SAND2016-2463C

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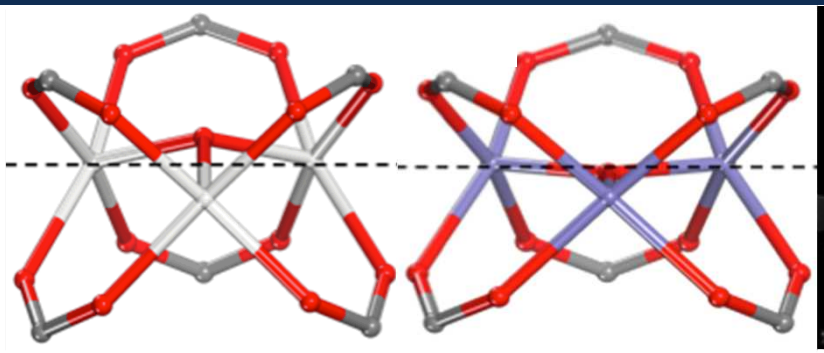

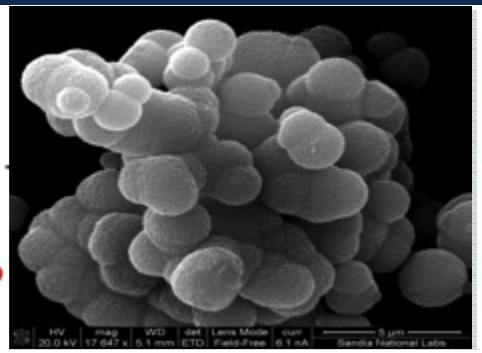

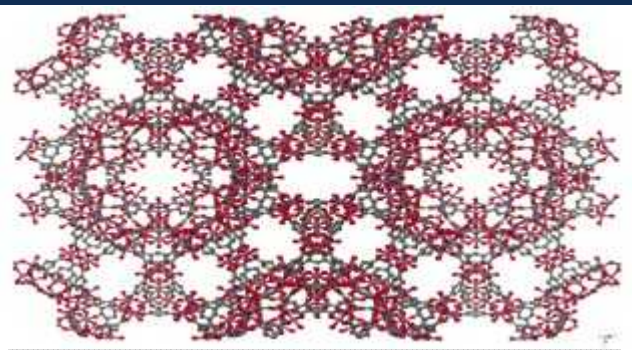

Light Gas Separations with MOFs via Predictive Modeling and Tuned Synthesis

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2016 Spring ACS Meeting,
San Diego, CA March 17, 2016

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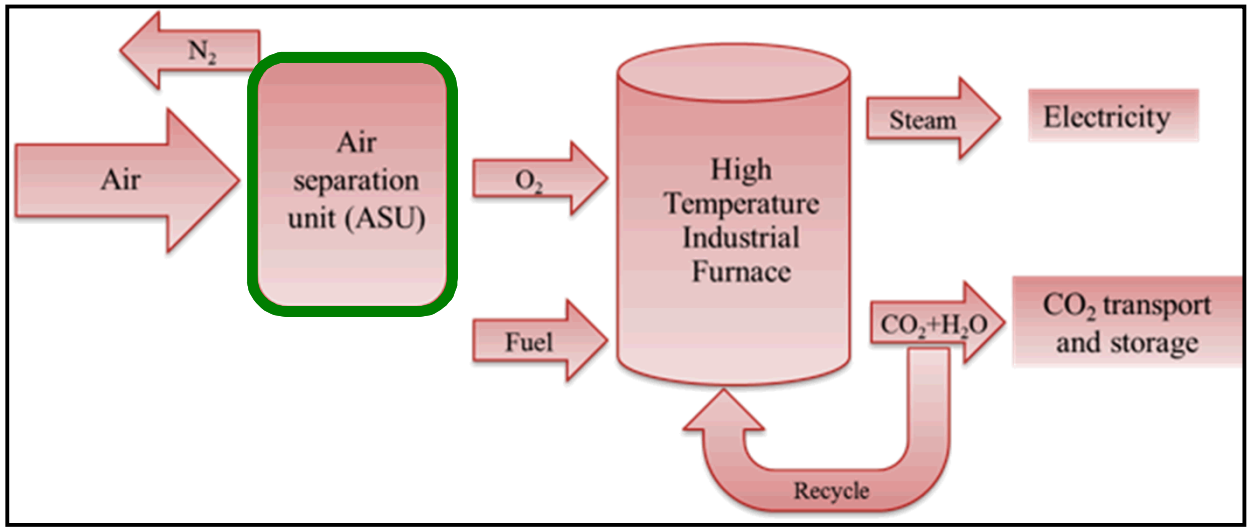
U.S. DEPARTMENT OF ENERGY

NNSA

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 Oxygen Purification Steps: **Cryogenic** ASU, a costly and energy intensive process (primarily compression) for 99+% purity, or **zeolites + PSA** for ~90-95% purity

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

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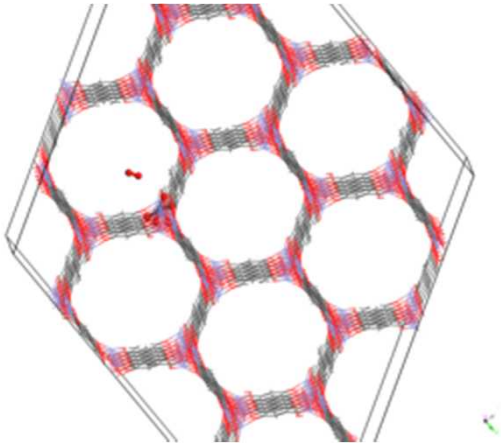
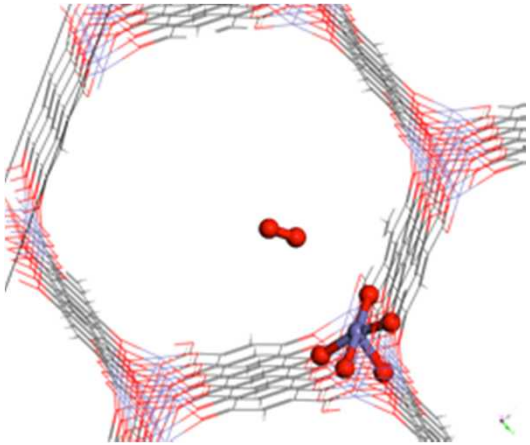
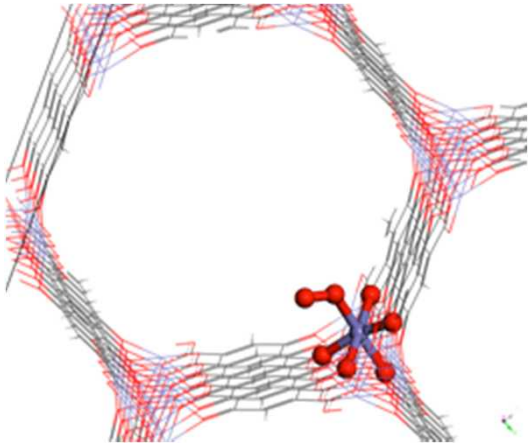
- MOFs with coordinatively unsaturated metal centers are promising materials for O_2/N_2 separations
- Two prototypical MOFs from this category, $Cr_2(BTC)_3$ (*J. Am. Chem. Soc.* **2010**, *132*, 7856–7857) and $Fe_2(DOBDC)$ (*J. Am. Chem. Soc.* **2011,** *133*, 14814-14822) both show preferential adsorption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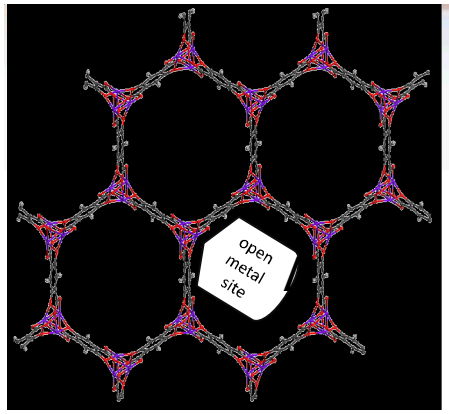
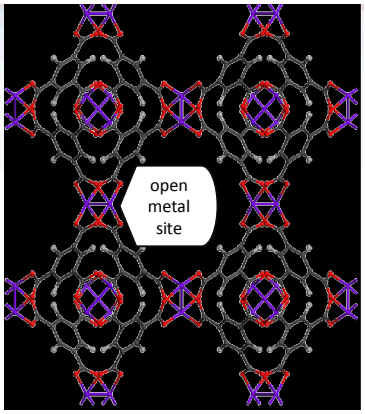
DFT modeling of of Oxygen Adsorption in Varied Metal-Centered MOFs



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

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

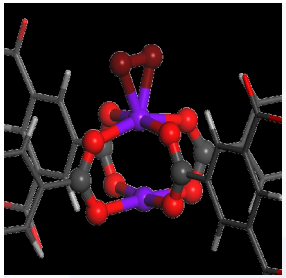
The **differences in binding energies ($\Delta\Delta$ E)** for oxygen and nitrogen were calculated by

