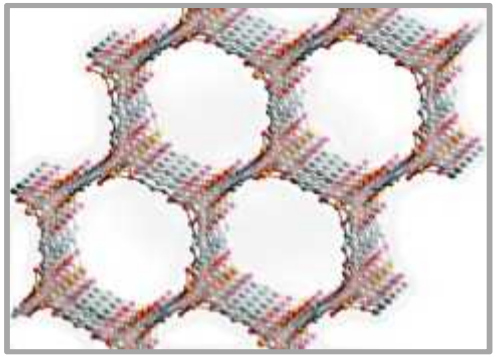
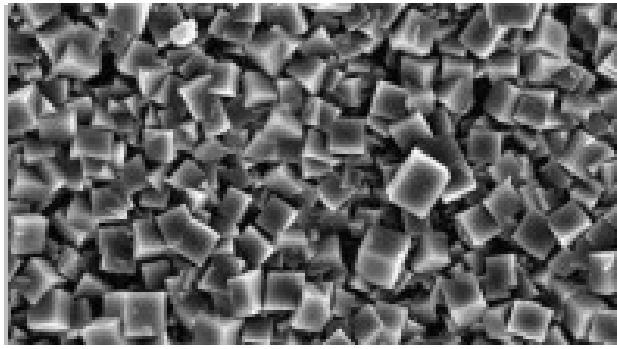
SAND2016-5724C

SAND2017-3123C





# Design and Synthesis of Novel Porous Materials for Energy and Environmental Applications

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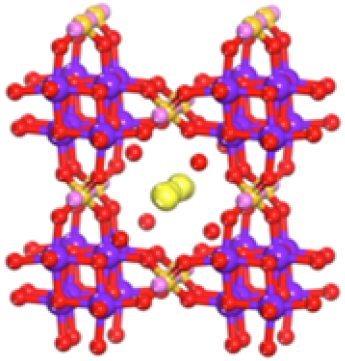
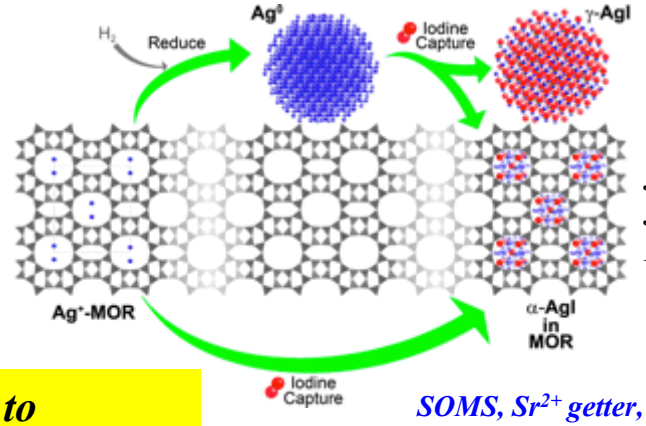
# Novel SNL Separations and Waste Forms: Technologies for Environment and Energy Applications

Sandia National Laboratories

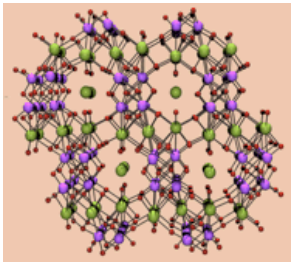


R&D100 1996
*JACerS*, 2009, *92(9)*, 2144
*JACerS*, 2011, *94(9)*, 3053
*Solvent Extr. & Ion Exch*, 2012, *30*, 33

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



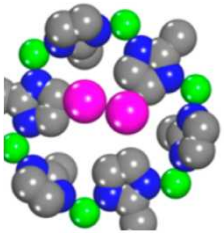

***Ag-MOR $I_2$(g) capture & mechanisms***
*JACS*, 2010, *132*(26), 8897
*J Phys Chem Lett*, 2011, *2*,2742
*I&ECR* 2017, *56*(8), 2331

