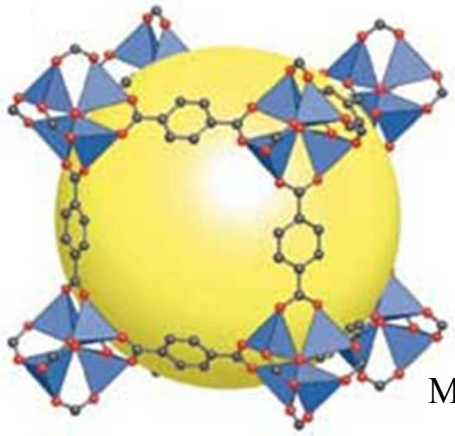


Zeolite 5A, opening ~3.5Å
$Na_{12}Al_{12}Si_{12}O_{48}\cdot 27H_2O$
commonly used in
PSA O_2 separations

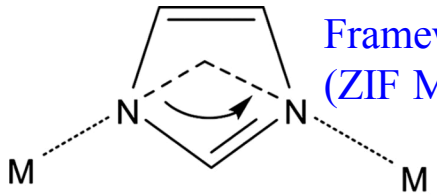


Si - O - Si

- Possible to build Metal-organic Frameworks (MOFs) with higher adsorption and selectivity by replacing zeolite linkers with transition metals and organics: Ultra high surface areas >1000 m^2/g

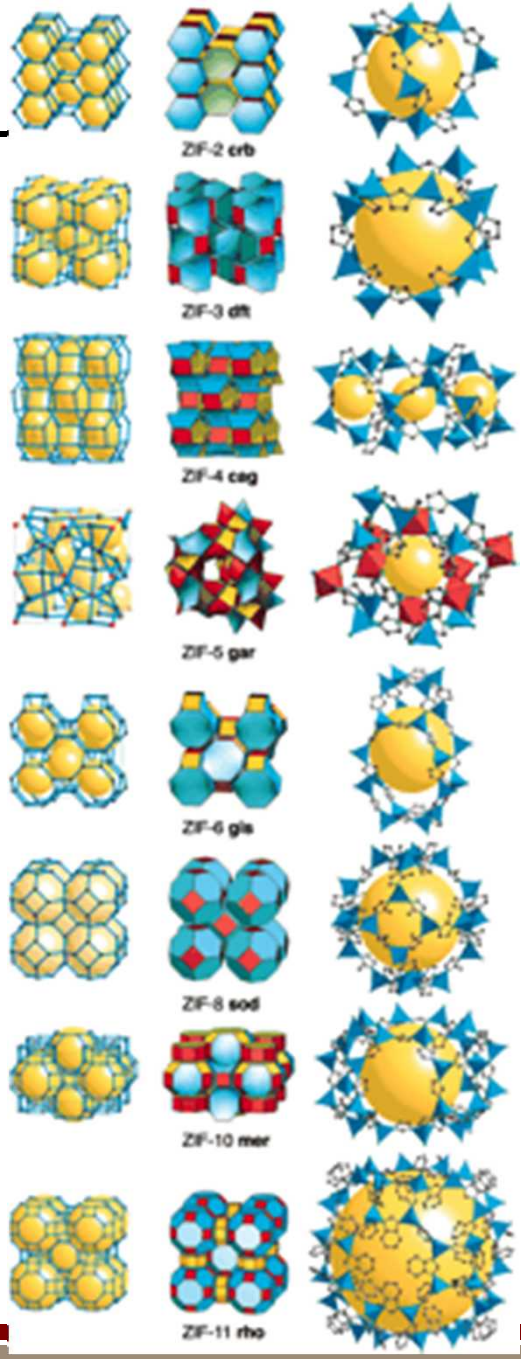


MOF-5: **$Zn_4O(BDC)_3$**, opening 13.8Å
BDC^{2-} =1,4-benzenedicarboxylate

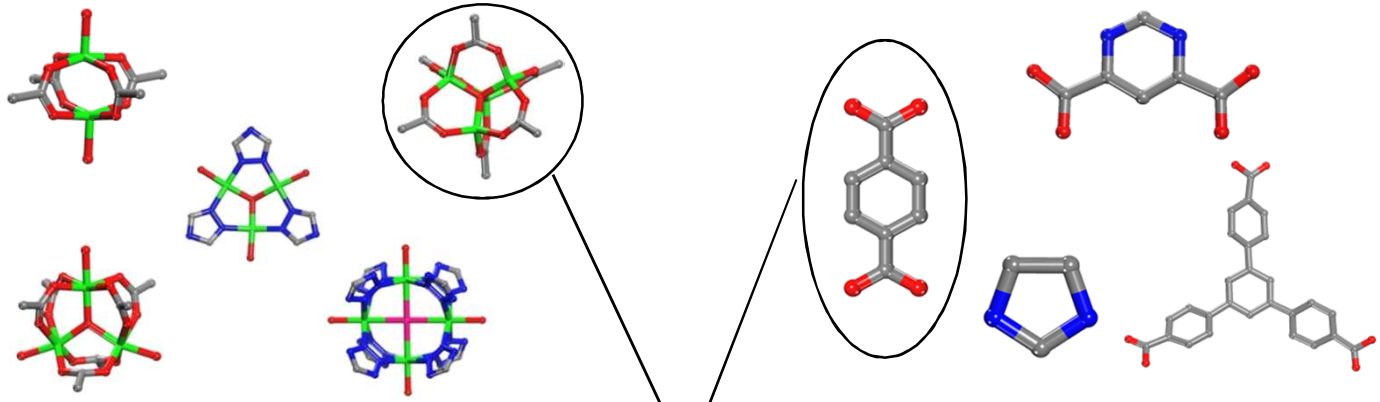


M - IM - M

eg. Zeolitic Imidazolate Frameworks (ZIF MOFs)

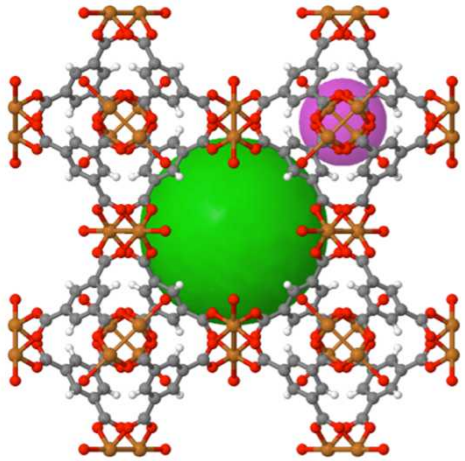


Metal-Organic Frameworks (MOFs)



Common metal clusters (molecular building blocks)

Organic Linking Units



HKUST-1 (Hong Kong University of Science and Technology), (Cu-BTC), is a metal organic framework (MOF) made up of copper nodes with 1,3,5-benzenetricarboxylic acid struts between them. The spheres represent the pore size within the framework which can be used for gas storage.

Mild Synthesis:[1]
Cupric nitrate, H_2O
BTC, EtOH/H_2O,
Solutions mixed
110°C, 18 hrs
Xtals washed in H_2O/EtOH
Air dried

1. Chui, et. al., Science 1999, 283(5405), 1148-1150

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IIIa. Introduction: O_2 Separations for Oxyfuel Combustion

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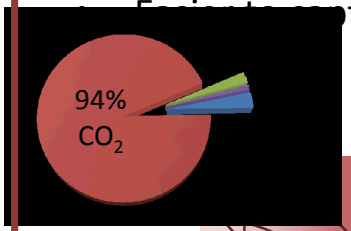
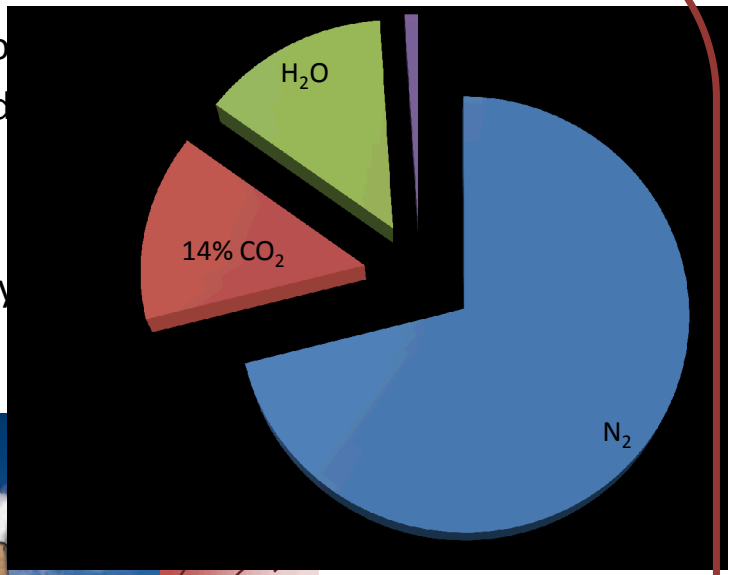
Oxyfuel for cleaner power plants

Benefits of using **oxyfuel** in po

- Flue gas volume decreased
- Decreased NO_x emissions
- Greater thermal efficiency
- Increased energy efficiency
- Easier to capture CO_2





Oxyfuel (95% O_2)

Air (78% N_2, 21% O_2)

Stock photo from www.shutterstock.com.

The generation of **oxygen-enriched air** is currently done by cryogenic distillation, an energy-intensive and expensive process.[2]

1. Hu, Y. CO_2 Capture from Oxyfuel Combustion Power Plants, Licentiate Thesis, KTH Royal Institute of Tech, Stockholm, Sweden, 2011
2. Wang, W.; Yang, J; Li., L.; Li, L. *J Funct. Mater. Lett*. 2013, *6*(1), 1350004.

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Potential Efficiency Improvement of MOFs Oxygen-from-Air-Separation Relative to State-of-the-Art

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Cryogenic Air-Separation Unit (ASU) is state-of-the-art, but suffers from high power losses (primarily compression)

For example, for a 600 MW_e (gross) oxy-fuel power plant, 100 MW_e will be consumed by air-separation, resulting in an efficiency decrease of 10 percentage points [1-2]

Similarly, for application to a glass melting furnace, Schepp[3] estimates oxygen production accounts for ≈ 10% of energy use

MOFs-based air separation, with its minor power requirements for pressurization, is anticipated to ensure major energy and cost savings

target: 25% savings

Air Liquide cryogenic ASU at Callide 30 MW_e Oxy-Fuel Power Plant Demonstration

1. Pfaff, Kather, *Energy Procedia*, 2009, 1(1), 495; 2. Xiong et al., *Energy & Fuels*, 2011, 25(5), 2405;
3. Schepp, *69th Glass Conf.*, 2009

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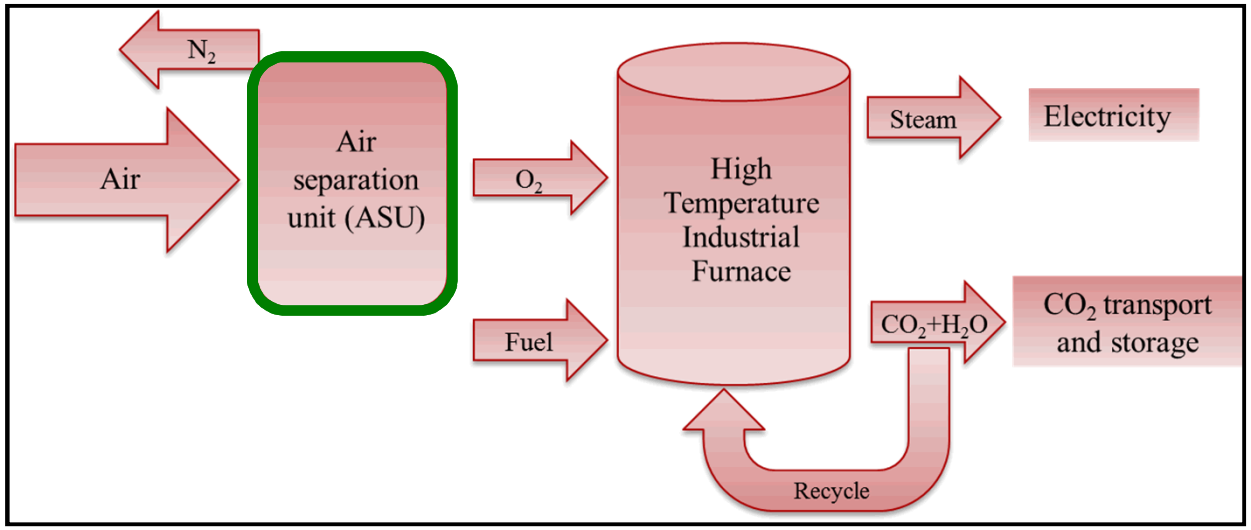
O_2/N_2 air separations with MOFs to Increase the Efficiency of the *ASU*



Process Development:
MOFs to replace zeolites in PSA Processes for the energy efficient production of pure O_2 from air at temperatures up to ambient.