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

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

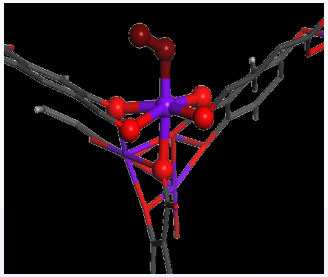
Attention Paid to Bonding Geometries

Side-on bonding
∡M-X-X 67° - 71°



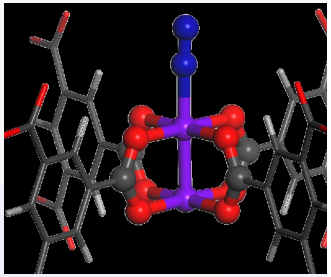
$Cr_3(btc)_2(O_2)$

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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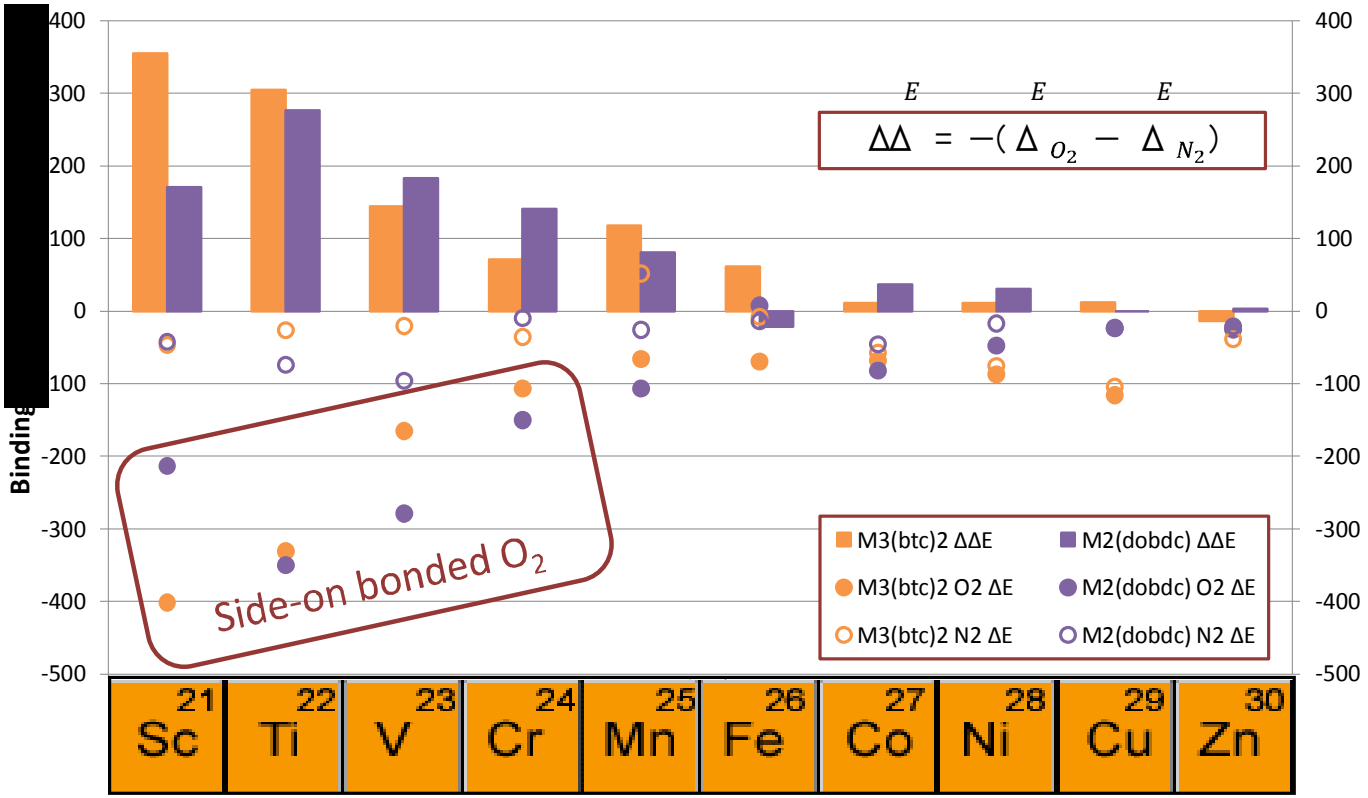
Binding Energy Calculated as a Function of Metal Site



Current Study: Parkes, M.; Sava Gallis, D. F.; Greathouse, J.A.; Nenoff, T.M. "Using Ab Initio Molecular Dynamics to Examine Gas Adsorption on Open Metal Sites of M_2(dobdc)" **2016**, submitted.

Parkes, M.; Sava Gallis, D. F.; Greathouse, J.A.; Nenoff, T.M. *J. Phys Chem C*, **2015**, *119*, 6556.
Sava Gallis, D. F.; Parkes, M.; Greathouse, J.A.; Nenoff, T.M. *Chem. Mater.*, **2015**, *27*(6), 2018.

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MD Simulation Inspired MOF Synthesis: Sc/BTC/DMF/HCl

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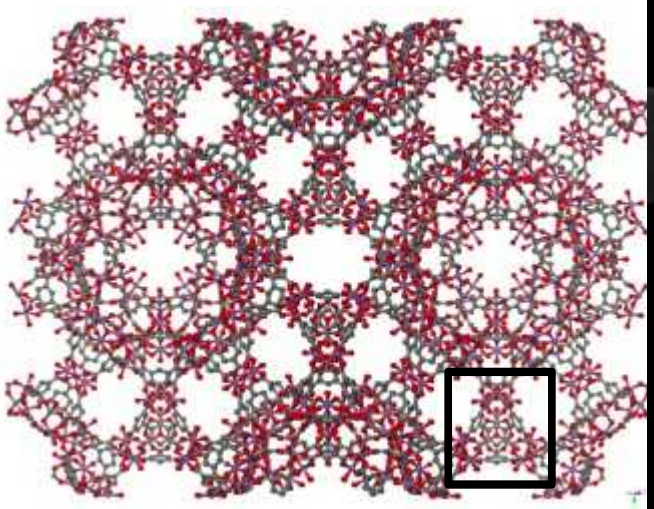
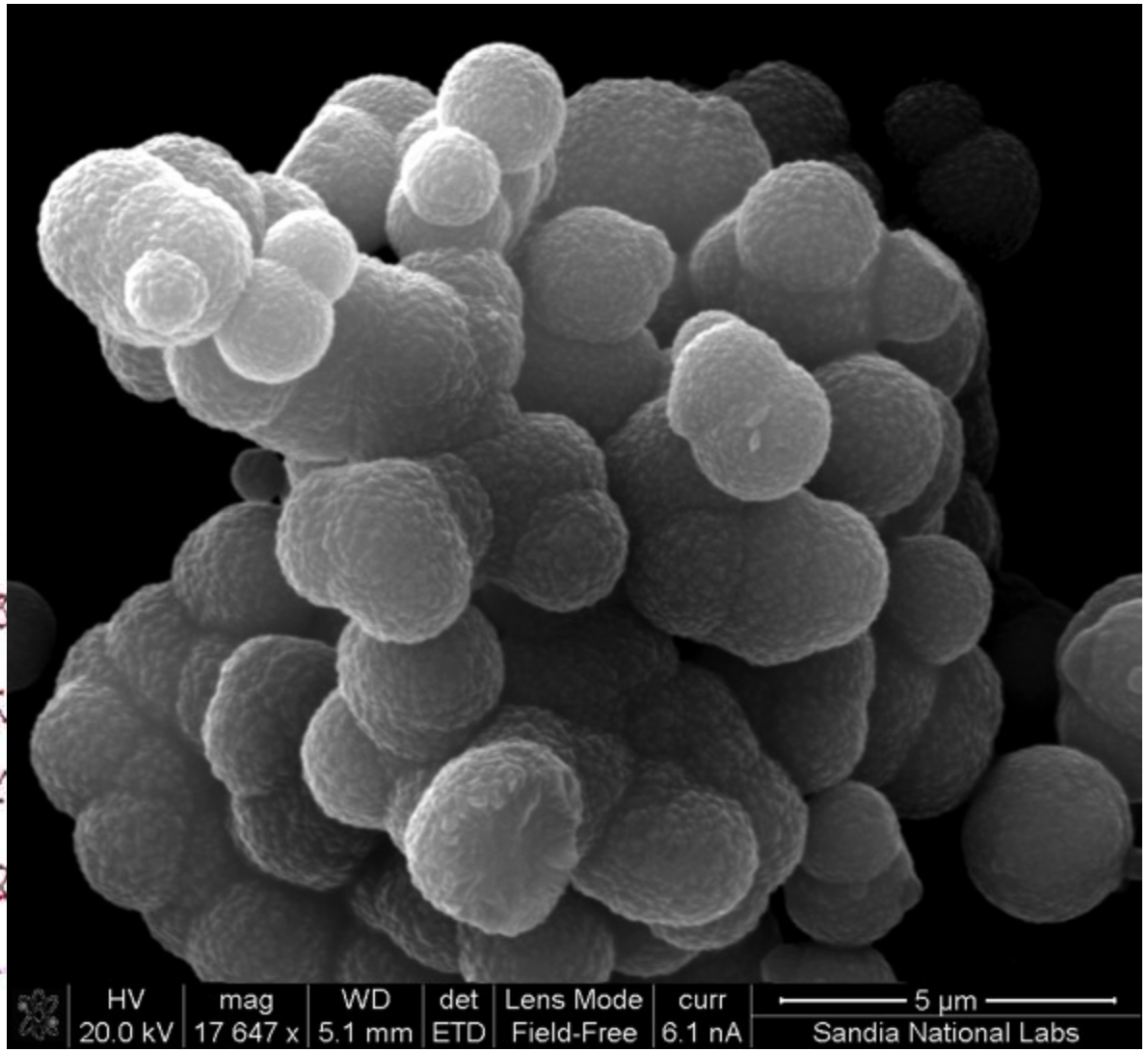
Sc-MIL-100

Unique synthesis:

Mixed $Sc(NO_3)_3 \cdot xH_2O$ and 1,3,5–benzetricarboxylic acid in N,N'-dimethylformamide and HCl.

Heated to 373K overnight





Sava Gallis, D. F., Greathouse, J.A.; Rodriguez, M.A.; Parkes, M.V.; Chapman, K.W.; Nenoff, T.M. **2016**, submitted.