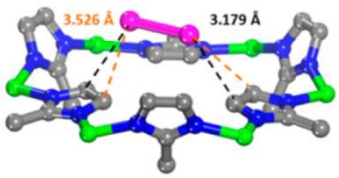


***SOMS, $Sr^{2+}$ getter, 1-step to Perovksite WF***
*JACS*, 2002,*124(3)*, 1704
US Patent *7,122,164*

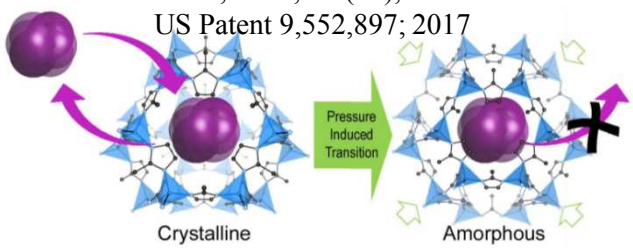
***Fundamental Research to Applied to Commercial Products***
***Design the Separation Material To Develop the Waste Form***

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

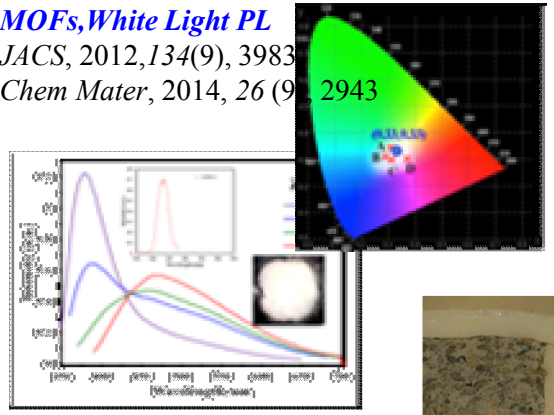


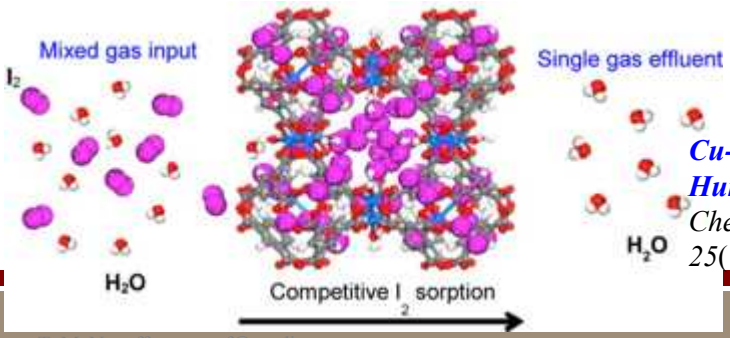



***MOF Amorphization for Gas Storage***
*JACS*, 2011,*133*(46),18583
US Patent 9,552,897; 2017

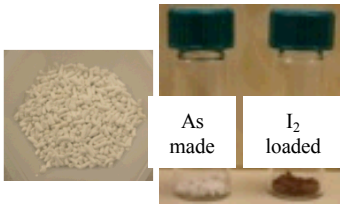



***MOFs,White Light PL***
*JACS*, 2012,*134*(9), 3983
*Chem Mater*, 2014, *26* (9), 2943

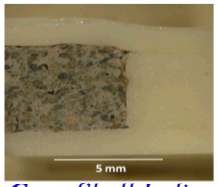





***Cu-BTC: $I_2$ from Humid Gas Stream***
*Chem. Mater.* 2013, *25*(13), 2591

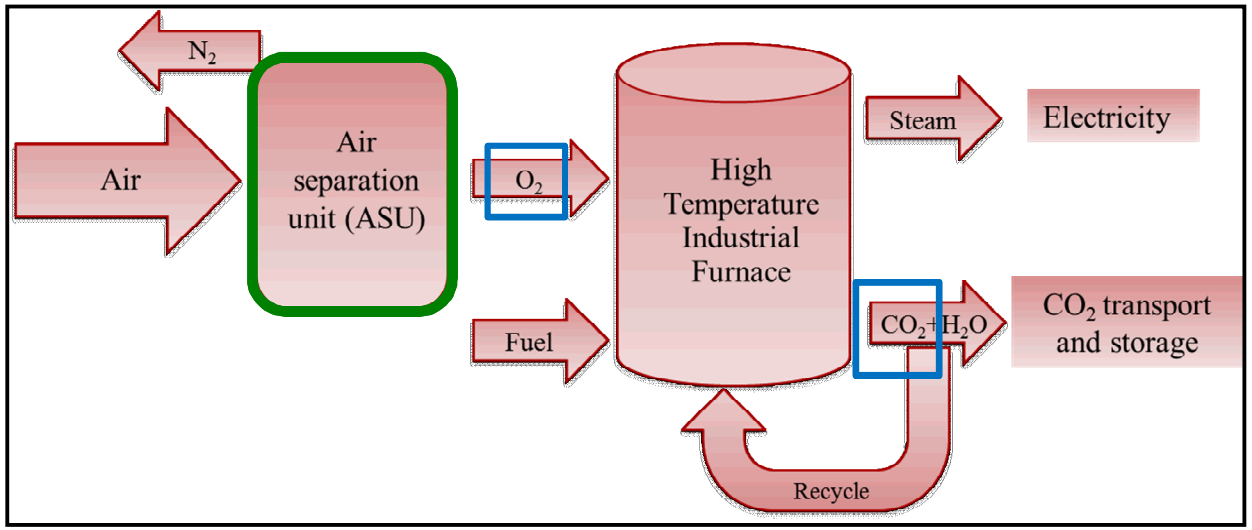



*Binder Free MOF Pelletization*
US Patent 2015 *9,117,560*




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

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