- Oxygen-enriched (oxy-fuel) combustion: burning the fossil fuel in an O_2 rich atmosphere resulting in high efficiency burning, easily captured CO_2, little/no NO_x production
- Purification of O_2 limiting step:
  (1) Cryogenic, costly & energy intensive process (primarily compression) for high purity O_2 (99.9%),
  (2) Pressure Swing Adsorption (PSA), use of zeolites for less costly separation but lower purity O_2 (94%)
- Replace Zeolites in PSA with ***high surface area, high capacity and high selectivity***
  Metal-organic Framework (MOFs) for O_2 separation from air

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

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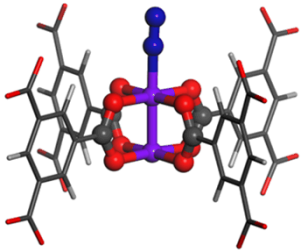
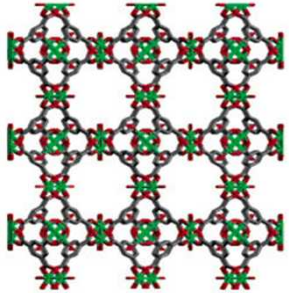
Predictive molecular modeling

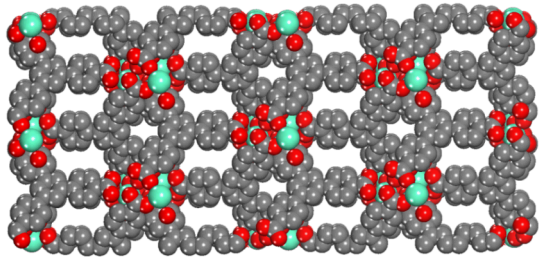
Predictive molecular modeling designed to *measure the binding energy for O_2 and N_2* on coordinatively unsaturated metal sites in MOFs

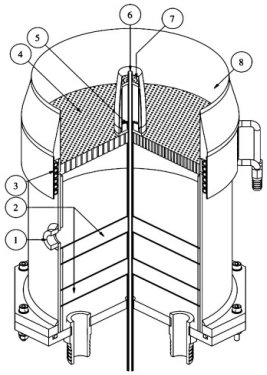


Materials development

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







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

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

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

Techno-Economic Modeling

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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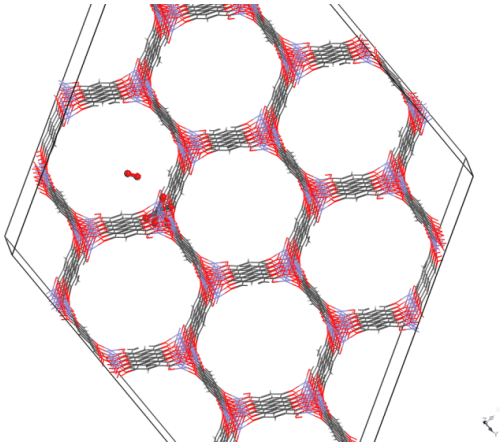
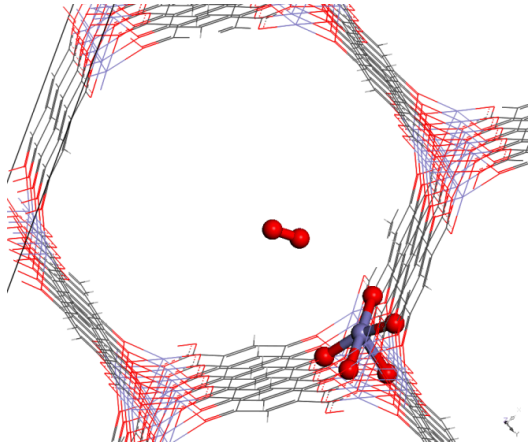
III b. Modeling: DFT Simulations

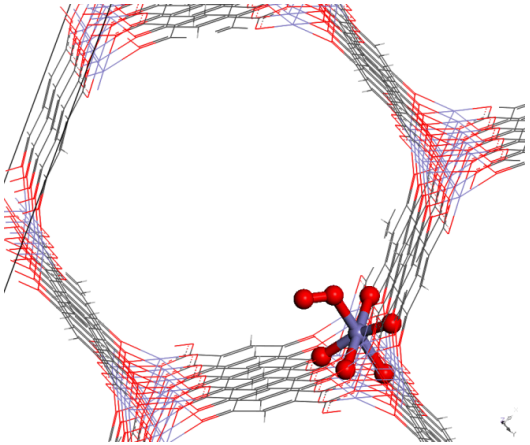
- ***Molecular-level Details of Metal-O_2 and Metal-N_2 Binding Energies and Geometries***
- MOFs with coordinatively unsaturated metal centers are promising materials for O_2/N_2 separations
- Two prototypical MOFs from this category, $Cr_2(BTC)_3$[1] (***HKUST-1***) and $Fe_2(DOBDC)$[2] (***MOF-74***)
- 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

1. *J. Am. Chem. Soc.* **2010**, *132*, 7856–7857
2. *J. Am. Chem. Soc.* **2011,** *133*, 14814-14822

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

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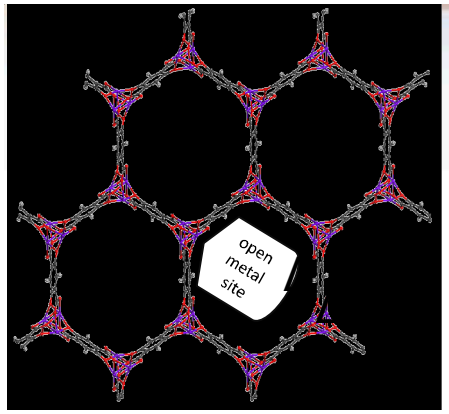
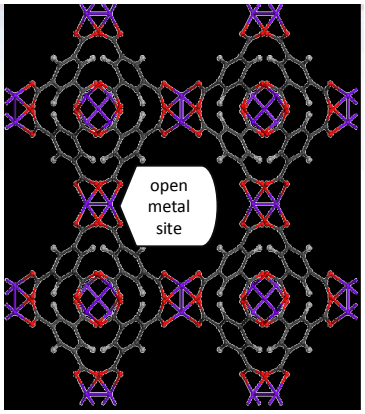


M_2(dobdc)



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

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

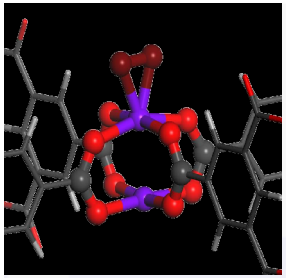
The **differences in binding energies ($\Delta\Delta$ E)** for oxygen and nitrogen were calculated by

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

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

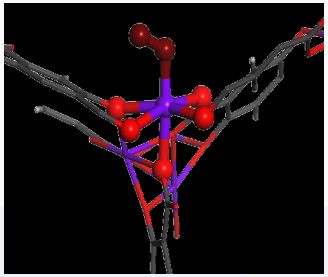
Attention Paid to Bonding Geometries

Side-on bonding
∡M-X-X 67° - 71°



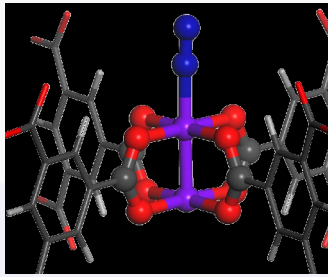
$Cr_3(btc)_2(O_2)$

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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Sandia Red Sky Super Computer: Transition Metal-MOF-O_2 or N_2 Screening

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Bonding geometry as a function of metal

Bonding geometries of O_2 binding to $M_3(btc)_2$

Metal (M)	Binding Energy (kJ/mol)	M-O Distance (Å)	Bonding Mode*
Sc	-402	1.91	Side-on
Ti	-331	1.85	Side-on
V	-165	1.83	Side-on
Cr	-107	1.98	Side-on
Mn	-66	1.87	Bent
Fe	-70	1.97	Bent
Co	-68	1.93	Bent
Ni	-87	1.95	Bent
Cu	-116	2.32	Bent
Zn	-25	2.27	Bent

Bonding geometries of O_2 binding to $M_2(dobdc)$

Metal (M)	Binding Energy (kJ/mol)	M-O Distance (Å)	Bonding Mode*
Sc	-214	1.93	Side-on
Ti	-350	1.83	Side-on
V	-279	1.86	Side-on
Cr	-150	1.83	Side-on
Mn	-107	1.88	Bent
Fe	7	2.04	Bent
Co	-82	1.84	Bent
Ni	-48	1.95	Bent
Cu	-23	2.35	Bent
Zn	-25	2.28	Bent

Bonding geometries of N_2 binding to $M_3(btc)_2$

Metal (M)	Binding Energy (kJ/mol)	M-N Distance (Å)†	Bonding Mode*
Sc	-47	2.24	Bent
Ti	-27	2.36	Bent
V	-21	2.28	Linear
Cr	-36	2.73 (nb)	Bent
Mn	52	2.32	Linear
Fe	-8	1.96	Linear
Co	-57	1.95	Linear
Ni	-76	1.99	Linear
Cu	-105	2.34	Bent
Zn	-39	2.22	Linear

Bonding geometries of N_2 binding to $M_2(dobdc)$

Metal (M)	Binding Energy (kJ/mol)	M-N Distance (Å)†	Bonding Mode*
Sc	-43	2.36	Linear
Ti	-74	2.07	Linear
V	-96	1.98	Linear
Cr	-10	1.88	Linear
Mn	-26	2.37	Bent
Fe	-14	3.58 (nb)	Bent
Co	-46	1.93	Linear
Ni	-17	2.92 (nb)	Bent
Cu	-24	2.92 (nb)	Bent
Zn	-22	2.64 (nb)	Linear

* Side-on bonding mode corresponds to M-X-X angle 67°-71°; Bent bonding mode corresponds to M-X-X angle 94°-159°; Linear bonding mode corresponds to M-X-X angle 165°-179°.

† (nb) indicates that the M-X interatomic distance is too long to represent a bonding interaction.

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Transition to Quantum Calculations to Estimate Metal-Oxygen Binding Energy

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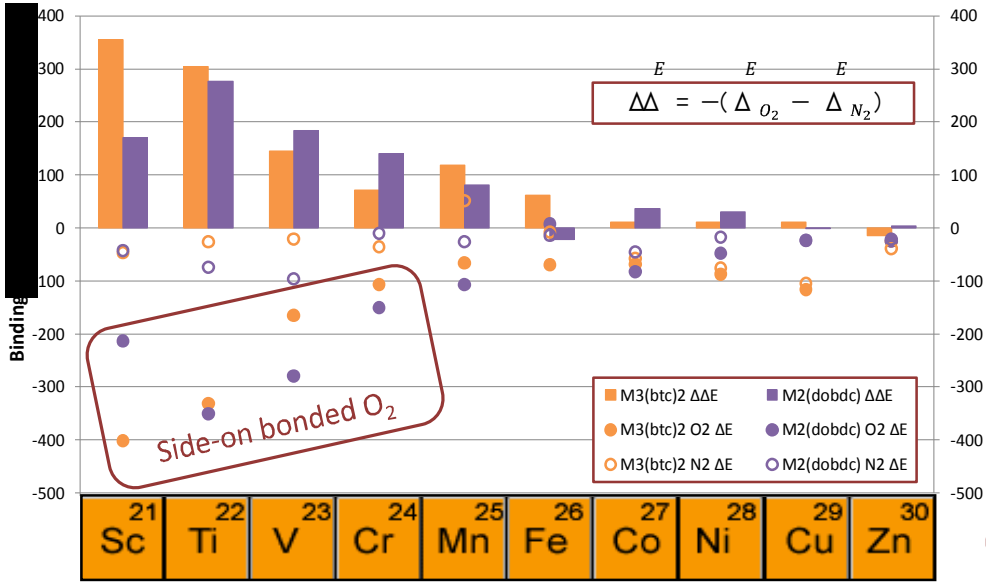
Binding Energy Calculated as a Function of Metal Site

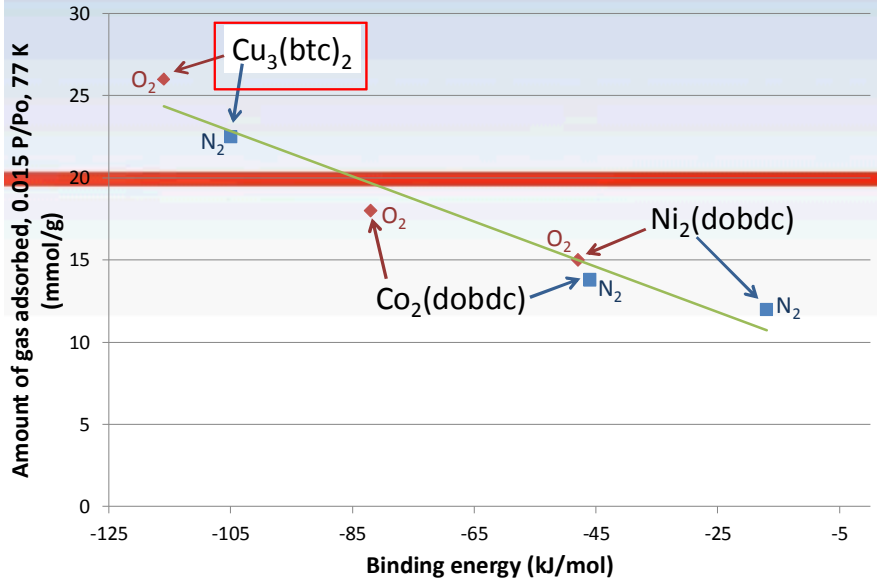


Parkes, M.; Sava Gallis, D. F.; Greathouse, J.A.; Nenoff, T.M. "Screening MOFs for O_2/N_2 Separations: Role of MOF Metal Center", **2014**, in preparation.