US Provisional Patent 2015

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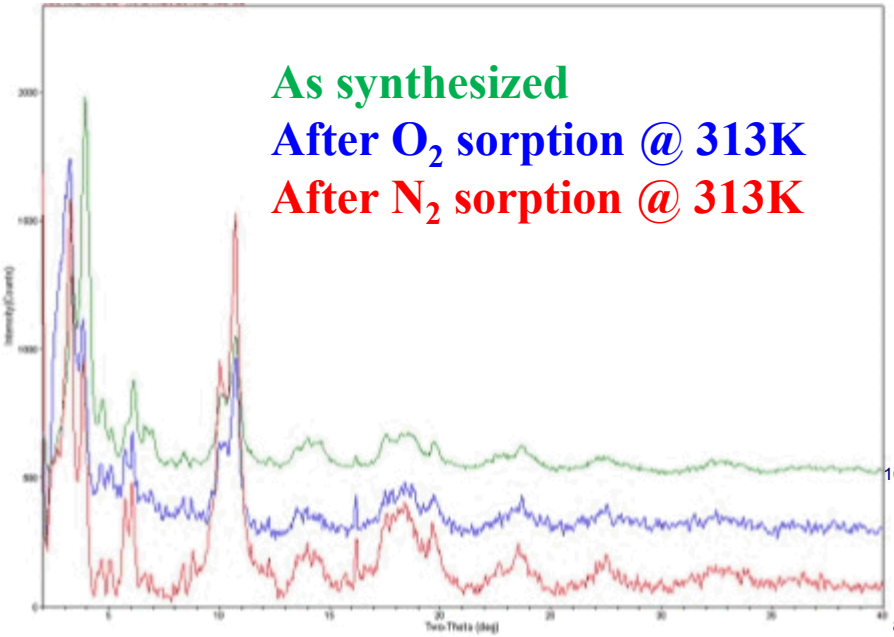
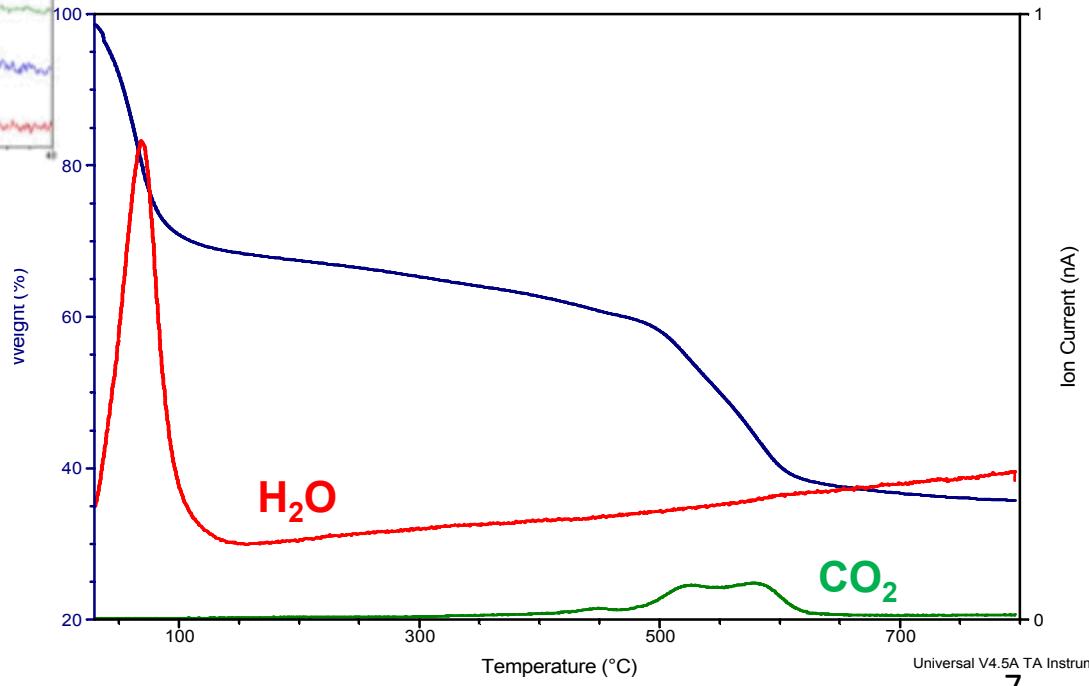
Sc-MIL-100



XRD

Stable MOF framework over Wide Temperature Range and with Exposure to Variety of Gases

TGA-MS



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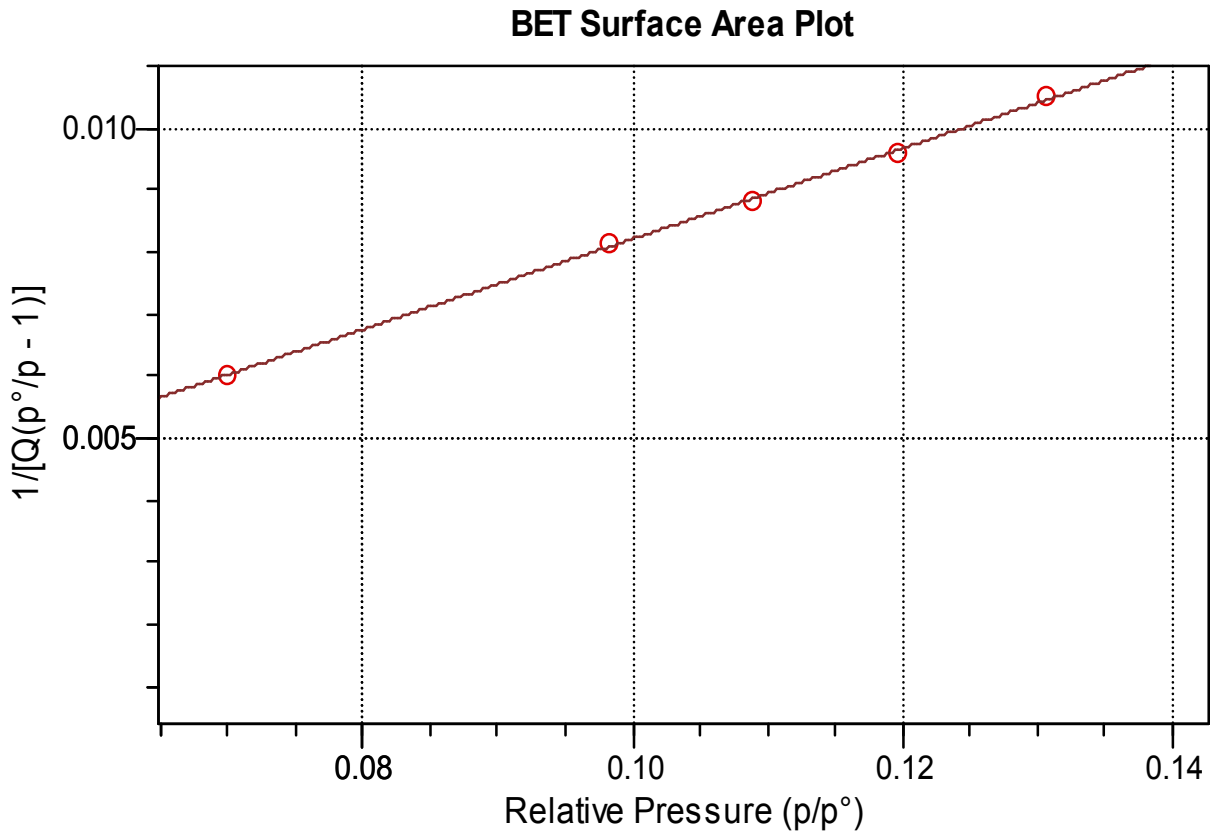
Sc-MIL-100: High Surface Area with Accessible Metal Centers



BET surface area: 1321.7194 ± 24.4623 m²/g

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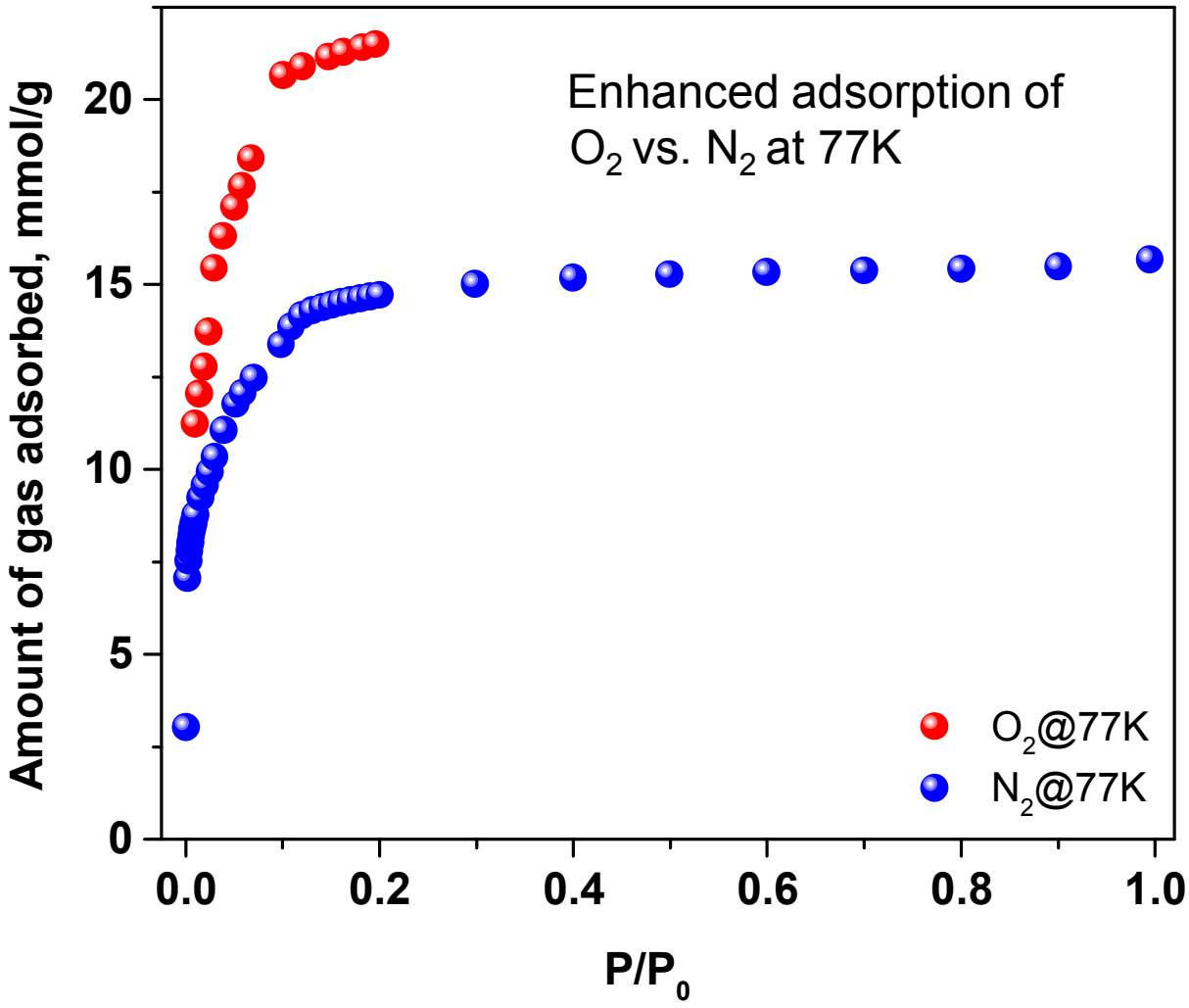
Sc-MIL-100: Metal-Center has a role at 77K



How does Sc-MIL-100 behave at more realistic operational temperatures?