- Oxygen-enriched (oxy-fuel) combustion: burning the fossil fuel in an $O_2$ rich atmosphere results in a flue gas composed mainly of $CO_2$ and water (little or no $SO_X$ and $NO_X$ emissions)
- The limiting factor of this technology is the efficiency of the cryogenic ASU, a costly and energy intensive process (primarily compression)
- Our study is focused on new highly selective materials to increase the efficiency of this separation process

Goal: determine the $O_2$ and $N_2$ uptake dependency with temperature in MOFs with coordinatively unsaturated metal sites



*tmnenof@sandia.gov*

# Feng, Bu, et. al.: Tuned $CO_2$ uptake with MOFs via Mixed Metal Centers

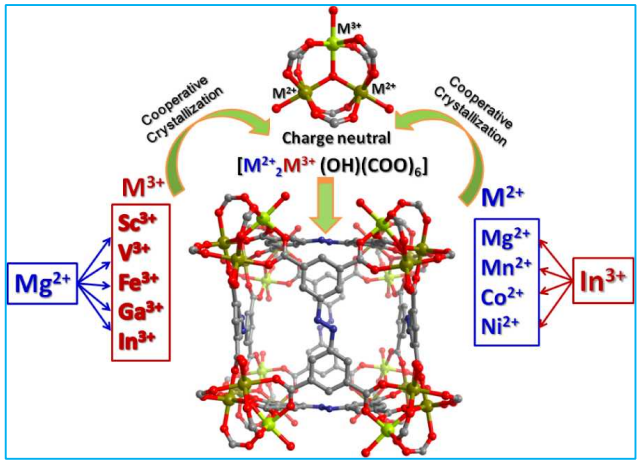
Sandia National Laboratories

JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

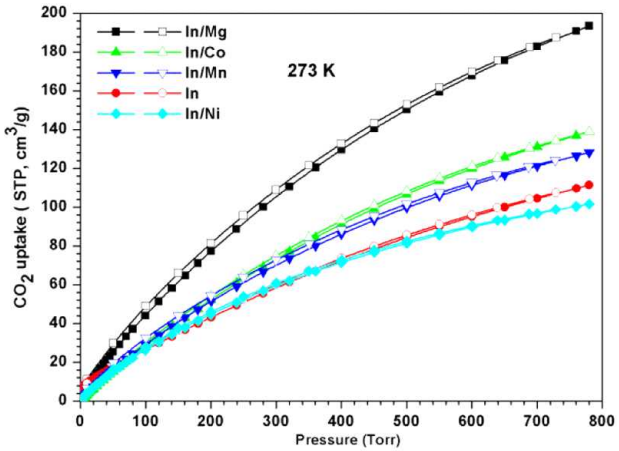
Up to 207.6 cm3/g @ 273K, 1 bar

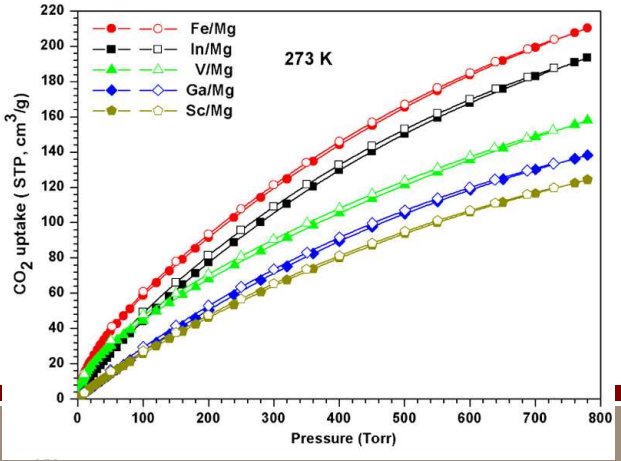
## Systematic and Dramatic Tuning on Gas Sorption Performance in Heterometallic Metal–Organic Frameworks