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.

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MOFs Platforms Used for O_2/N_2 Sorption Studies: Known/Literature and Sandia

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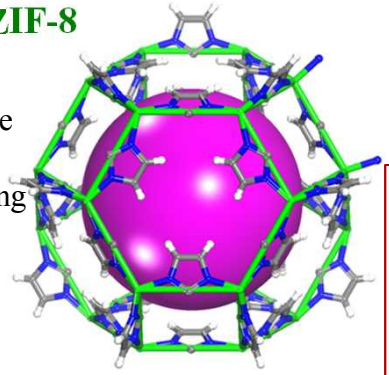
O_2: 3.46Å ; N_2: 3.64Å

Al-MIL-53

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

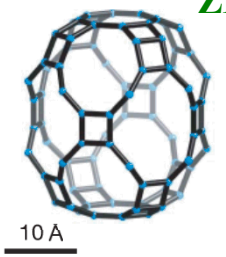
Open Metal Centers

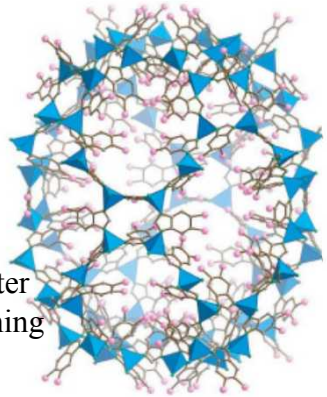
ZIF-8



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

ZIF-95



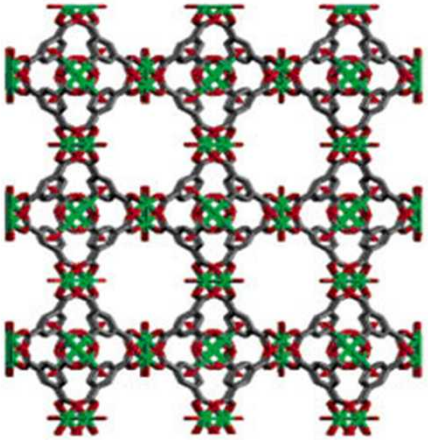


24 Å pore diameter
3.65 Å pore opening
1240 m^2/g

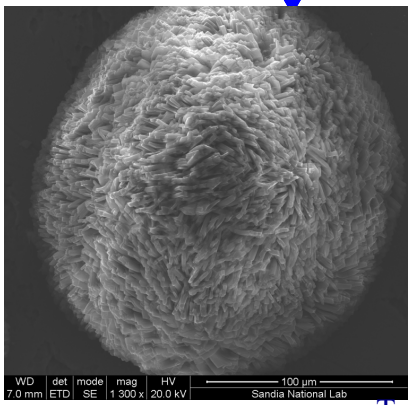
Fe-HKUST

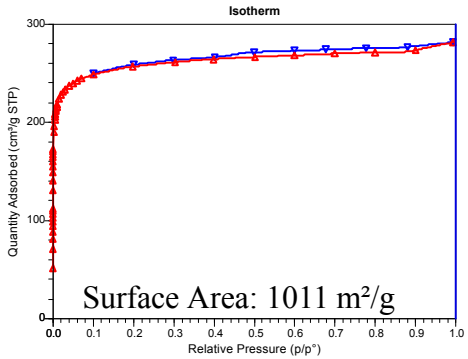
Fe-BTC

Cu-BTC



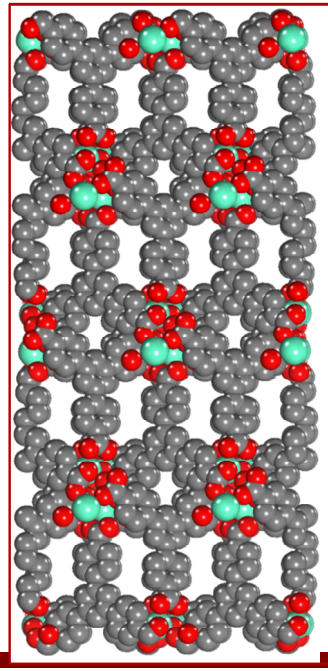
SMOF-3





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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III c. Metal Substituted MOFs: Targeted Synthesis of Porous Mn-, Fe- and Co- Cu-BTC

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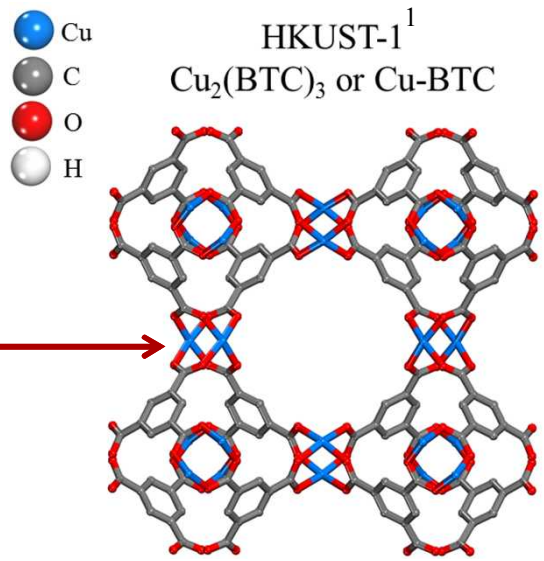
MOF metal centers can be considered as ***Site isolated molecular units.*** Mild reaction ***ion exchange*** without detriment to the entire MOF framework unit

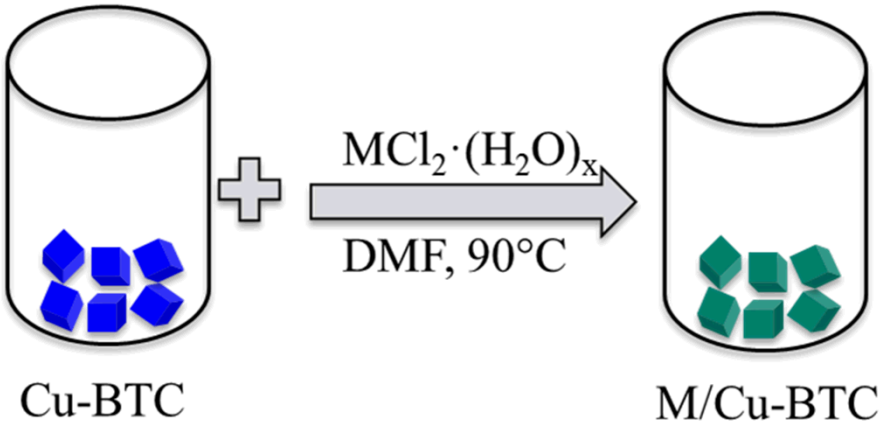


MOF metal Substitution with Retention of Porosity: 2 approaches

1. M-substituted Cu-BTC: Cr, Mo, Ru, Ni (Ru & Ni much lower than expected surface area of ~1100 m^2/g)

2.Porphyrin-templated Mn-, Fe- & Co-Cu-BTC analogues[2] known, *no measurable accessible porosity*

Postsynthetic metal ion exchange[3]



***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**, submitted, *Chem. Mater.*

1. Chui, S. S. Y et.al *Science* **1999**, 283, 1148.; 2. *J. Am. Chem. Soc.* **2012**, *134*, 928−933
3. Dinca, et al., *J. Am. Chem. Soc.* 2006, 128, 16876-16883.

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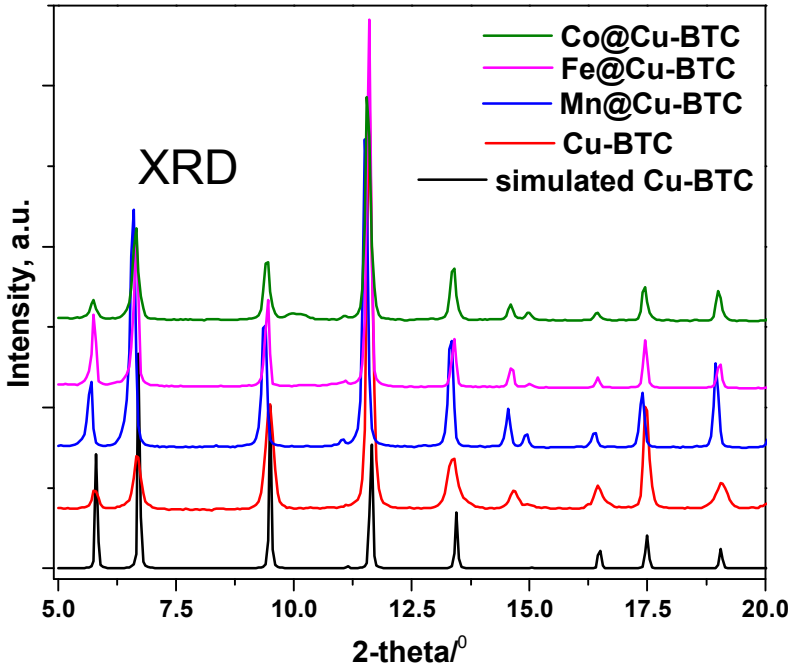
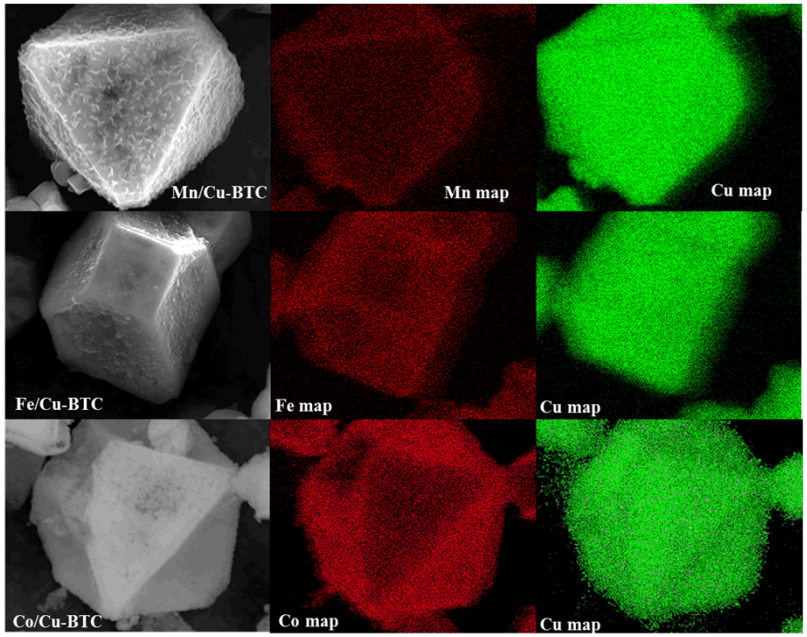
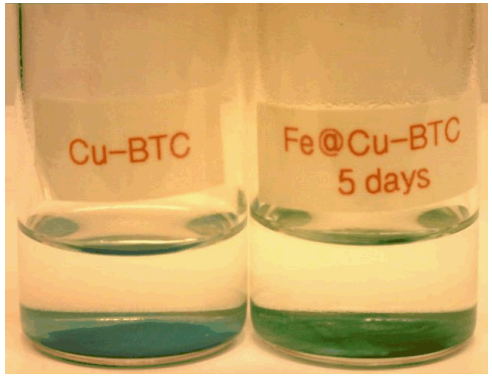
Confirmation of In-Framework Metal Substitution – Unit Cell Expansion & Elemental Mapping