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Sc-MIL-100: GCMC Isotherm Calculations at 258K and 298K

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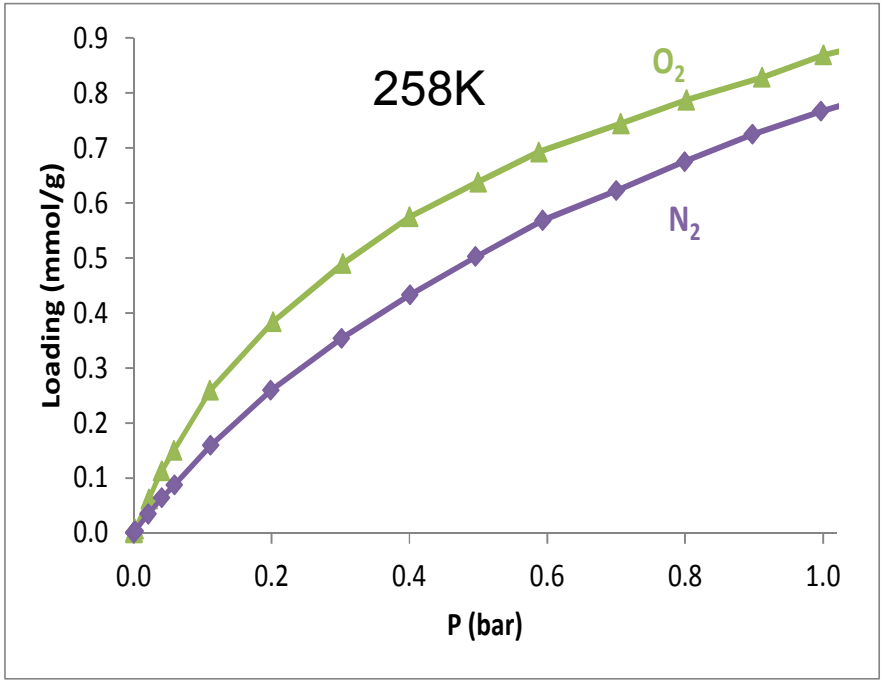
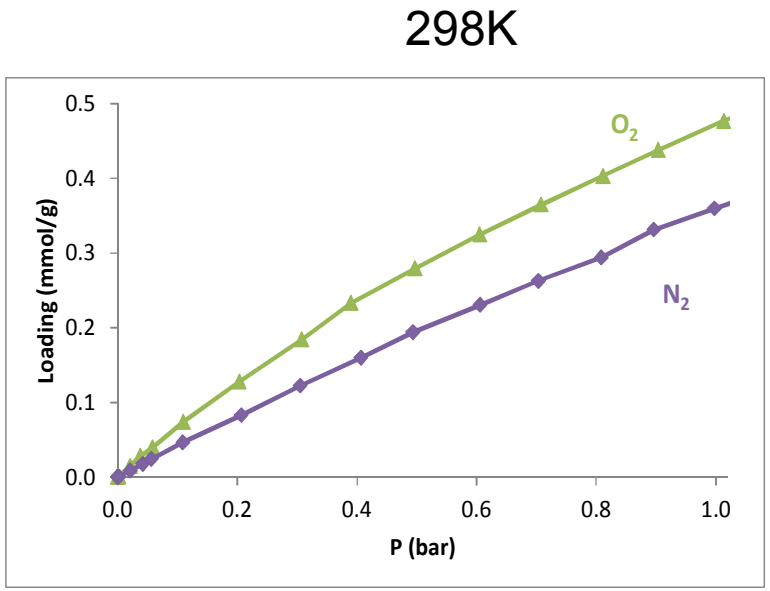
- **Grand Canonical Monte Carlo (GCMC) Simulations**
- Pure gas (N_2 or O_2) adsorption over pressure range 0 - 1 bar.
- Temperature range matched with experiment: 258 K, 298 K, 313 K.
- Grand canonical ensemble (constant chemical potential, temperature, volume) using the Towhee code (Martin, *Mol. Sim*. **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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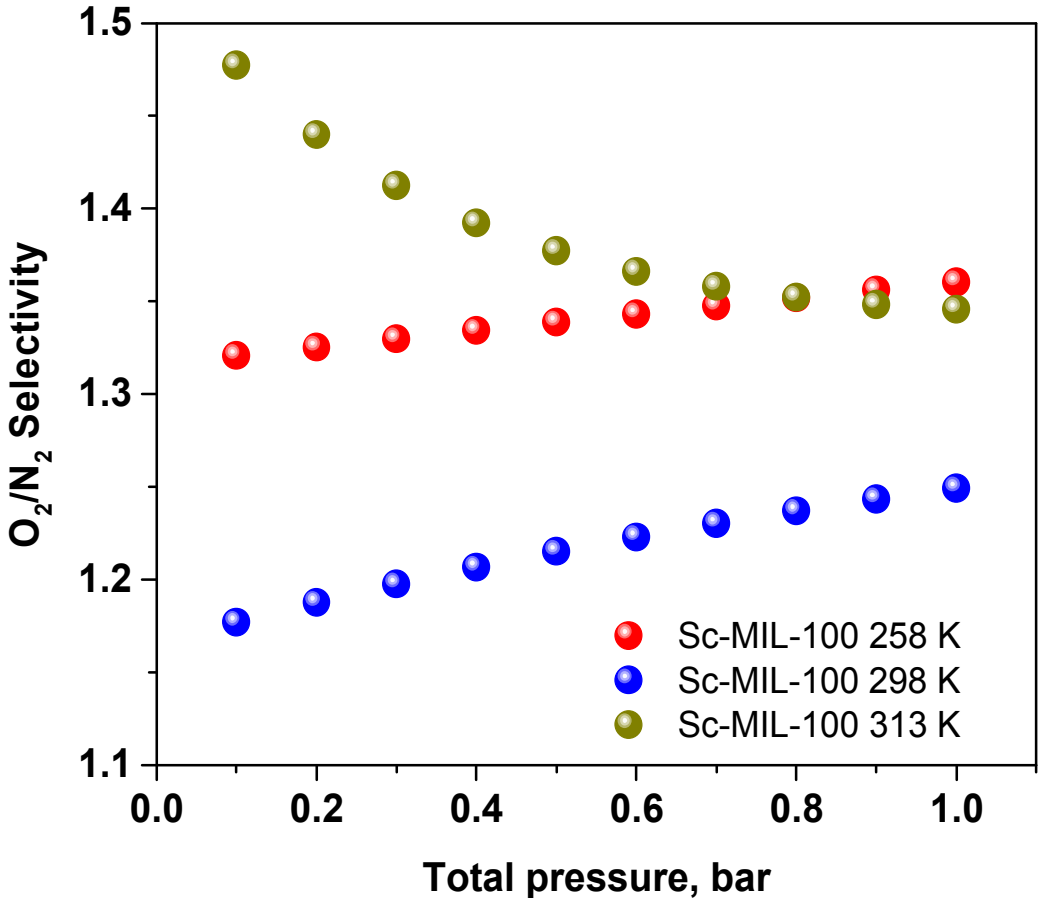
Simulations of Competitive Gas Adsorption: based on GCMC data, 298K



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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Sc-MIL-100: Enhanced Quantity of O_2 vs N_2 Adsorbed over Wide Temperature Range (at least to 313K)

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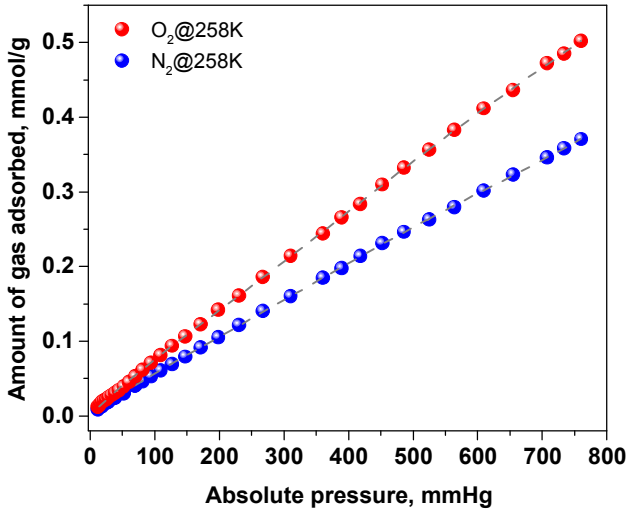
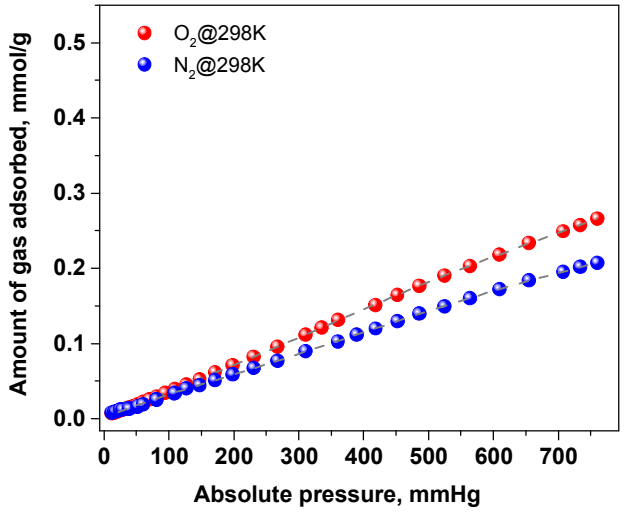
Fit using the virial eq.