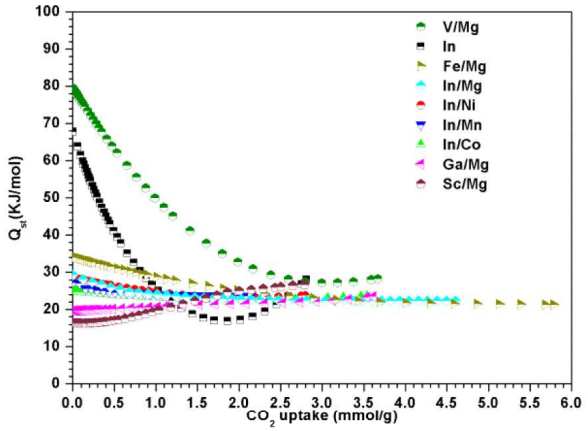
Quan-Guo Zhai,[†] Xianhui Bu,*[,‡] Chengyu Mao,[†] Xiang Zhao,[†] and Pingyun Feng*[,†]

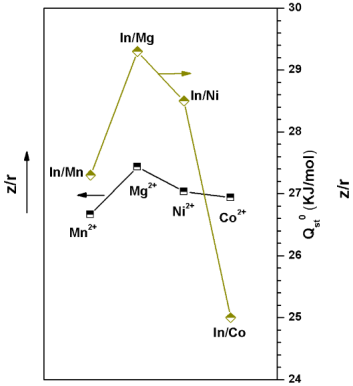


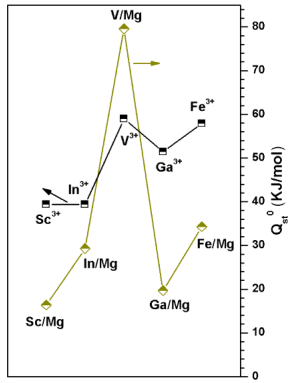

$M^{2+}$ and $M^{3+}$ combinations for CPM-200s




Correlation between isosertic heat at zero loading of $CO_2$ and charge-to-radius ratio of metal ions

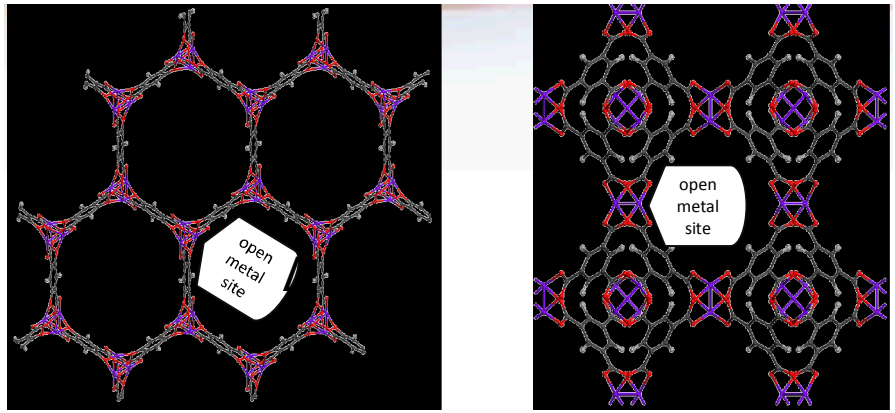


*tmnenof@sandia.gov*

# Target $O_2$ Selective Separations Materials, DFT & Experiments

*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], $Fe_2(DOBDC)$[2] both show preferential adsorption $O_2$ vs $N_2$
- Plane wave DFT calculations on periodic structures: 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
- Use of DFT to determine M-$O_2$ vs M-$N_2$ binding energies