	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

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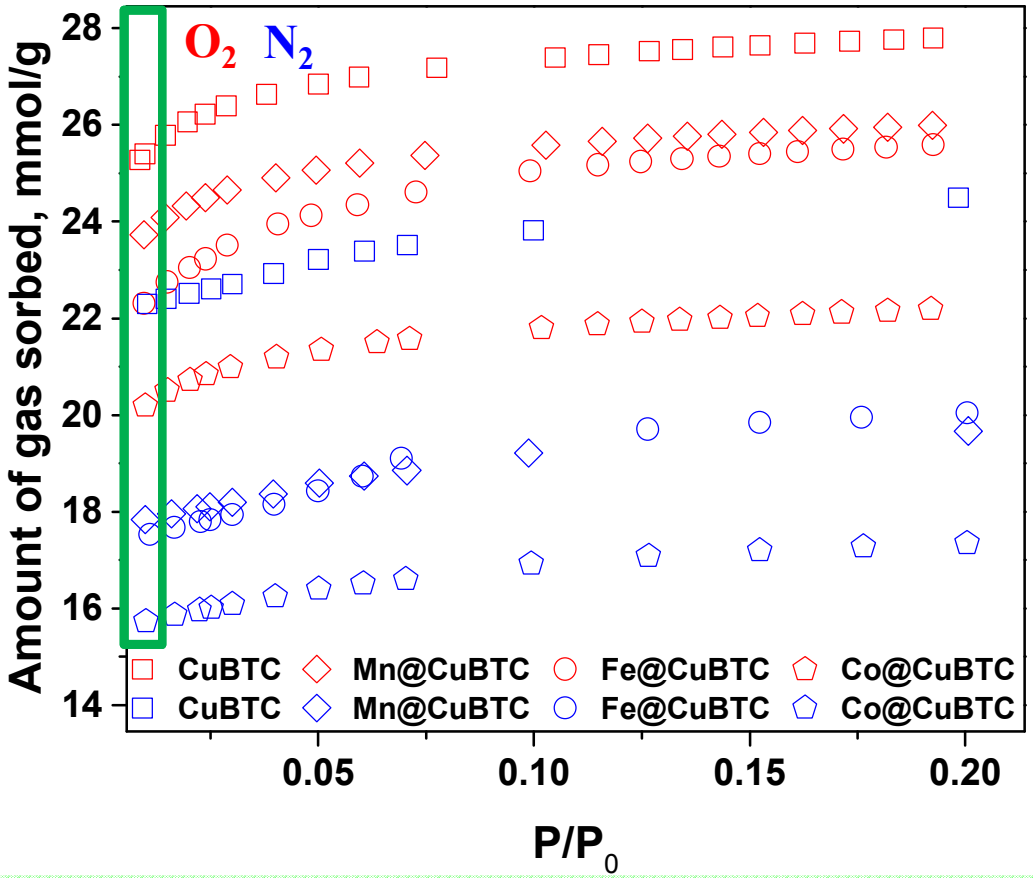
Cu>Mn>Fe>Co (DFT)
Cu>Mn>Fe>Co (exp)

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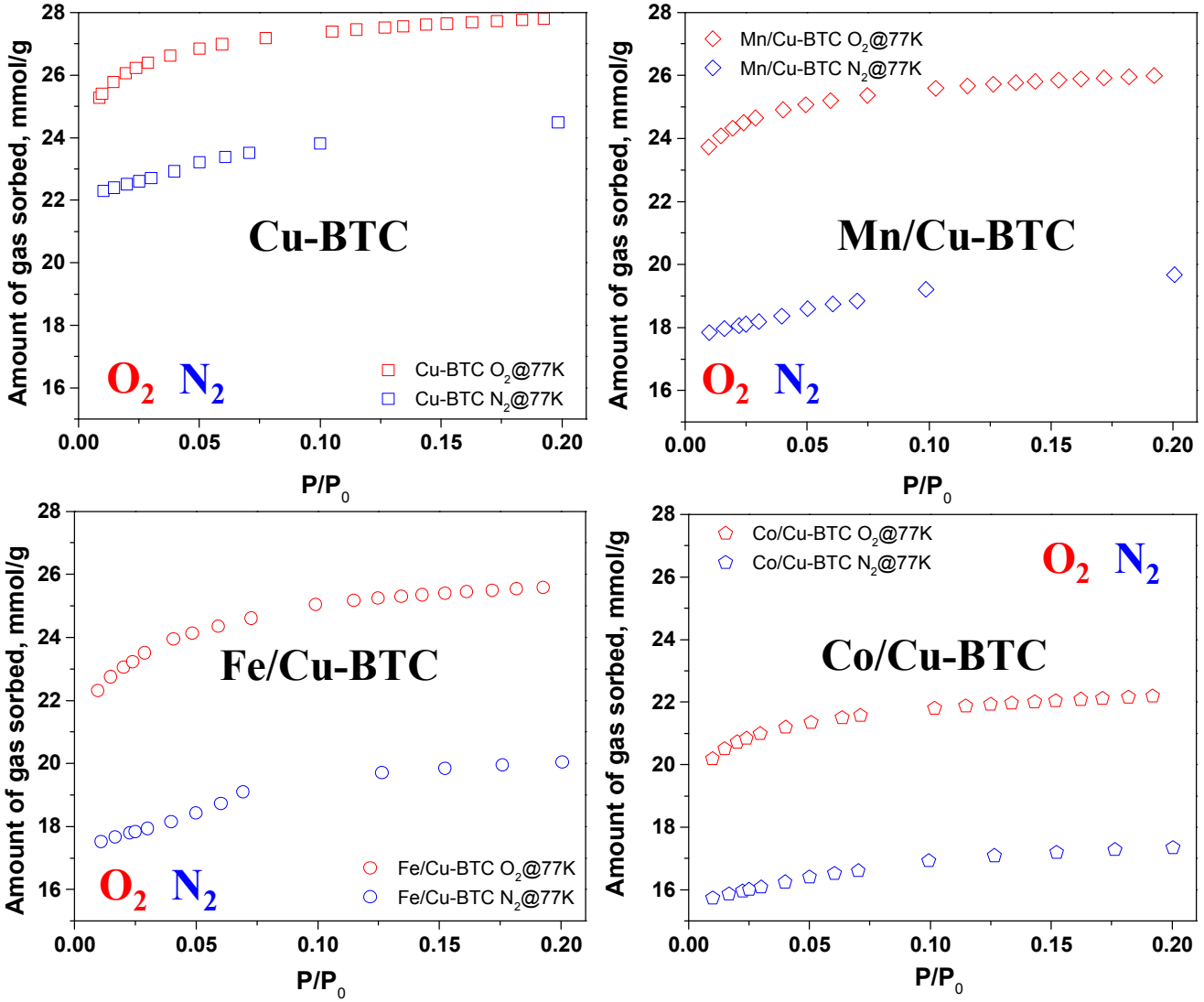
77 K: All Samples have ***Higher*** O_2 Loadings over N_2



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

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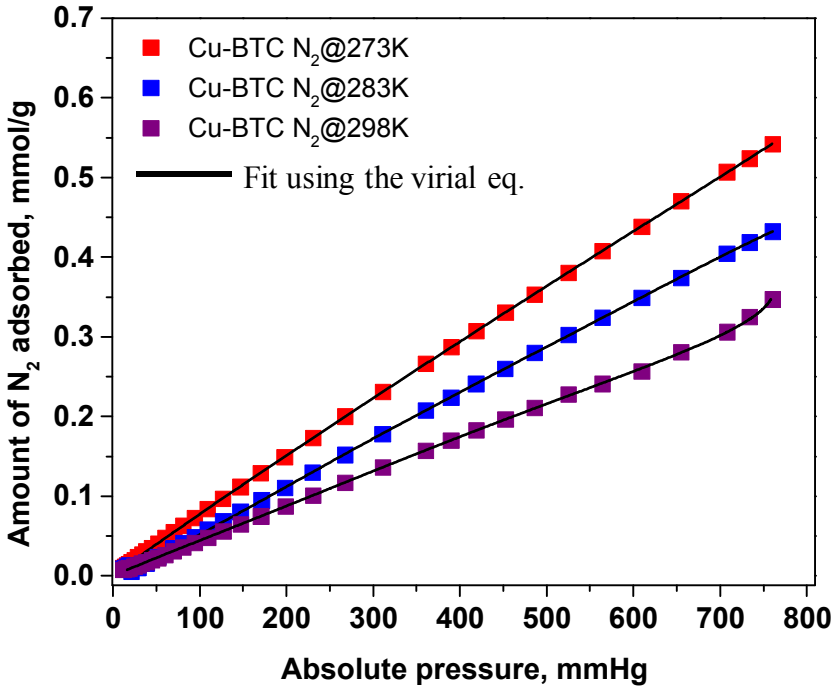
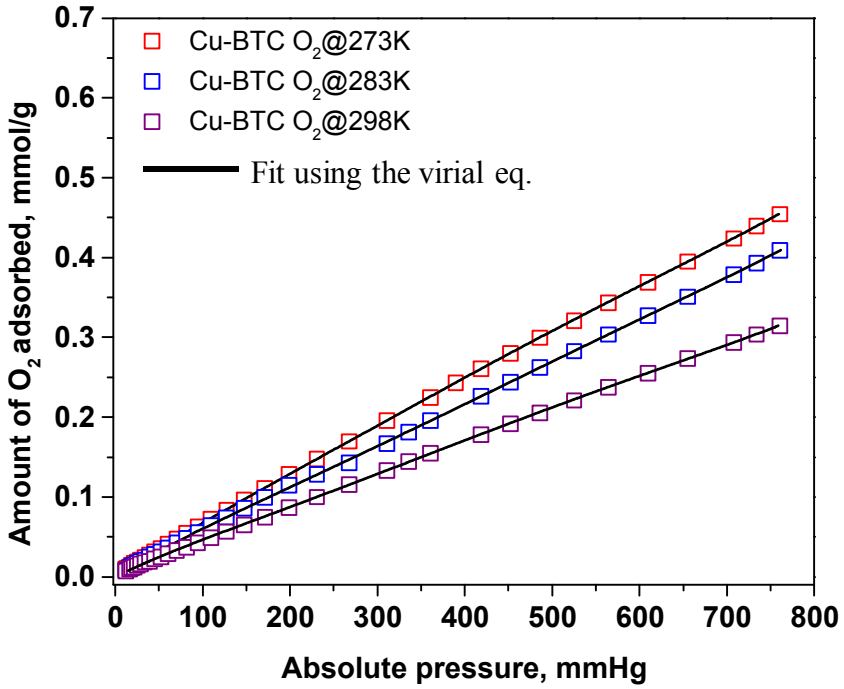
273-298 K: As Temperature Increases, O_2 Loadings Decrease Relative to N_2

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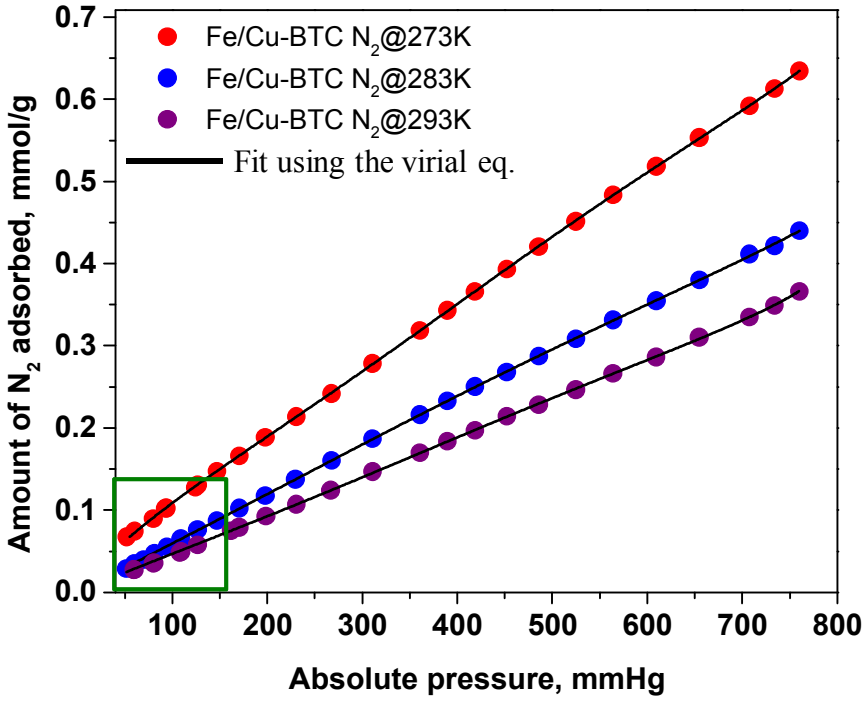
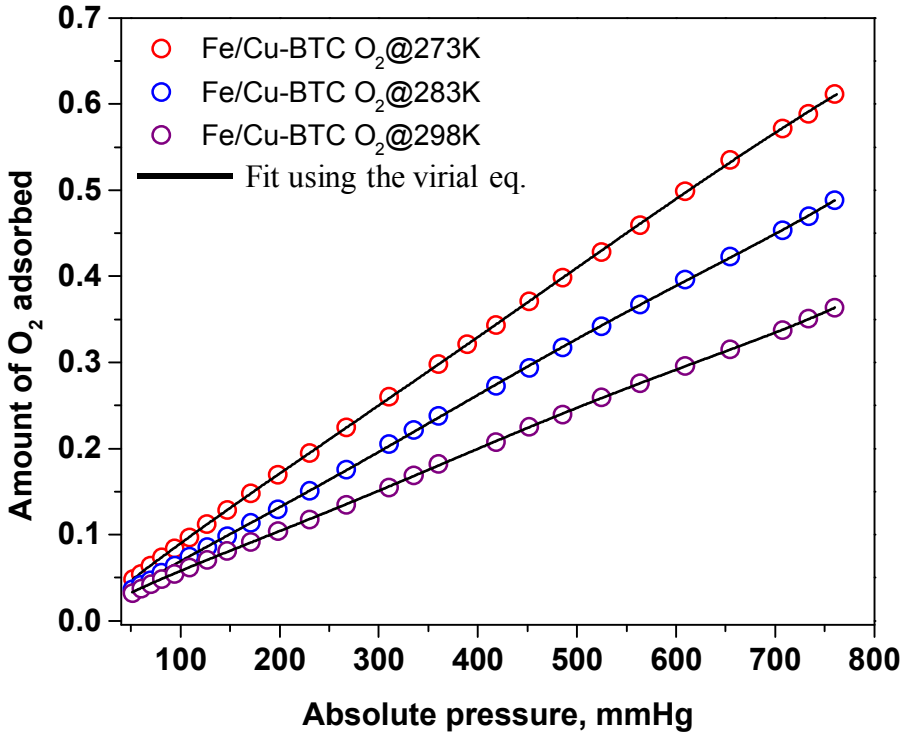
N_2@273 K in Fe/Cu-BTC Trend Deviation: Slightly Higher N_2 Uptake at Lowest Loading Levels (at lowest pressures)