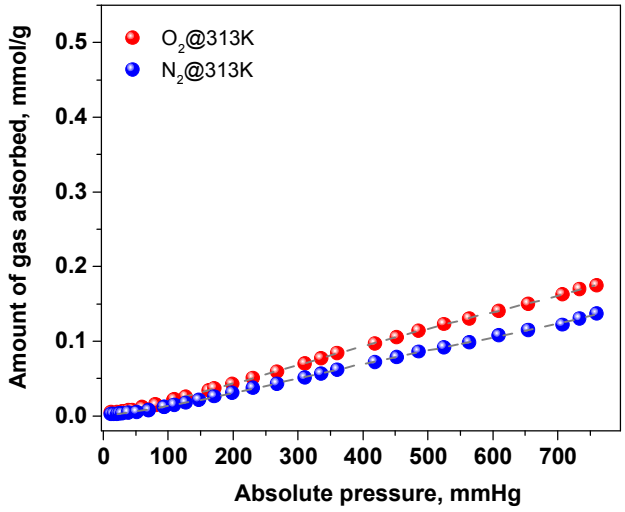
O_2 vs. N_2 @**258K**



O_2 vs. N_2 @**298K**



O_2 vs. N_2 @**313K**



Isotherm trends mimic those predicted by GCMC

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Sc-MIL-100: Enhanced Quantity of O_2 vs N_2 Adsorbed over Wide Temperature Range (at least to 313K)

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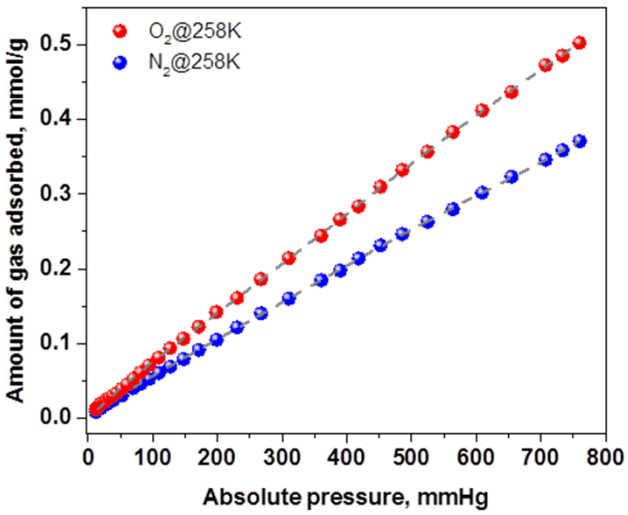
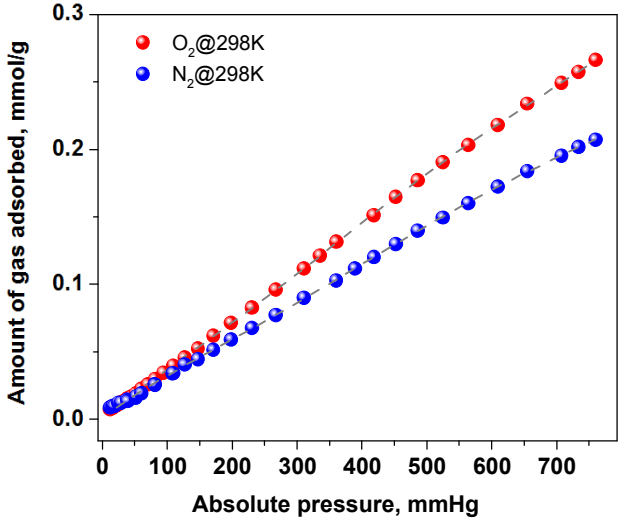
Fit using the virial eq.

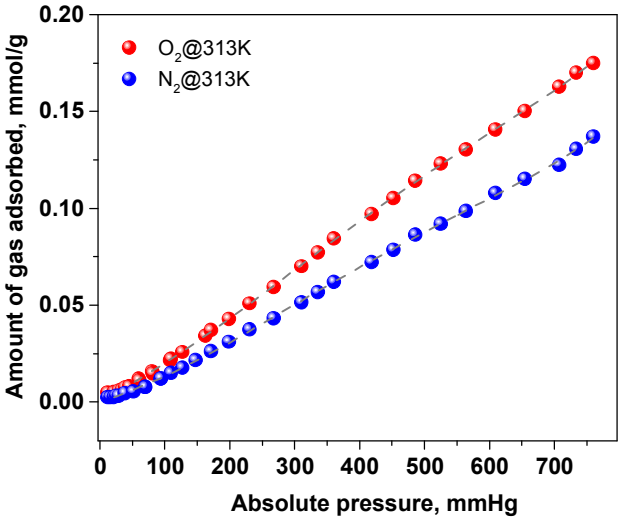
O_2 vs. N_2 @**258K**



O_2 vs. N_2 @**298K**



O_2 vs. N_2 @**313K**



Isotherm trends mimic those predicted by GCMC

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Sc-MIL-100: Isosteric Heat of Adsorption (kJ/mol) Higher Binding Energy in SMOF-8 for O_2 vs N_2

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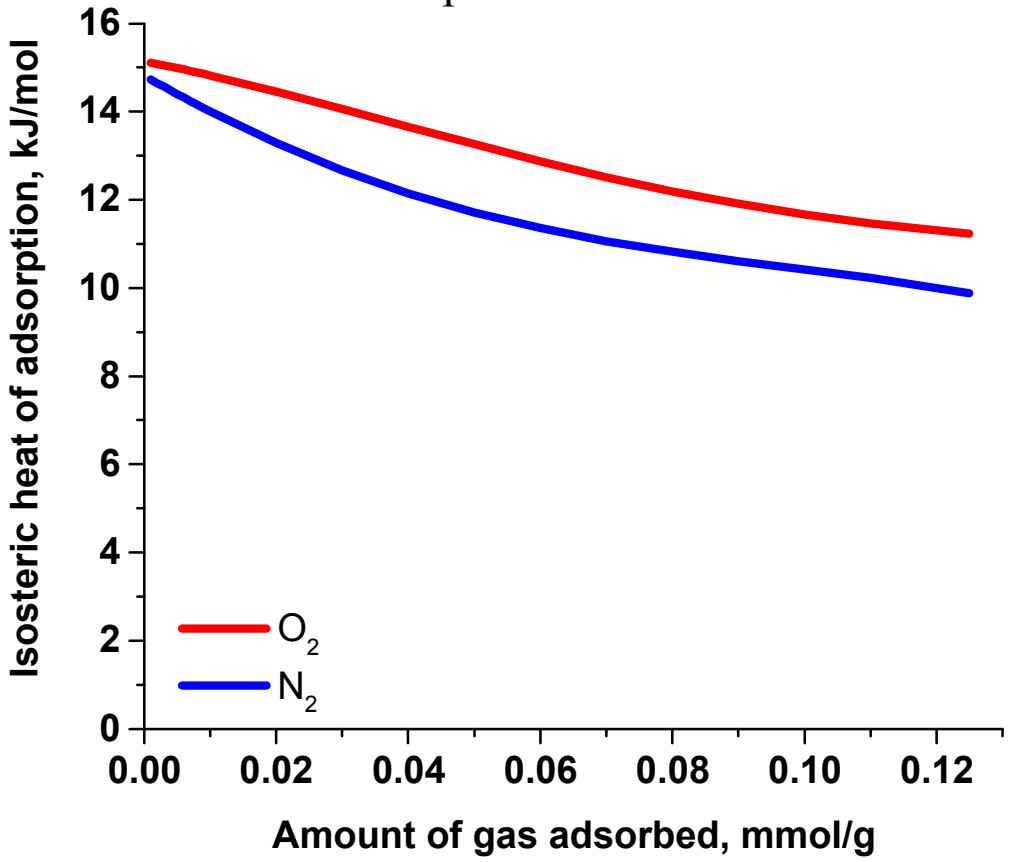
Qst derived from 258K, 298K and 313 K
Independent Virial Fit HOA



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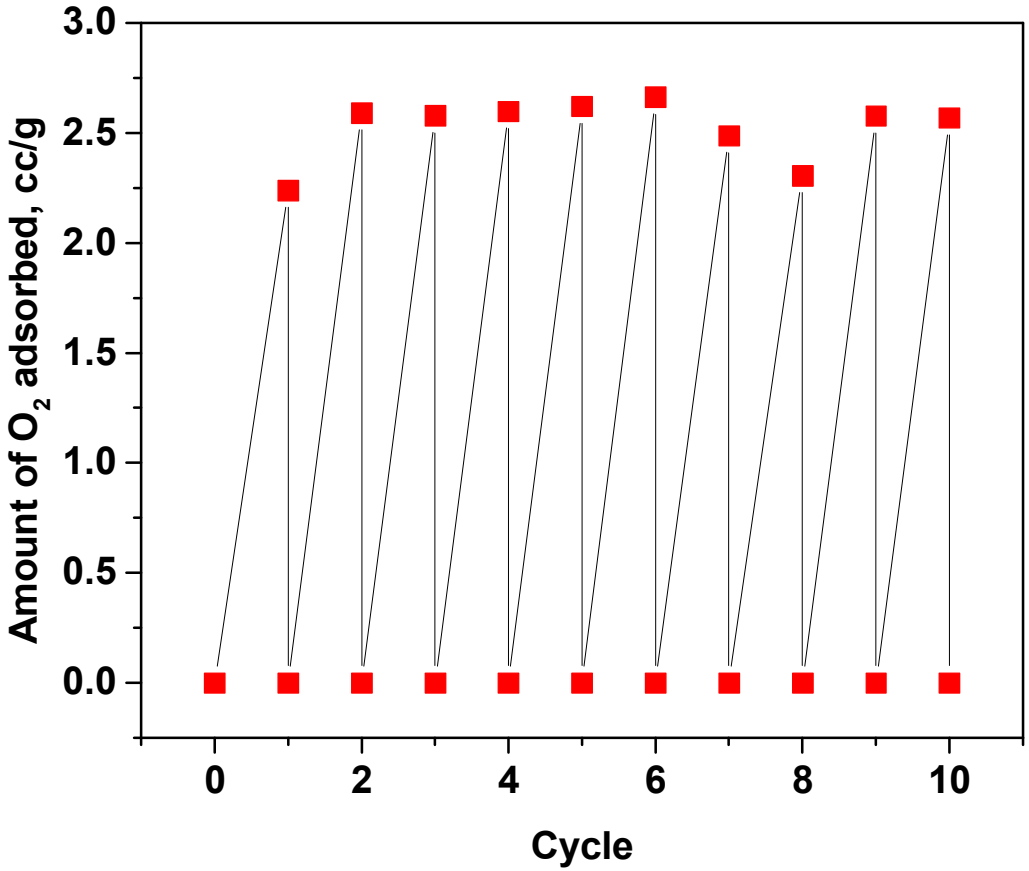
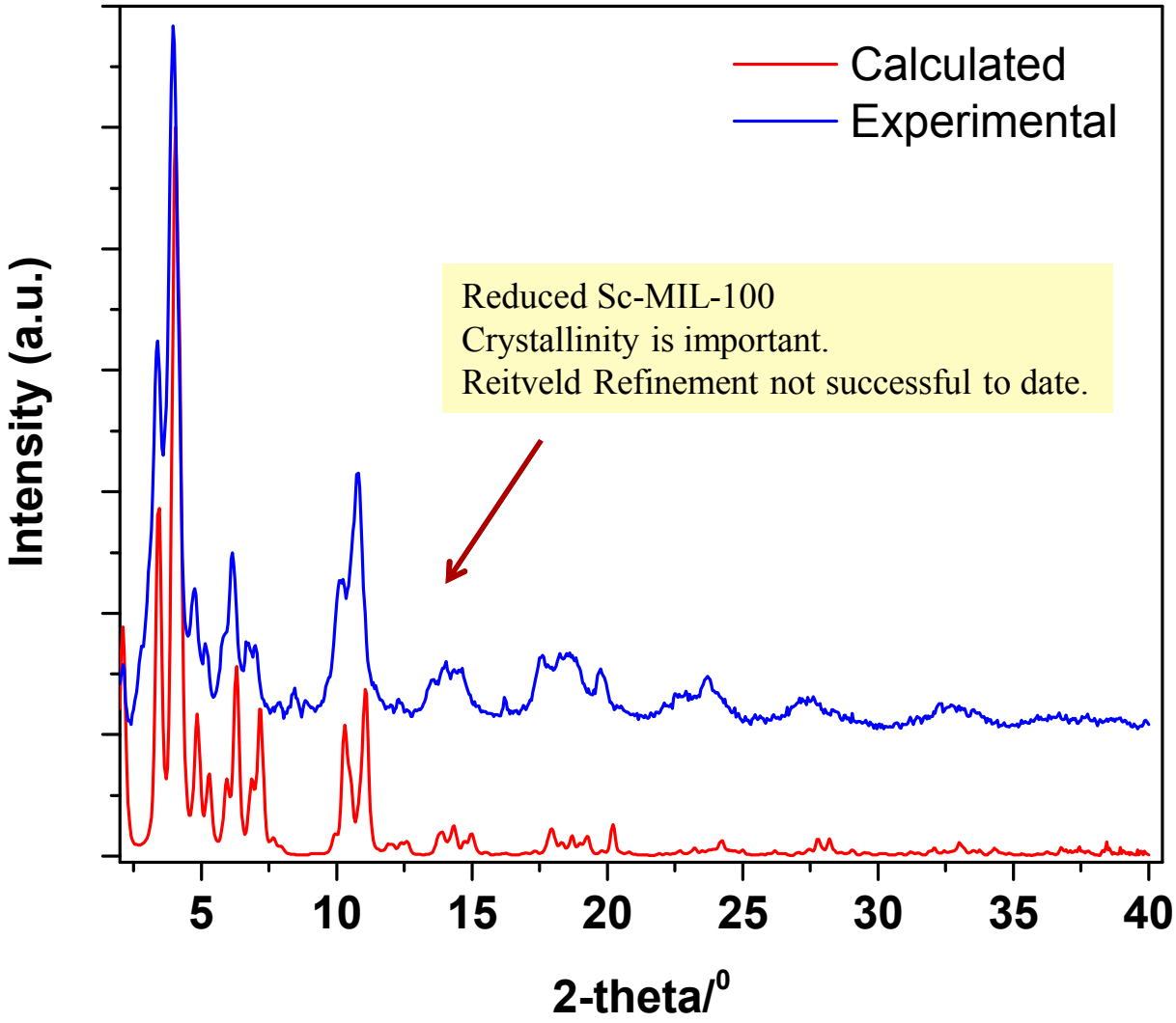
Sc-MIL-100 Performance:
O_2 adsorption and Desorption over 10 cycles, 298 K, 1 atm