$M_2(dobdc)$ $M_3(btc)_2$

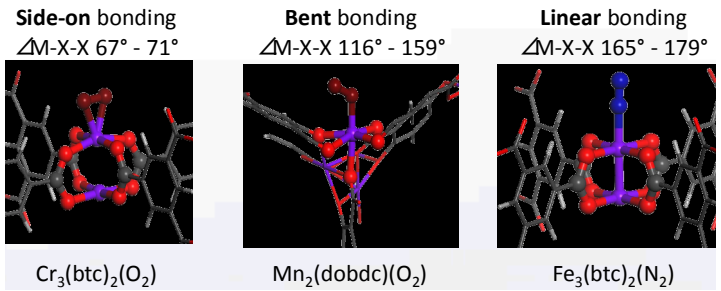
MOF metal sites = separate $O_2/N_2$ by differences in bonding & electronic properties

**Plan wave density functional theory (DFT) calculations** were performed on periodic structures of each MOF in the Vienna ab initio simulation package **(VASP)** with the Perdew-Burke-Ernzerhof **(PBE)** functional including dispersion corrections **(DFT-D2)**. Geometries were optimized and **static binding energies ($\Delta E_{O2}$, $\Delta E_{N2}$)** 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

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




Attention Paid to Bonding Geometries



[1]*JACS* **2010**, *132*, 7856–7857; [2]*JACS* **2011,** *133*, 14814-14822

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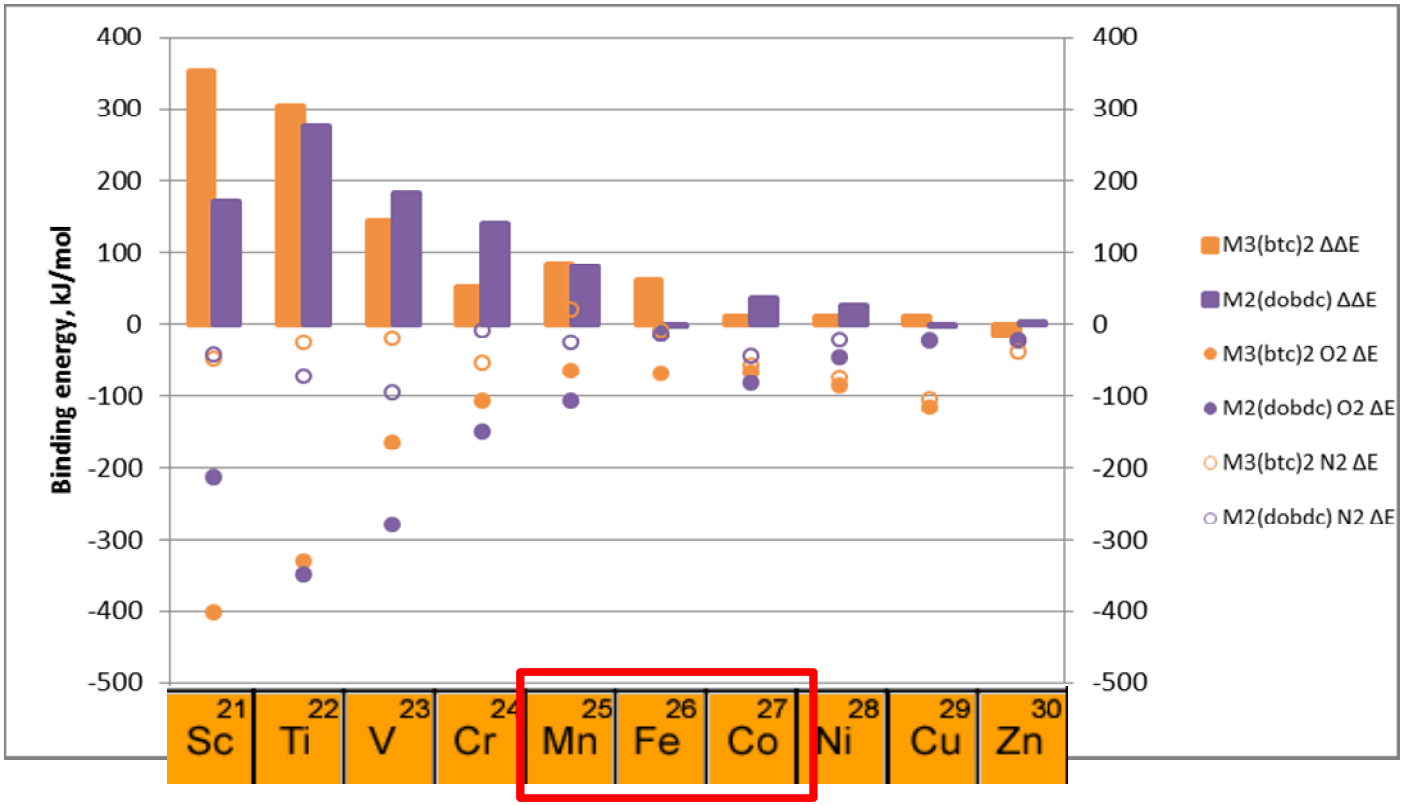
# $O_2$ and $N_2$ Binding Energies Trends Across the First Row Transition Metal Series