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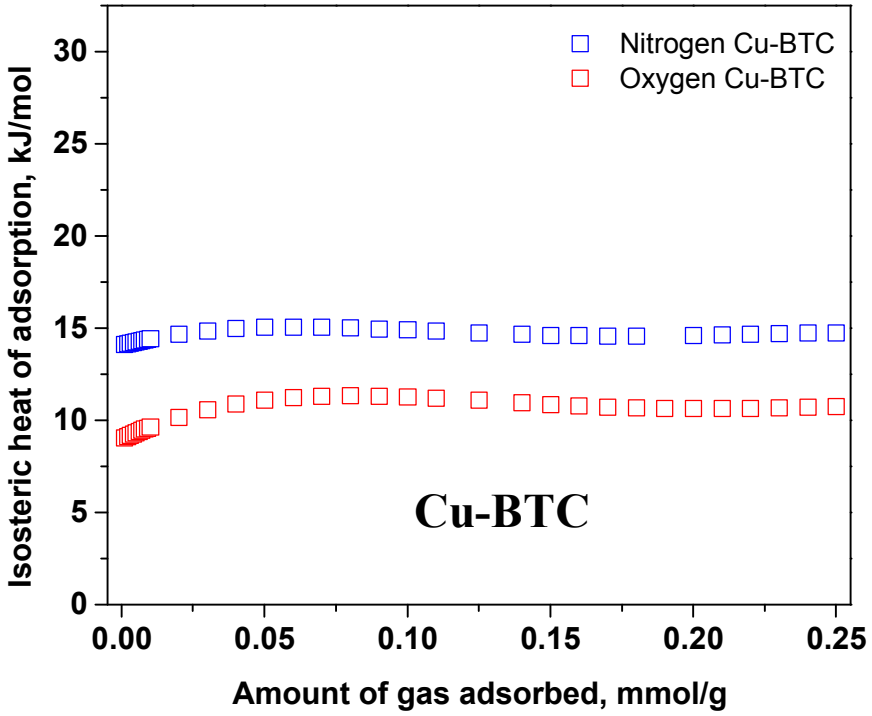
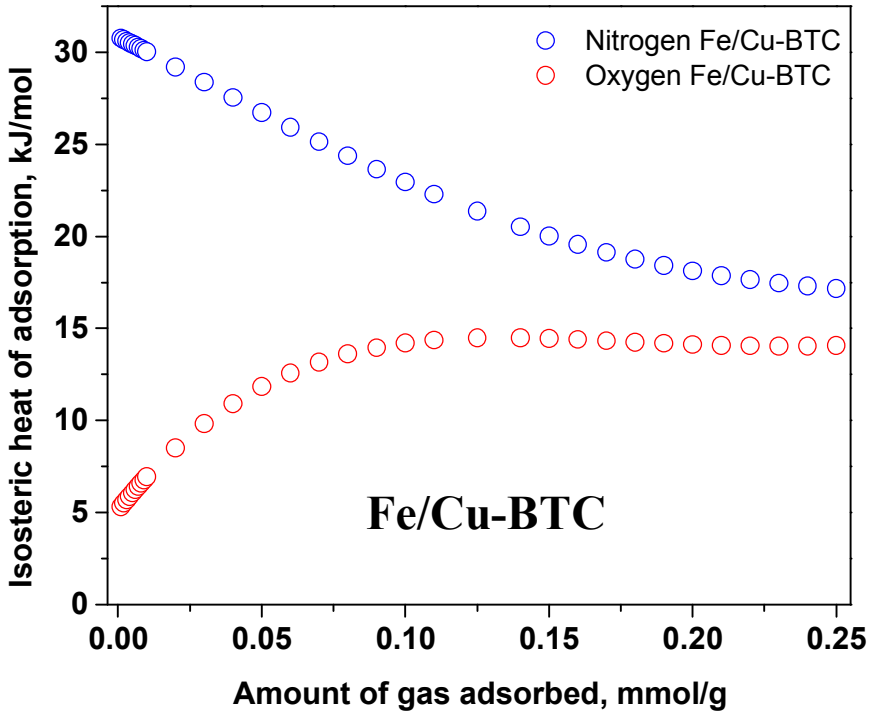
Isosteric Heats of Adsorption for O_2 (red) and N_2 (blue) Comparison of Cu-BTC vs Fe/Cu-BTC Data





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

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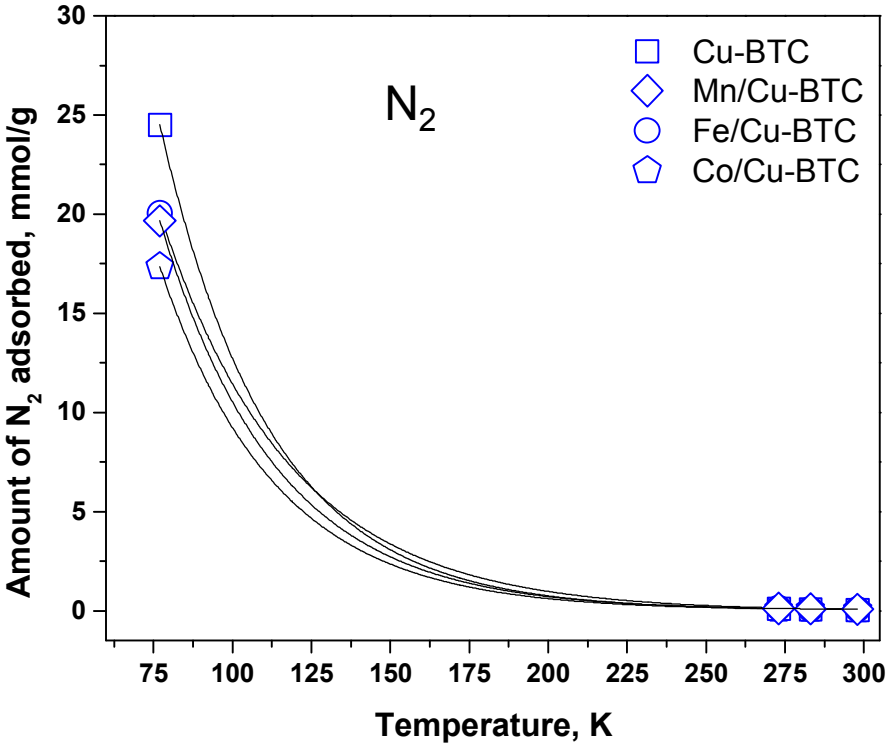
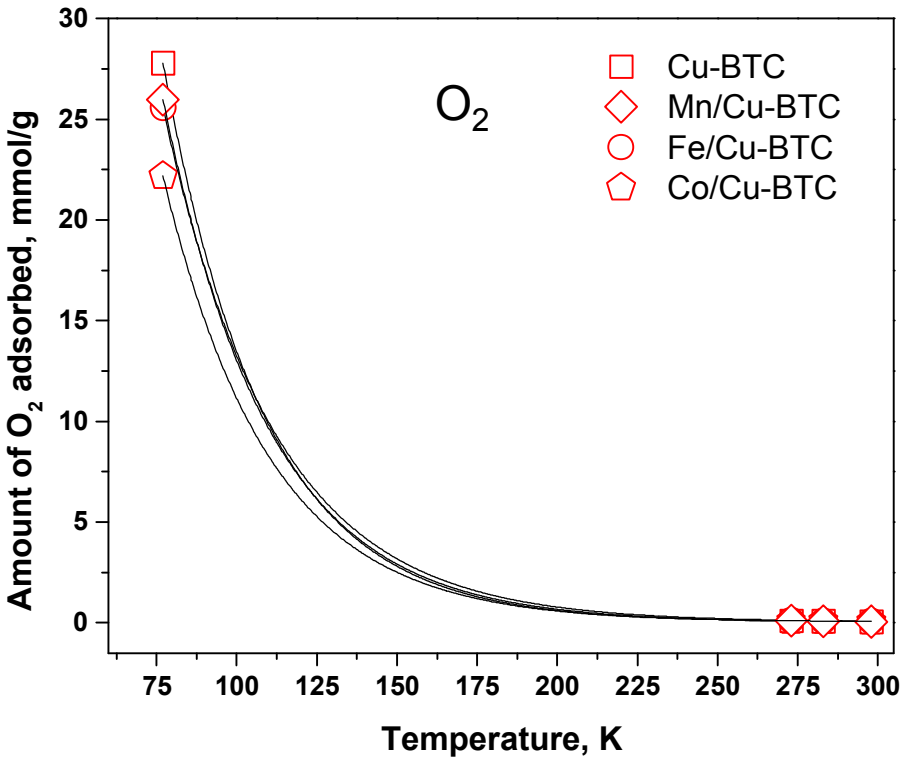
At 77K, Metal Sites Play an Important Role, while at *273 - 298 K* Metal Sites have a *Smaller Effect*

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

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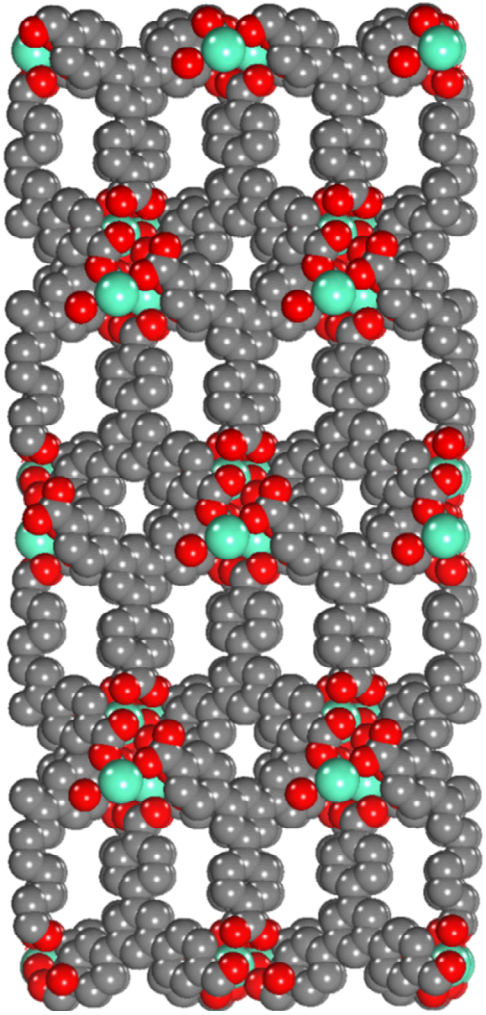
III d: SMOF-7, High Selectivity, Low Capacity for O_2

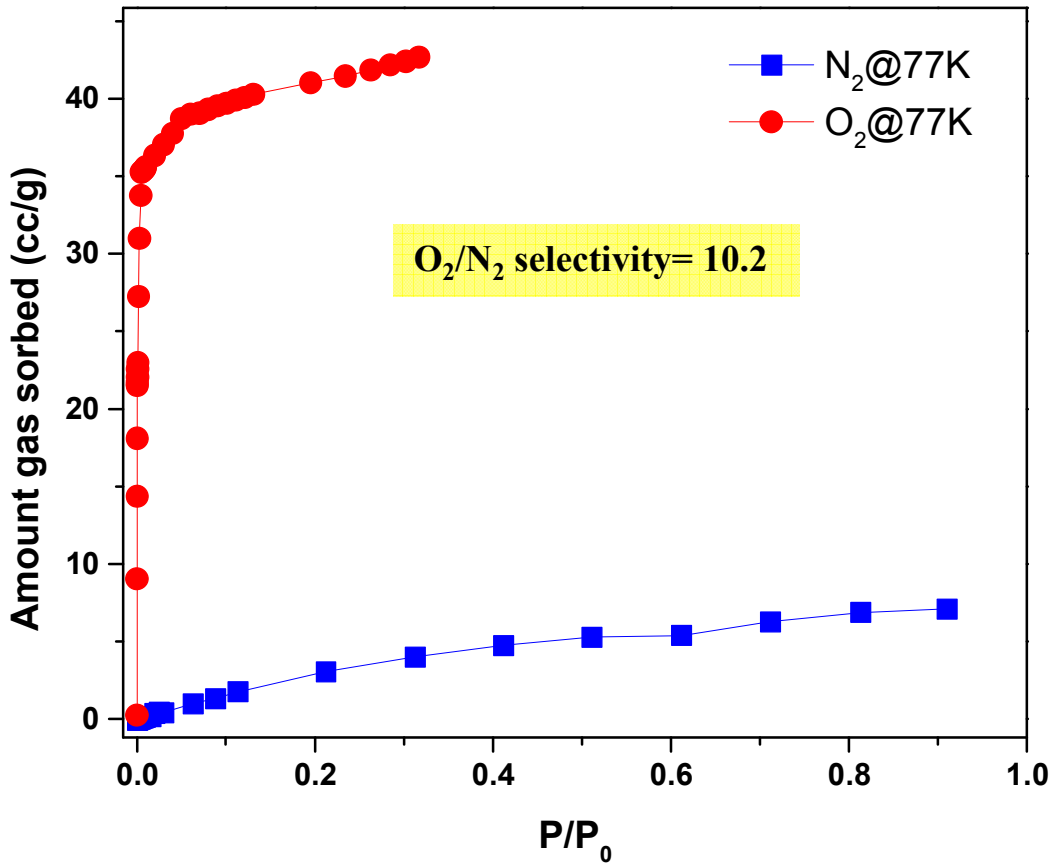
Sandia National Laboratories

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



O_2 vs. N_2 Single Gas Sorption Isotherm, at 77K

IIIe.: Oxyfuel, Combustion & Techno-economic Analysis

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Combine Experiment MOFs Gas Separations Data into Flame / Combustion Testing