What about the structure is making Sc-MIL-100 O_2 strongly sorbing?

Structure-Property Relationship Understanding of Sc-MIL-100 Oxygen Selectivity

High Energy Synchrotron X-ray, APS/ANL



Sava Gallis, D. F.; Parkes, M.; Greathouse, J.A.; Nenoff, T.M. **2015**, submitted. *US provisional Patent 2015* *tmnenof@sandia.gov*

Structure-Property Analysis:
Pair Distribution Function (PDF) Analysis

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The PDF, ***G(r)****,* is related to the ***probability*** of finding an atom at a distance ***r*** from a reference atom.
It is the Fourier transform of the total structure factor, ***S(Q)***.

$$\boldsymbol{G(r)} = 4\pi r\,\rho_0[\underbrace{\boldsymbol{g(r)}}_{\text{probability}}-1] = (2/\pi)\int Q[\underbrace{\boldsymbol{S(Q)}}_{\text{structure factor}} - 1]\sin(Qr)dQ$$

The structure factor, ***S(Q)***, is related to coherent part of the diffraction intensity

$$\boldsymbol{S(Q)} = 1 + [\underbrace{\boldsymbol{I^{coh}(Q)}}_{\substack{\text{diffraction intensity}\\ \text{(corrected)}}} - \sum c_i|f_i(Q)|^2]/\,|\sum c_i f_i(Q)|^2$$

Apply corrections for background, absorption, Compton & multiple scattering

Use of high energy X-rays and large area detectors key to structure resolution

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PDF measurements: APS/ANL Collaboration

Does it matter which synchrotron?

Yes. Only higher energy storage rings produce significant fluxes of high energy X-rays

High energy X-rays are a unique strength of the *Advanced Photon Source* (in the western hemisphere)

- 3 dedicated high energy beam lines
- 1 dedicated PDF beamline

APS 11-ID-B: Dedicated PDF facility
- 58 or 90KeV high energy X-rays
- typical wavelengths = 0.1 - 0.2Å

For our experiments:

$Q > 20Å^{-1}$; CuK_α to $2\Theta = 180$ results in $Q_{max} = 8Å$

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PDF: Insight Into Short Range Structural Order
eg., Amorphous SiO_2 (Glass)

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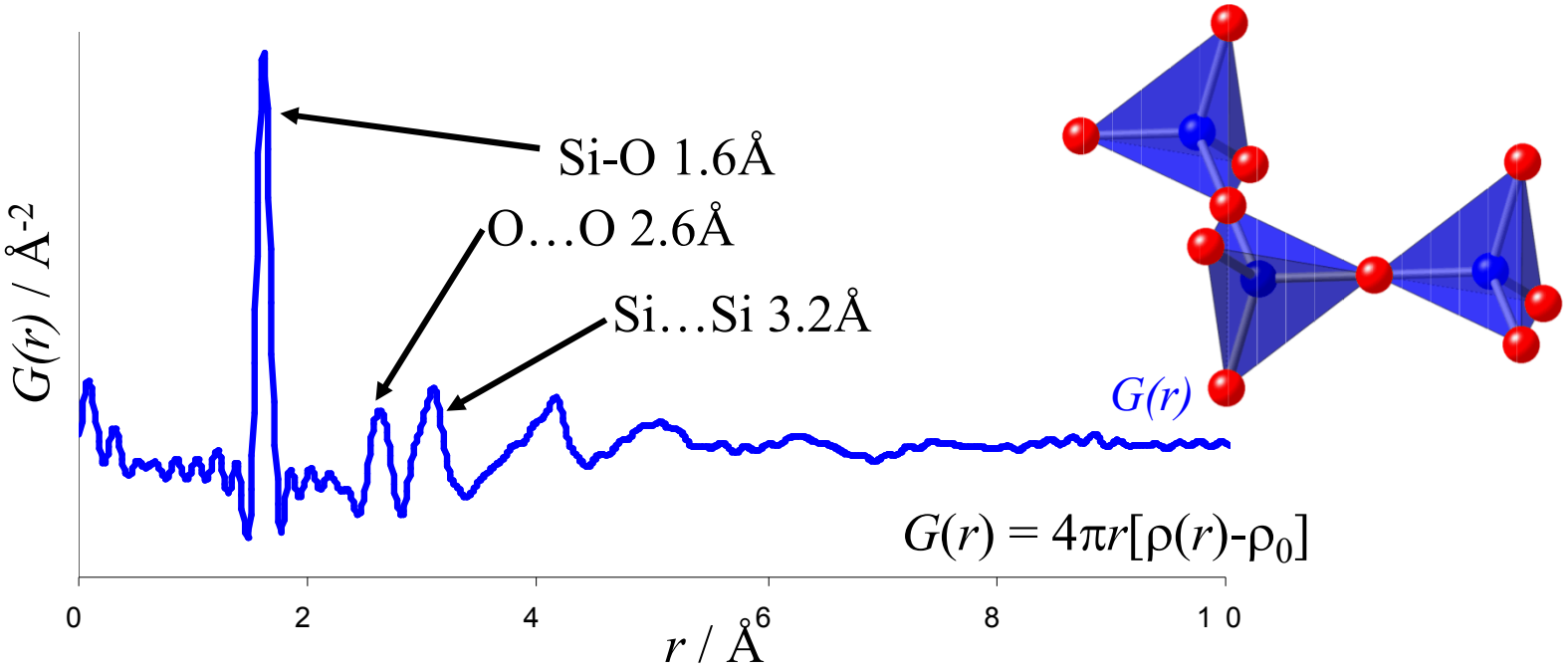
- a weighted histogram of ALL atom-atom distances



Peak position	⟷	Bond length / distance
Peak area	⟷	Coordination #, scattering intensity
Peak width	⟷	Disorder, bond angle distribution
Peak r_{max}	⟷	Particle size, coherence

→ **Structural Modeling**

Application to Nanoporous Materials to Examine Short Range Interactions

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Sc-MIL-100: Structure-Property relationship evaluated.