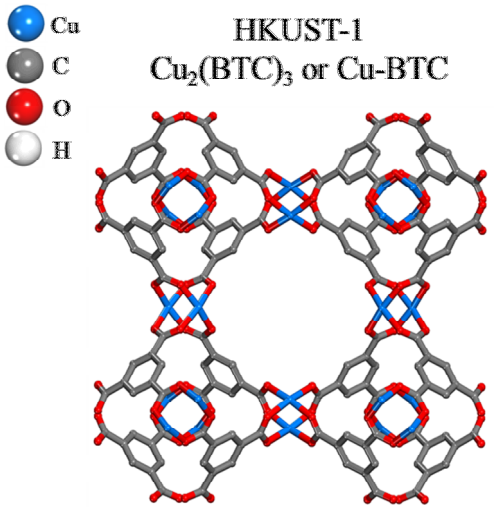

DFT predicts similar $O_2$ and $N_2$ binding to Mn, Fe, Co but with consistent stronger binding for $O_2$ to the metals



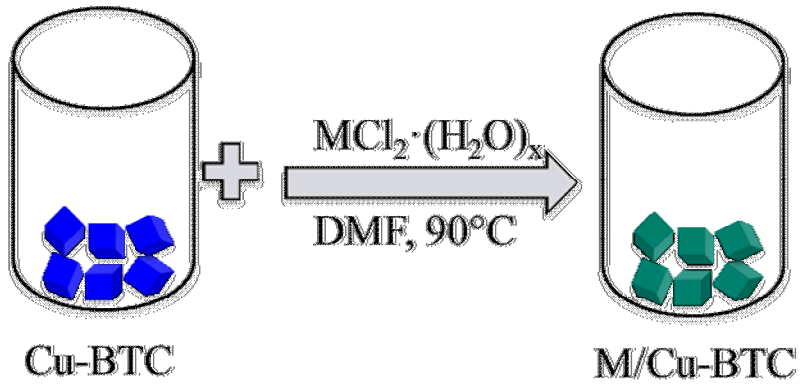
Parkes, M.; Sava Gallis, D. F.; Greathouse, J.A.; Nenoff, T.M. *J. Phys Chem C*, **2015**, *119*, 6556.

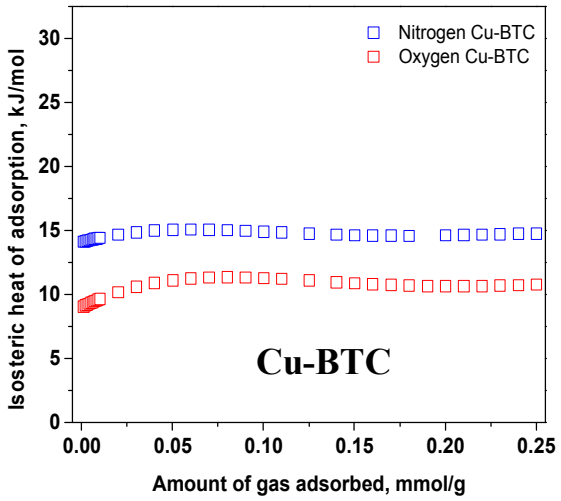
*tmnenof@sandia.gov*

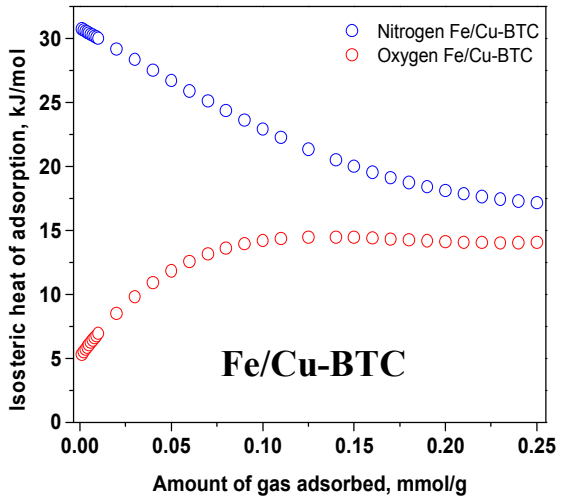
# Postsynthetic Metal Ion Exchange to form Porous Mn-, Fe- and Co- Analogues of Cu-BTC