Enhanced O_2/N_2 via MOF -> heat/radiation improvement w/oxyfuel -> improved efficiency

1) Study of non-premixed oxygen-enriched and oxy-fuel flames using a non-premixed turbulent jet flame burner

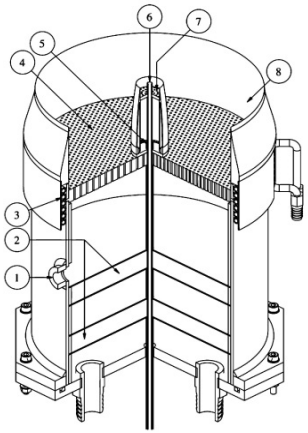
2) Measurement of radiant flux for accurate determination of flame radiation

3) Measurement of soot concentration in flames planar laser-induced incandescence measurements (LII)

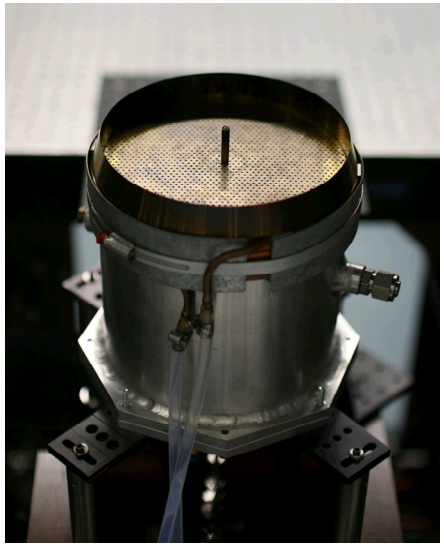
4) Allow for the calculation of the contribution of the soot to total radiant heat transfer of the flames

5) Data input to Systems Analysis for calculations of efficiency improvements of combined developed MOFs into Oxyfuel Process Stream

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



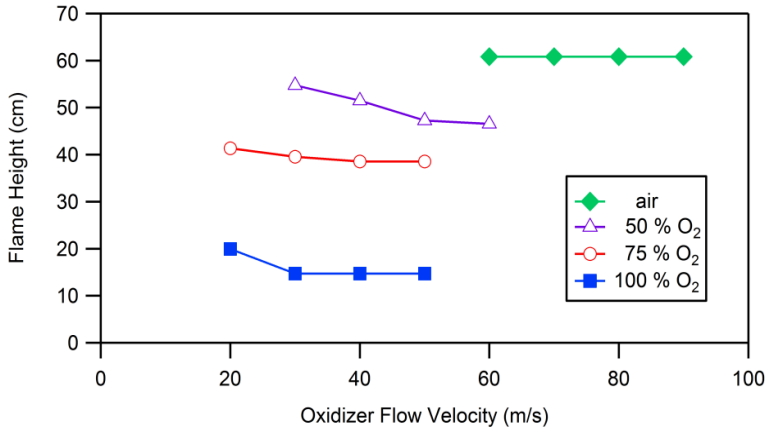
Balloon number	Description
1	Flashback over-pressure sensing port
2	Glass bead filled cavities
3	Cooling water coil
4	Coflow perforated baseplate
5	Pilot mixture feed exit
6	Central jet exit
7	Pilot perforated baseplate
8	Coflow collar



-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



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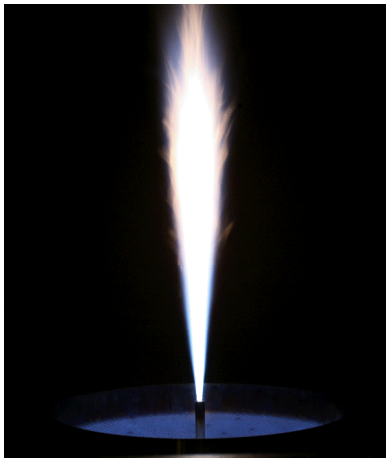
Performed preliminary testing performed with oxidizers of pure oxygen and with 50% O_2 in N_2, using an overall equivalence ratio of 1, with a constant methane flow

- 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)

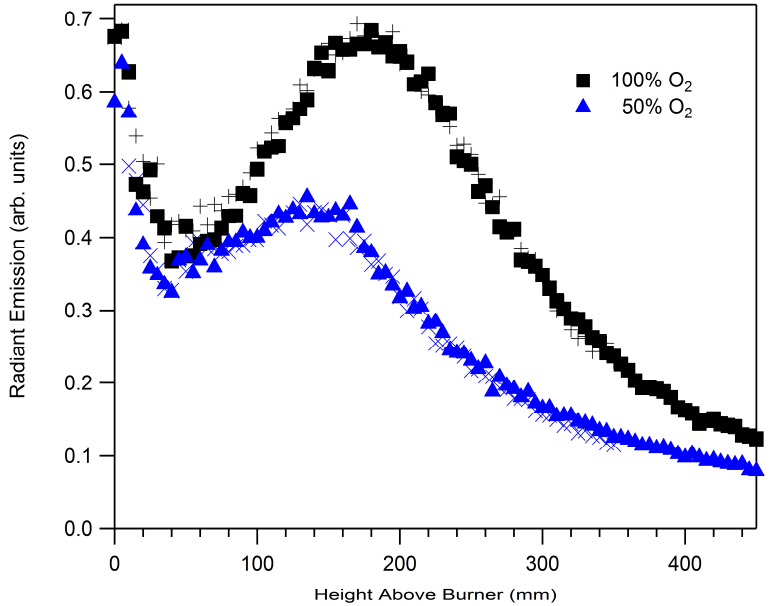
50% O_2 in N_2



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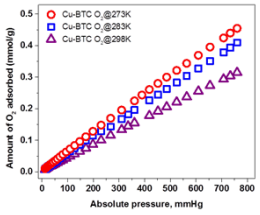
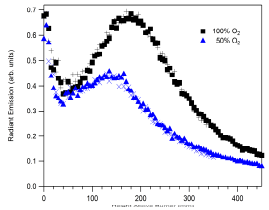
MOF adsorption isotherms (N_2 & O_2) (from MOF team)



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



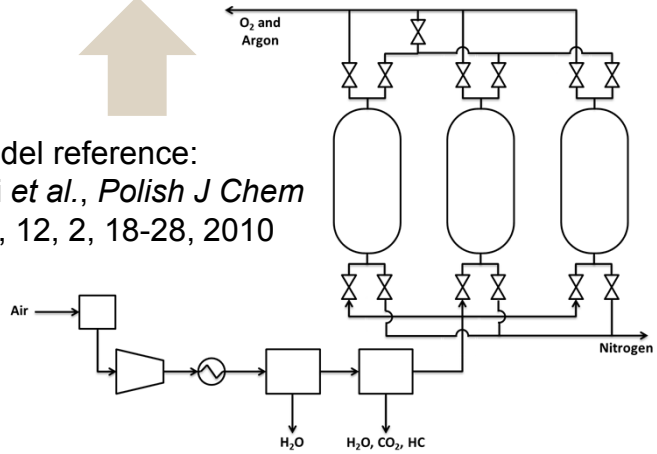
Can MOF-based PSA reduce energy consumption by 5% vs. conventional PSA air separation?

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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Outline

I. Nenoff Research Portfolio
II. Metal-organic Frameworks (MOFs) for Separations
III. O_2 separations for Oxyfuel Combustion
    a. Introduction
    b. Modeling
    c. Metal-substituted MOFs
    d. SMOF-7
    e. Oxyfuel, combustion and technoeconomic analysis
IV. Conclusions and Future Work

IV. Conclusions and Future work

Sandia National Laboratories

To Date: MOF Modeling (ab initio and MD Simulations) combined with Synthesis and Gas Sorption Testing, we identified and developed

- mixed metal MOFs for enhanced O_2 sorption over N_2 Co-, Fe- and Mn-analogues of Cu-BTC
- Novel MOFs (eg., SMOF-7) for enhanced O_2 separations

Future Direction: Process Development in which newly developed MOF materials replace zeolites in PSA processes for the energy efficient production of pure O_2 from air at temperatures up to ambient.

Target Results: Enhanced Energy Savings: up to 25%
Due to high selectivity and high capacity of the MOFs,
Plus increases in operating temperatures to near ambient

- Using previously studied/developed metal-organic frameworks (MOFs) tuned for O_2 selectivity
- Guided by techno-economic modeling
- Applied Energy R&D focus will be adsorption testing, primarily breakthrough systems up to ambient temperature
  - Complex gas stream mixtures of O_2, air, CO_2, Ar and H_2O
  - Development of cyclic adsorption processes

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Sandia Research -> Technology
Environmental and Energy Applications

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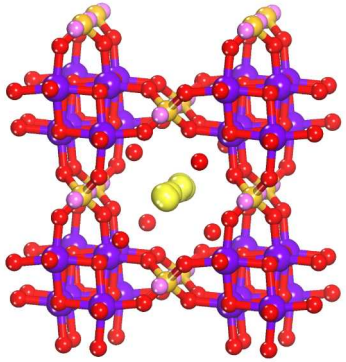
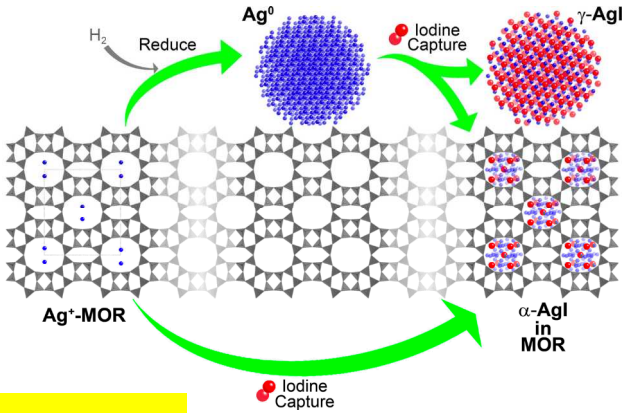


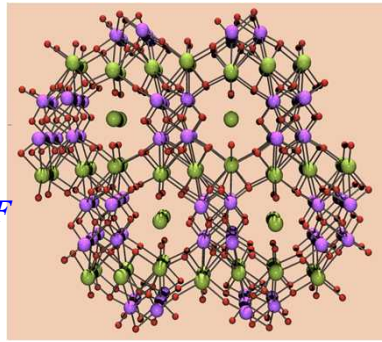
R&D100 1996
*JACerS, **2009**, 92(9), 2144*
*JACerS, **2011**, 94(9), 3053*
*Solvent Extr. & Ion Exch, **2012,** 30, 33*

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



Ag-MOR I_2(g) capture & mechanisms

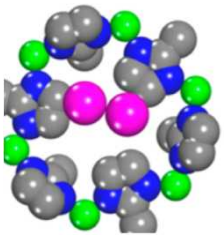
JACS, **2010**, *132*(26), 8897
J Phys Chem Letters, **2011**, *2*, 2742

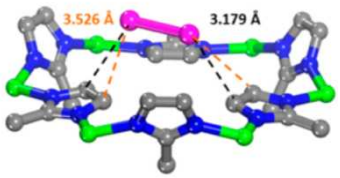


Fundamental Research to Applied to Commercial Products
Design the Separation Material To Develop the Waste Form

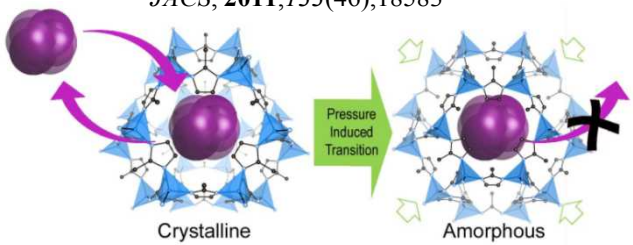
I_2/ZIF-8, Isolation to Waste Form
JACS, **2011**,*133(32)*,12398
US Patent filed 2012
JACS **2013**, *135*, 16256