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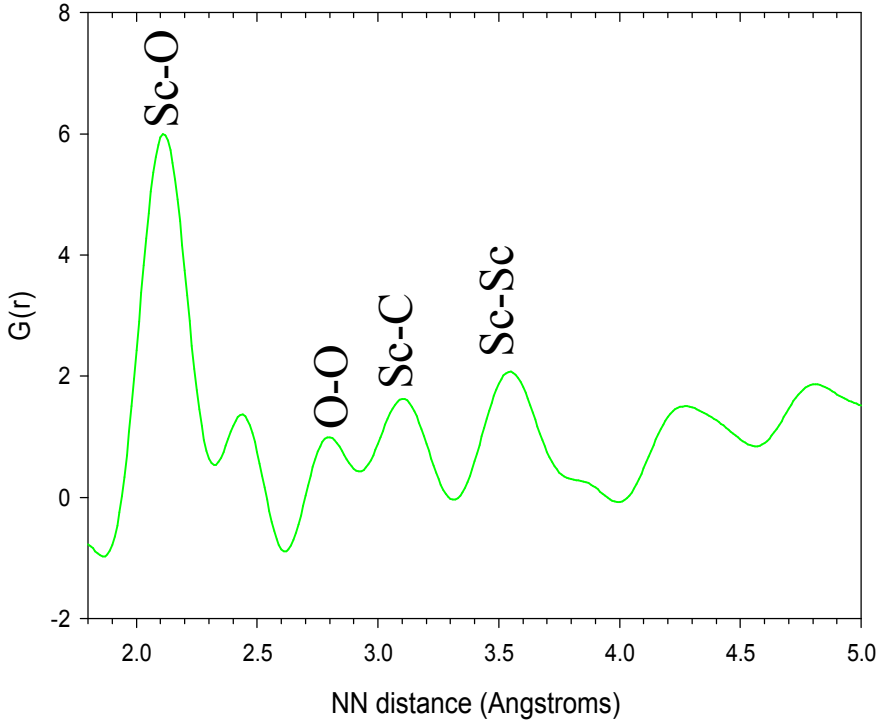
d-Pair Distribution Function (d-PDF)



Peaks shifted to longer distances
Consistent with larger Sc incorporation
(vs. Cr-MIL-100)

d-PDF peak analysis

Bond	NN distance (Å)	Area	FWHM (Å)
Sc-O	**2.11**	**1.5**	**0.19**
O-O	2.81	0.3	0.22
Sc-C	3.08	0.8	0.26
Sc-Sc	3.53	0.5	0.24

- Oxo-centered trimers at nodes of MIL-100 framework inferred from M-O and M…M distances
- Narrow Sc-O peak = narrow Distribution of bond lengths
- Single M-O bond length (M-O(μ_3) or M-O (carboxylate)), suggests **M-O-M angle of 113°** << 120° of a planer trimer

Sava Gallis, D. F.; Parkes, M.; Greathouse, J.A.; Nenoff, T.M. **2016**, submitted. *US provisional Patent 2015* *tmnenof@sandia.gov*

Sc-MIL-100: Structure-Property relationship evaluated. Preferred O_2 sorption – Large Sc Distorts Cluster

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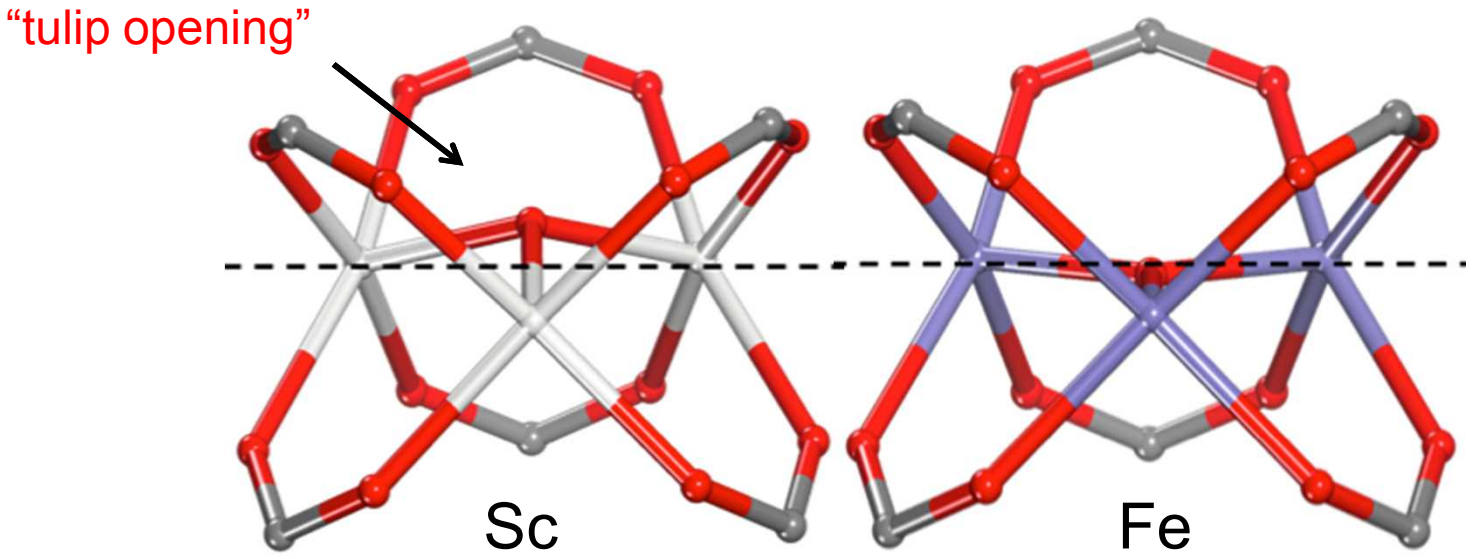
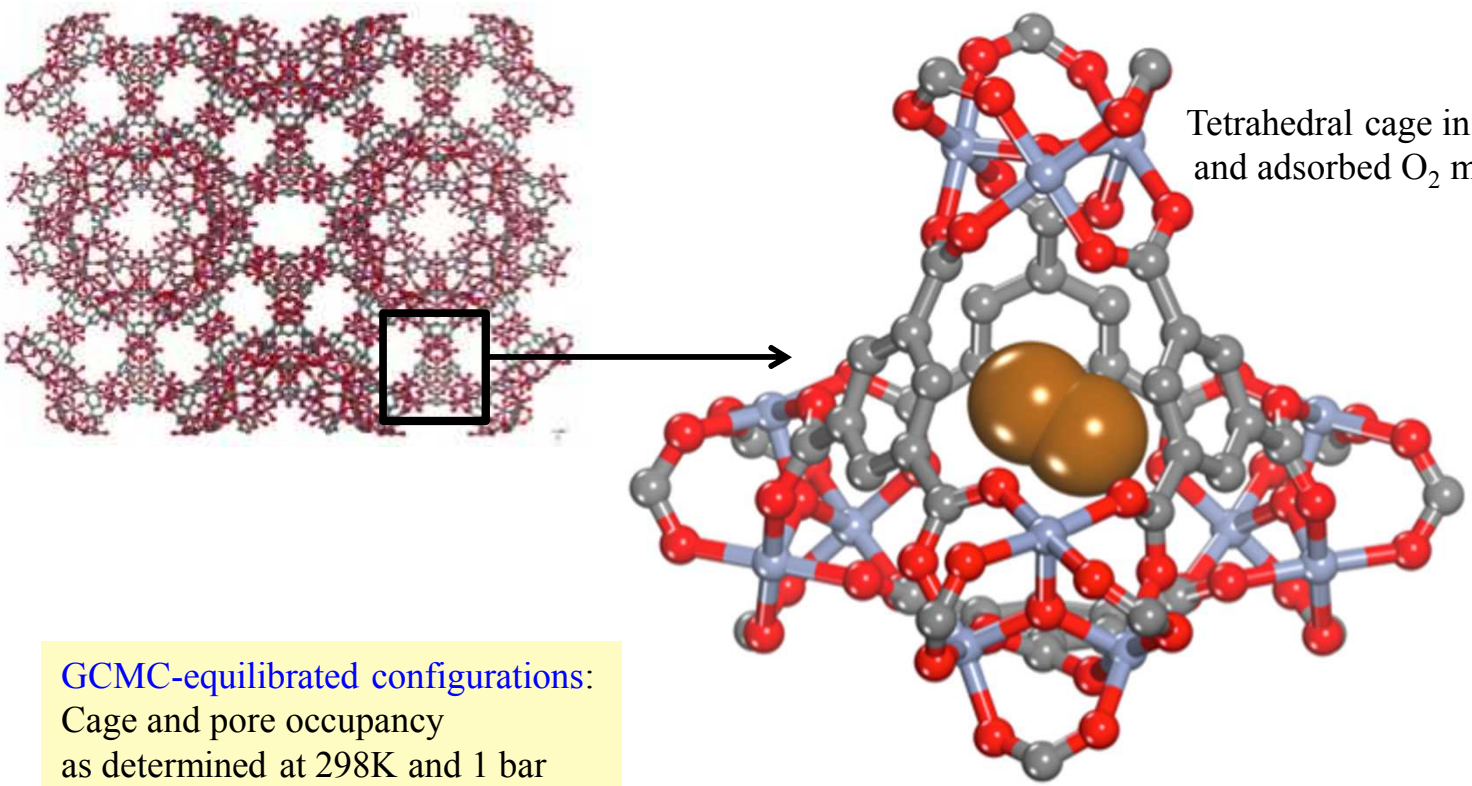
Large size of Sc atom requires **out of plane distortion** in the ozo trimer of the O(μ3) atom.

Resultant "**puckering**" of trimer and "bending" of ligand is probable route for enhanced O_2 sorption / insertion in Sc-MIL-100



Rietveld refinement unit cell for Sc-MIL-100: a = 74.518(31) Å, R = 10.7%

Sc-MIL-100: Probable Sc-O binding sites



Tetrahedral cage in the MIL-100 framework and adsorbed O_2 molecule (large spheres).

GCMC-equilibrated configurations:
Cage and pore occupancy
as determined at 298K and 1 bar

P (bar)	Gas	# in Cage	# in Pore	Total
1	N_2	21	27	48
1	O_2	47	20	67

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
- 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.
- **Sc-MIL-100**: 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.
- On-going Steps: Data transfer to *Technoeconomic Analysis* and *Burner Design* for Oxyfuel combustion applications; higher TRL testing

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Extra slides

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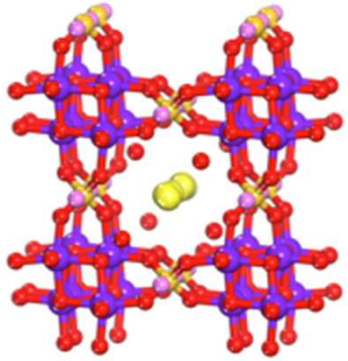
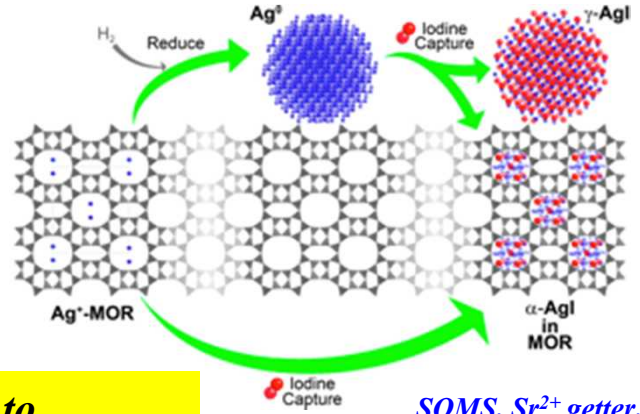
Novel SNL Separations and Waste Forms: Technologies for Environment and Energy Applications