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




**0 K *DFT binding energy*:** Excellent prediction for 77K experiments,

Do not correlate as well with experimental data 273-298 K
- $N_2$ is preferred over $O_2$



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

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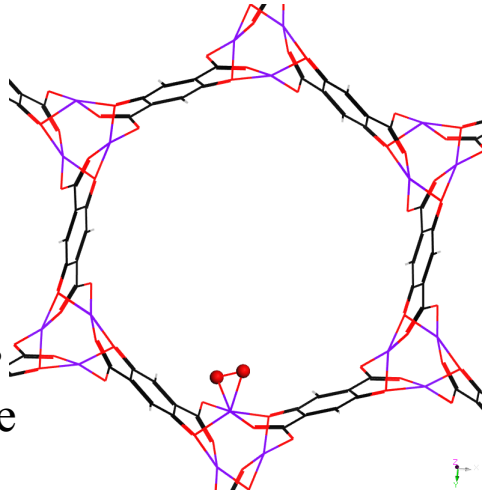
# Use of AIMD to Predict Behavior of Dynamic Gas Molecules

Vienna *ab initio* simulation package (VASP)



- MOF
  - $M_2$(dobdc) analogs
- Metals

| 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
|---|---|---|---|---|---|---|---|---|---|
| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |

- Effect of Temperature
  - 201 K
  - 258 K
  - 298 K

- AIMD simulations
  - NVT ensemble
  - 27.5 ps
  - 0.5 fs timestep
- PBE density functional with dispersion correction (PBE-D2), PAW potentials for core electrons, spin polarization



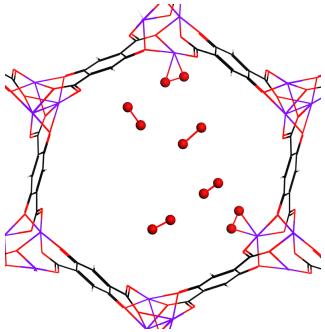
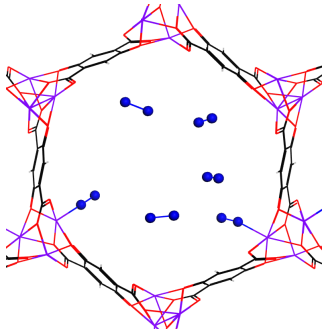
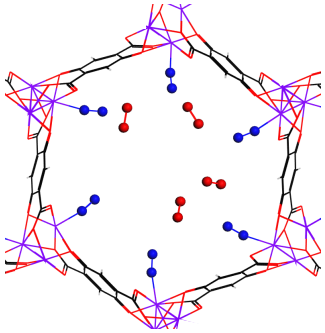
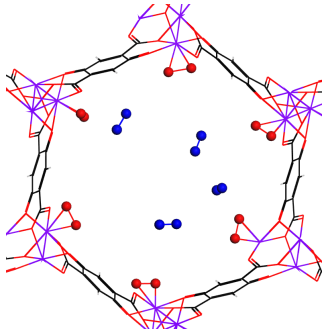
Parkes, M.V.; Sava Gallis, D. F.; Greathouse, J.A.; Nenoff, T.M. *PCCP*, **2016**, *18*, 11528.