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

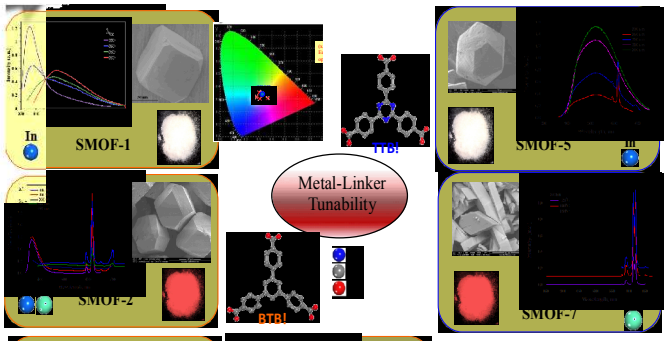


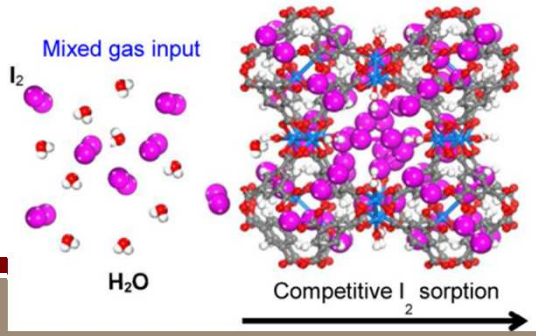


MOF Amorphization for Gas Storage
JACS, **2011**,*133*(46),18583



Highly Tunable PL MOFs





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

JACS, **2012**,*134* (9),3983
Chem.Mater. **2014**, *26*(9), 2943
US Patent filed 2013

Sandia National Laboratories

Thank You

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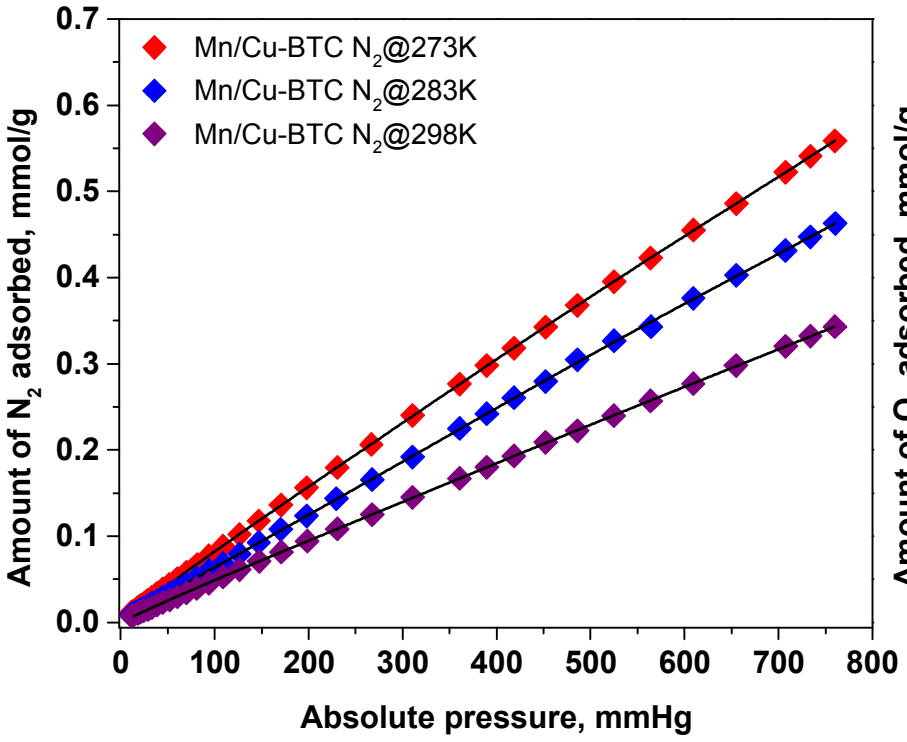
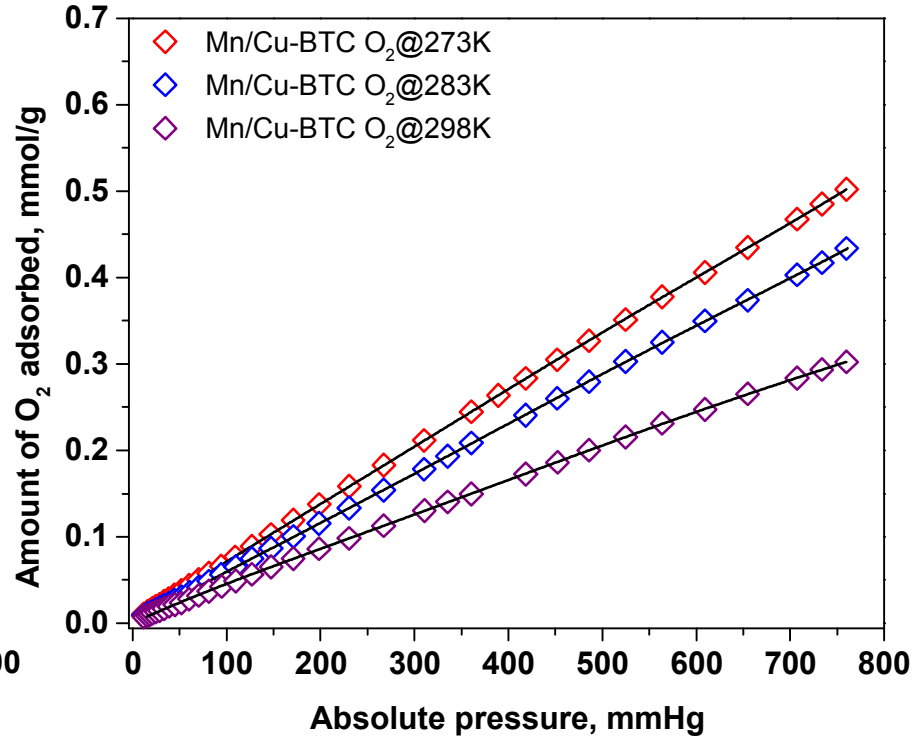
N_2 and O_2 adsorption isotherms measured at 273, 283, and 298K on pristine Mn/Cu-BTC





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

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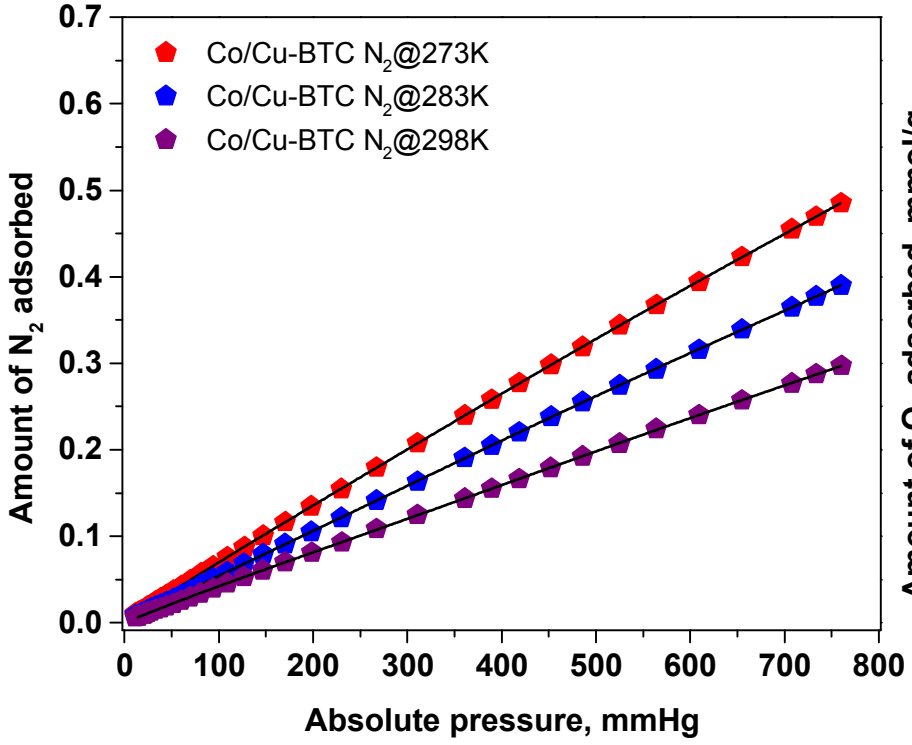
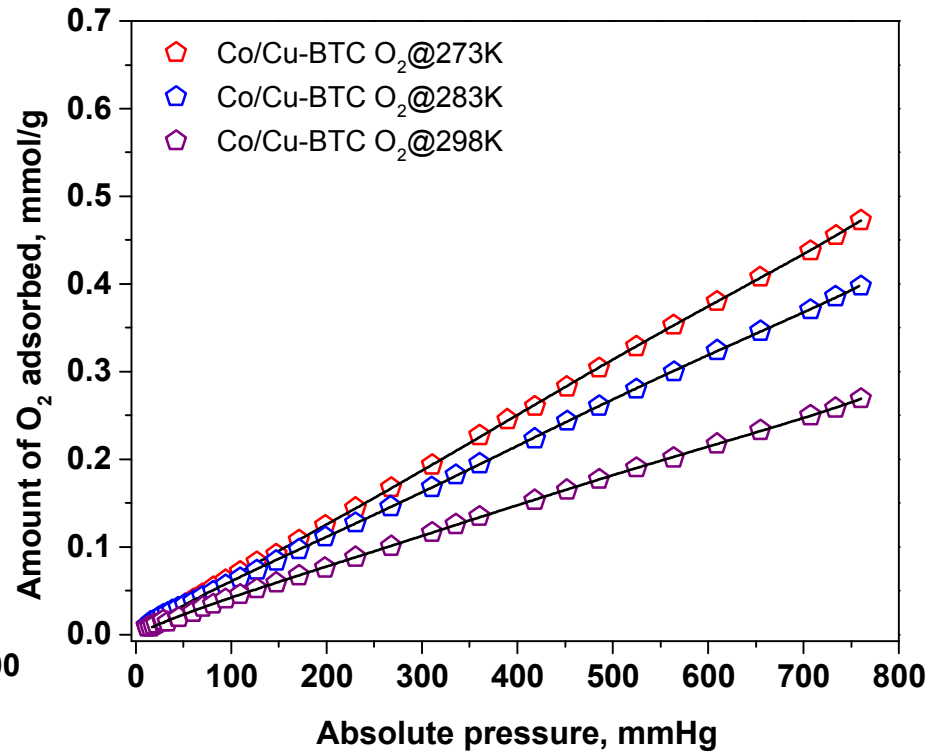
N_2 and O_2 adsorption isotherms measured at 273, 283, and 298K on pristine Co/Cu-BTC





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

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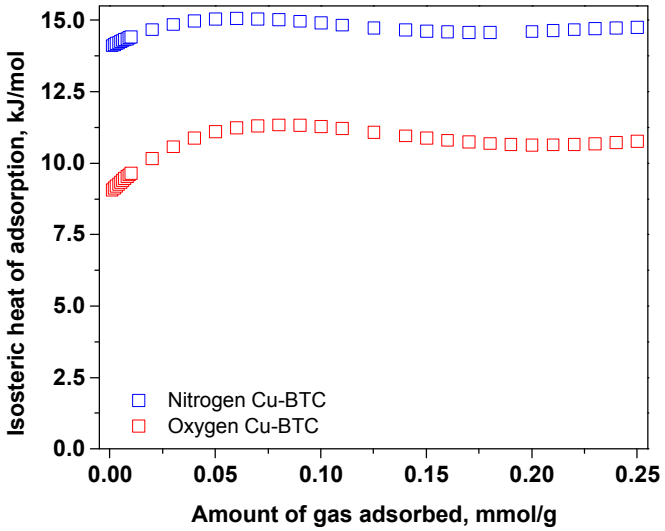
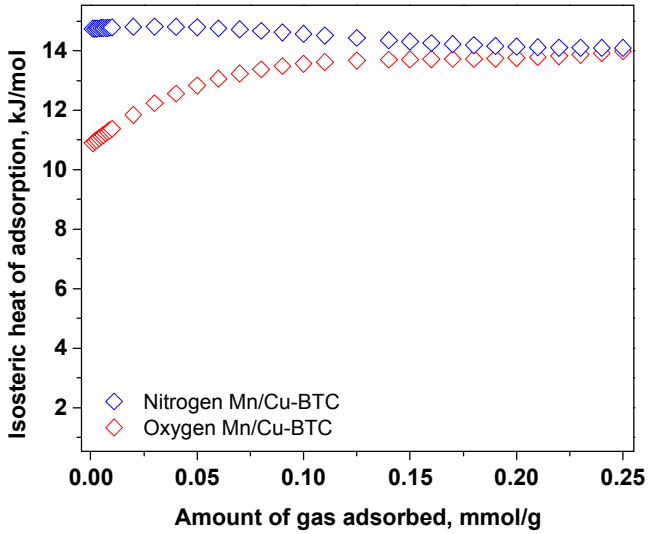
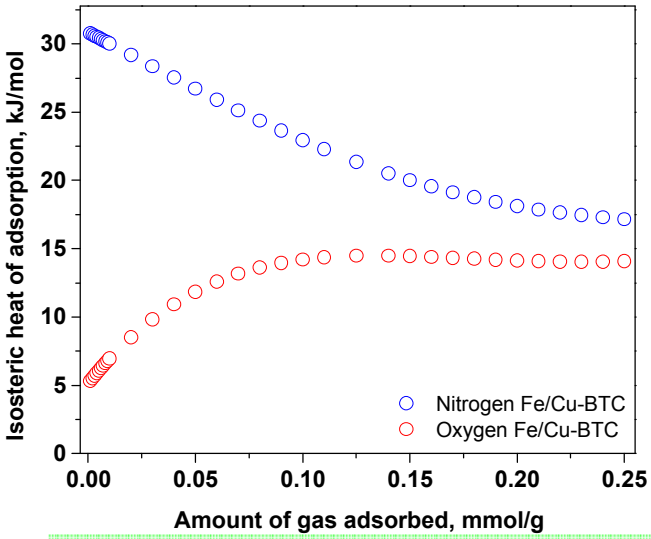
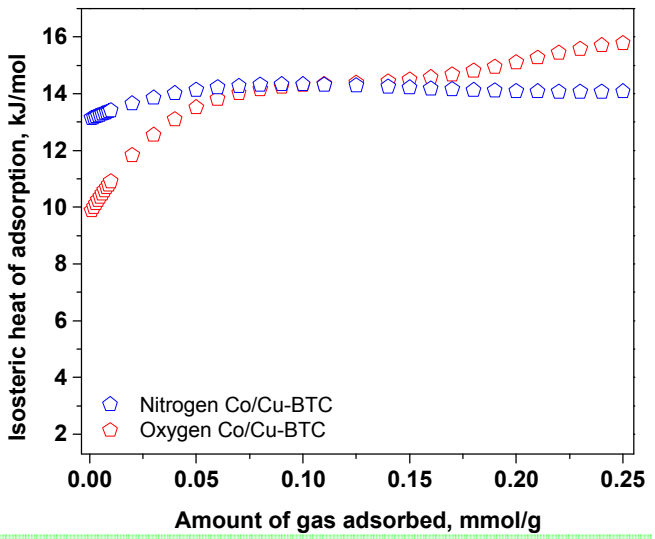
Significantly higher binding energy of N_2 over O_2 is noted for the Fe/Cu-BTC sample