Sandia National Laboratories

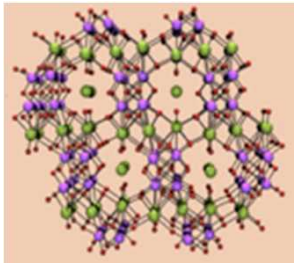


R&D100 1996
JACerS, 2009, *92(9)*, 2144
JACerS, 2011, *94(9)*, 3053
Solvent Extr. & Ion Exch, 2012, *30*, 33

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



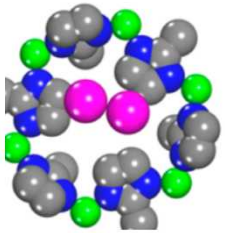
Ag-MOR I_2(g) capture & mechanisms
JACS, 2010, *132*(26), 8897
J Phys Chem Letters, 2011, *2*, 2742

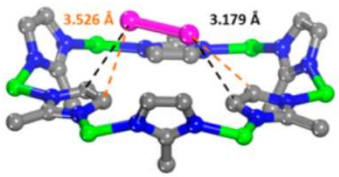


SOMS, Sr^{2+} getter, 1-step to Perovksite WF
JACS, 2002,*124(3)*, 1704
US Patent *7,122,164*

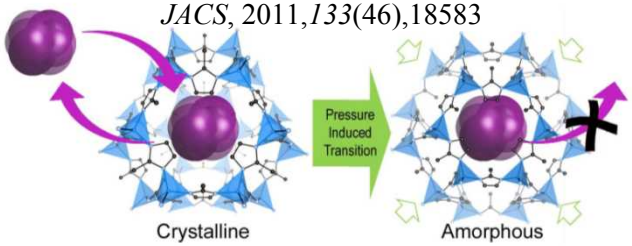
Fundamental Research to Applied to Commercial Products
Design the Separation Material To Develop the Waste Form

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

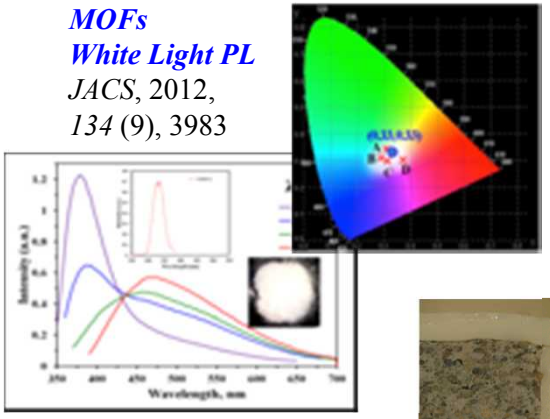


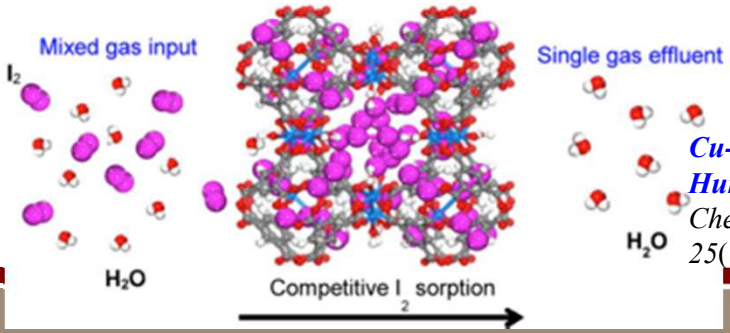


MOF Amorphization for Gas Storage
JACS, 2011,*133*(46),18583

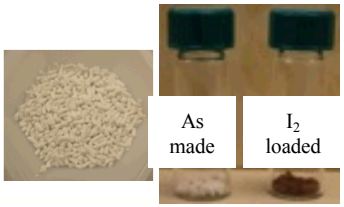


MOFs White Light PL
JACS, 2012, *134* (9), 3983

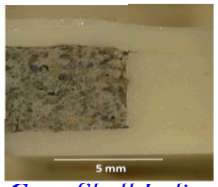




Cu-BTC: I_2 from Humid Gas Stream
Chem. Mater. 2013, *25*(13), 2591

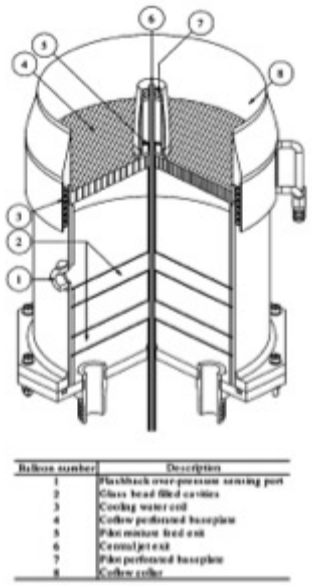


Binder Free MOF Pelletization
US Patent 2015 *9,117,560*

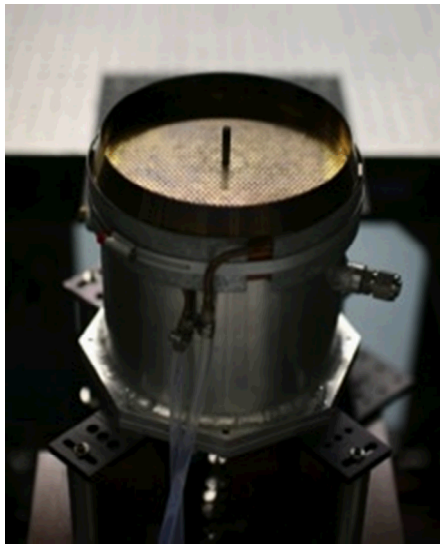


Universal Core-Shell Iodine Glass Waste Form & Getter
JACerS, 2011, *94*(8), 2412
US Patent 8,262,950; 2012

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



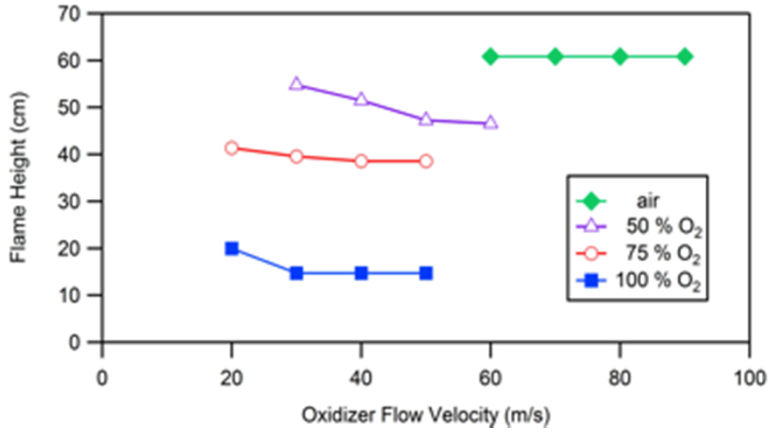
Balloon number	Description
1	Flashback over-pressure sensing port
2	Glass bead filled cavities
3	Cooling water coil
4	Coflow perforated baseplate
5	Pilot mixture feed exit
6	Central jet exit
7	Pilot perforated baseplate
8	Coflow collar



-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

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

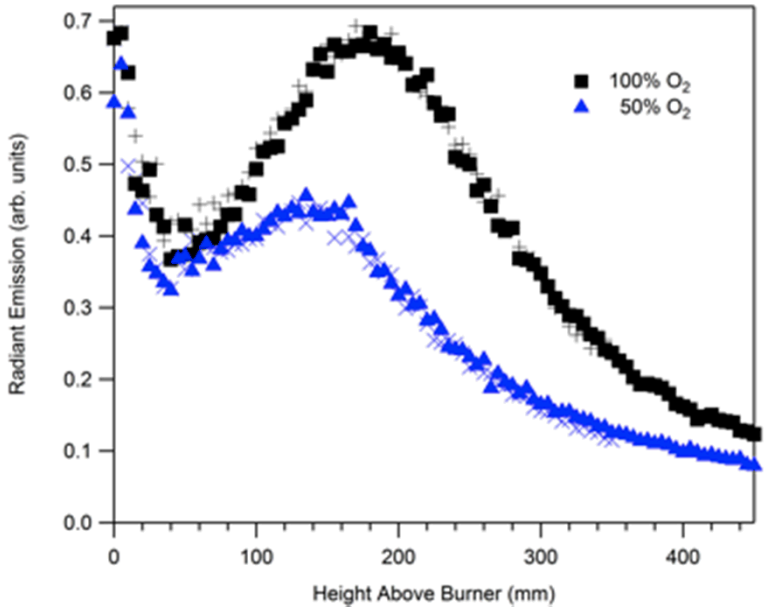
- Velocity (Re) of oxidizer flow is 50% lower when using pure O_2, making for taller flame (slower mixing)
- Soot formation is enhanced when using pure O_2 (higher temperatures, slower mixing)

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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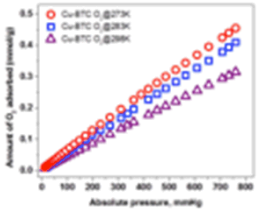
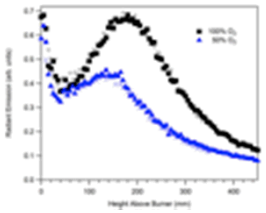
Systems Analysis of MOF-based Air Separation

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



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



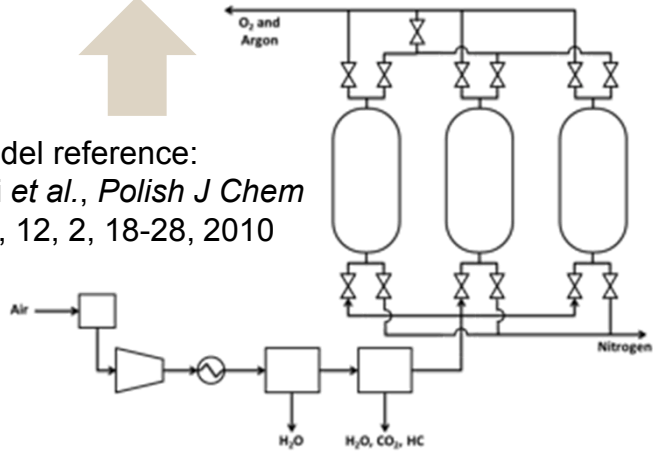
Can MOF-based PSA reduce energy consumption by 5% vs. conventional PSA air separation?

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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