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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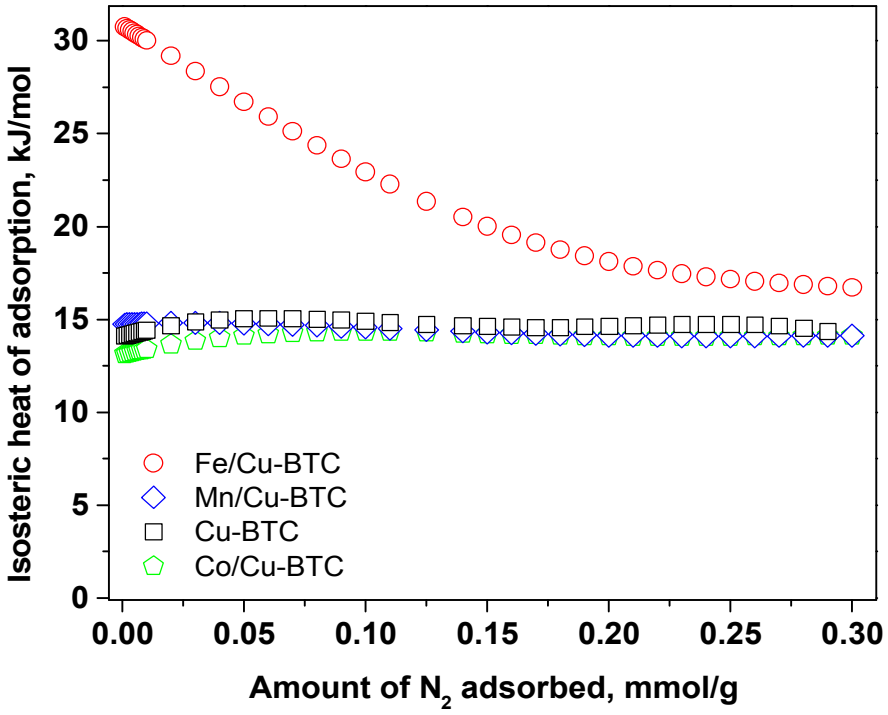

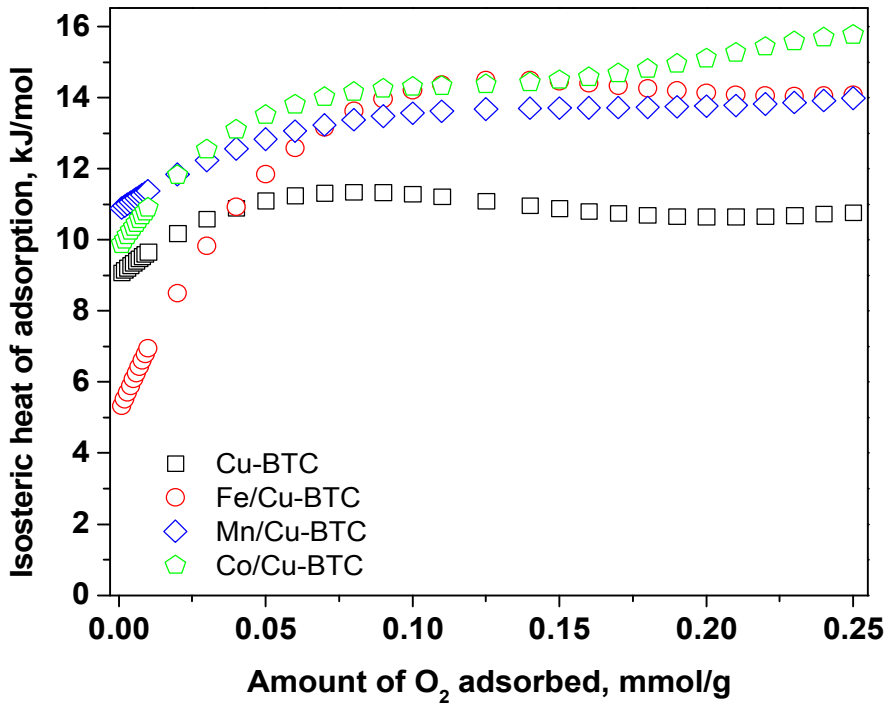

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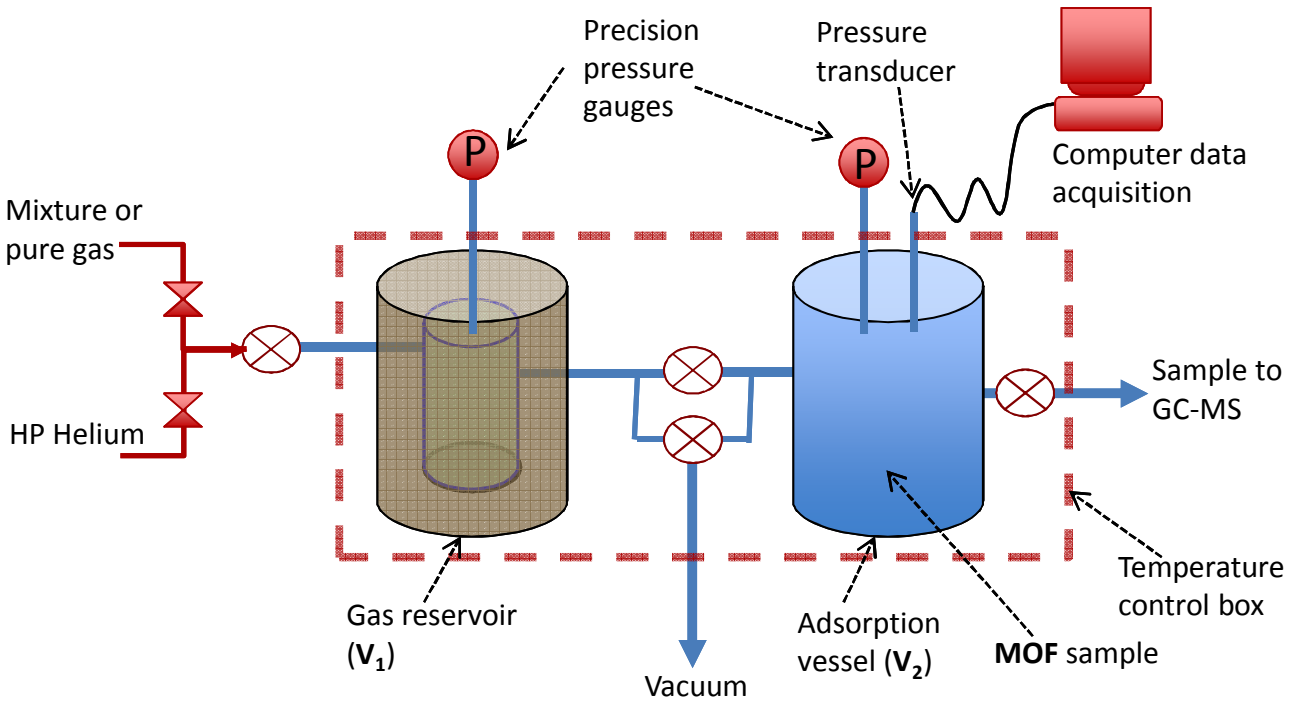
O_2/N_2 Gas mixture adsorption measurements containing 20% O_2 and 80% N_2

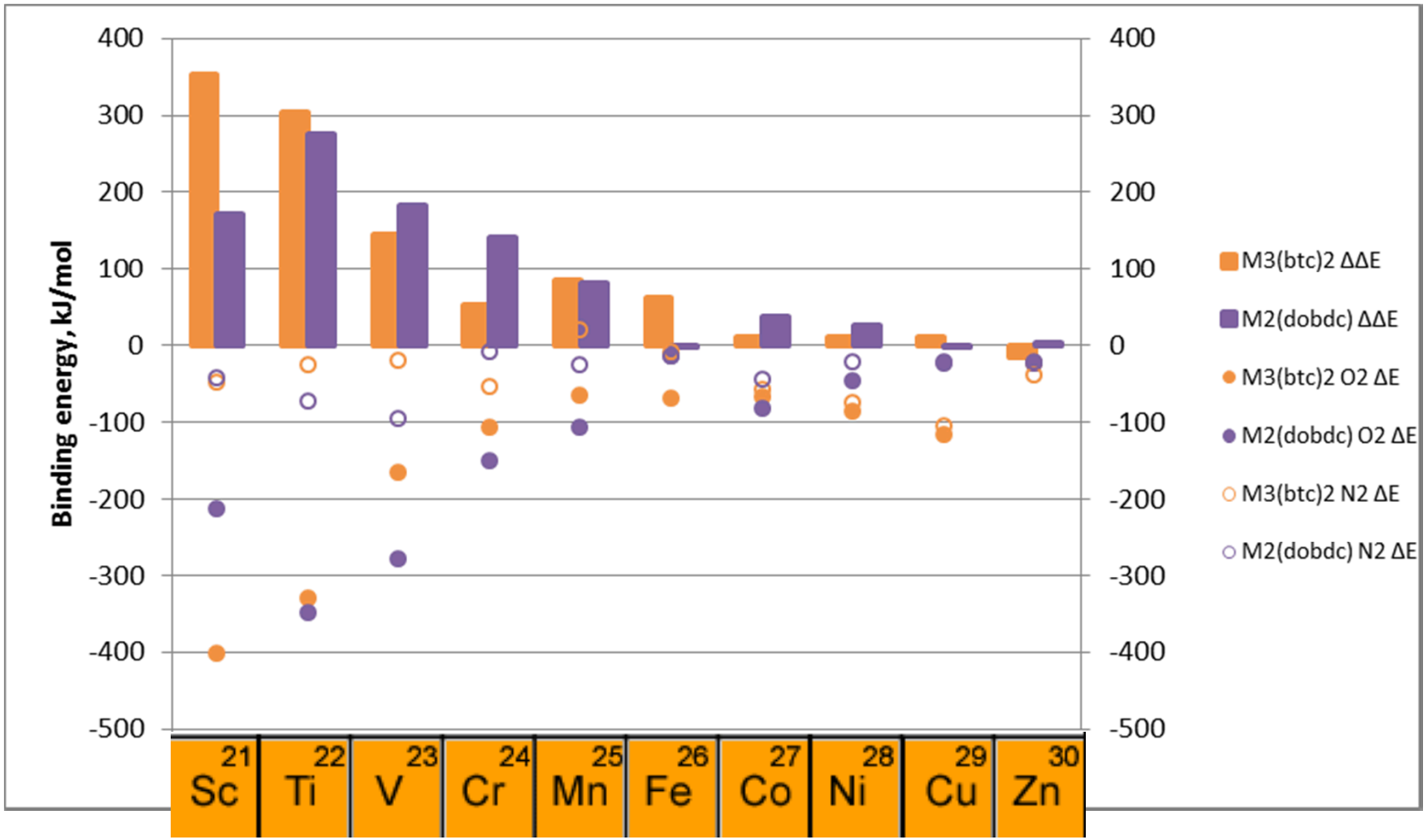


Room temperature (294K) in pressure range of 1.77 to 5.2 bars.

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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