*tmnenof@sandia.gov*

# Initial Gas Positions From Static DFT

Sandia National Laboratories

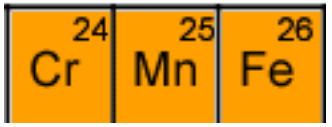
Guests

| | 2 $O_2$ bound<br>4 $O_2$ unbound | 2 $N_2$ bound<br>4 $N_2$ unbound |
|---|---|---|
| Single component |  |  |
| Mixed gas Competitive binding |  |  |
| | 6 $N_2$ bound<br>4 $O_2$ unbound | 6 $O_2$ bound<br>4 $N_2$ unbound |

## Temperatures

201 K
258 K
298 K

## Metals



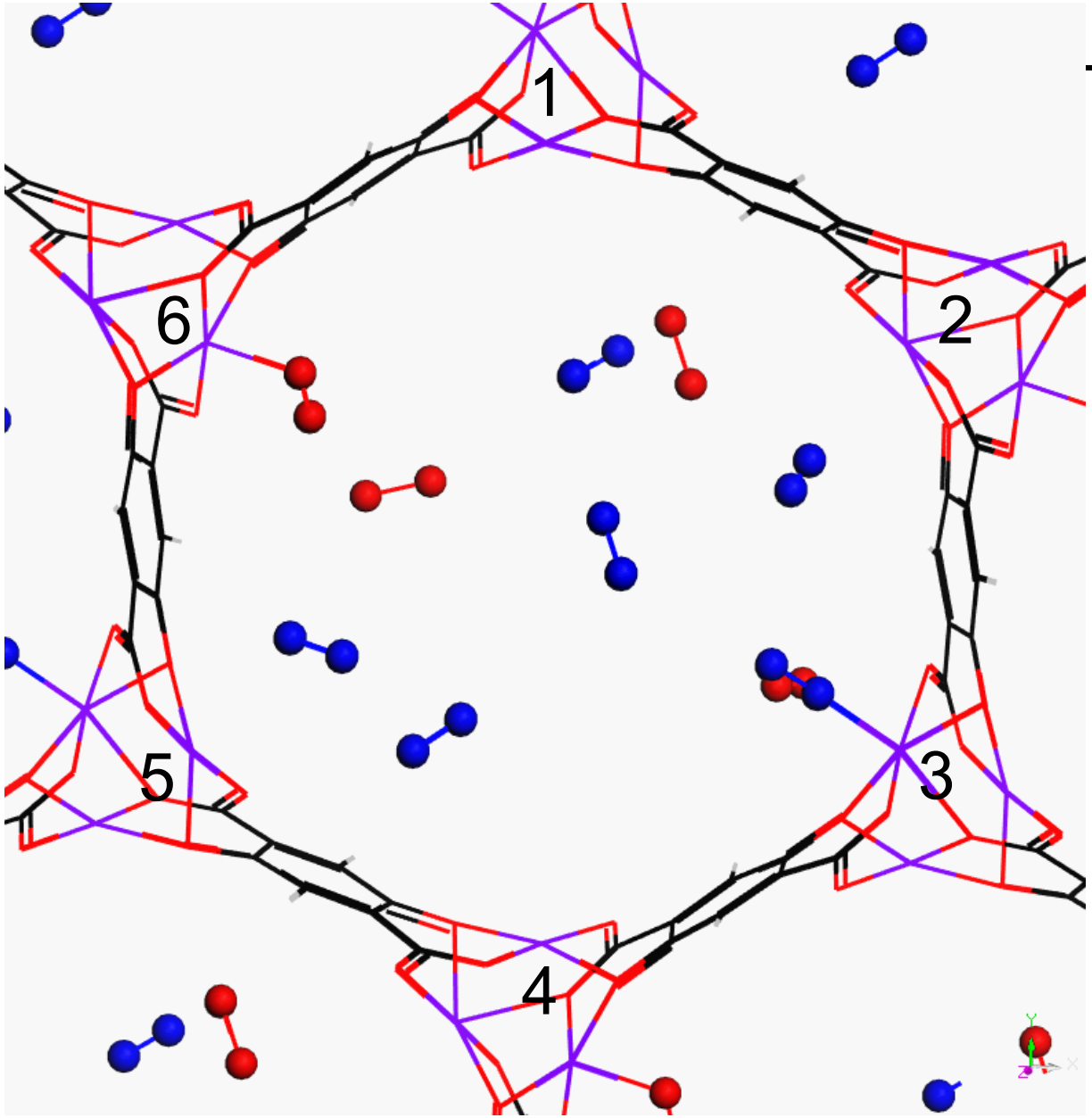

Red Sky Supercomputer
36 Simulations

3,800 processor-days each

http://hpc.sandia.gov/



tmnenof@sandia.gov




$Cr_2$(dobdc)
6 $N_2$ + 4 $O_2$
298 K

NVT
Time 2 ps – 15 ps

1 frame = 25 fs

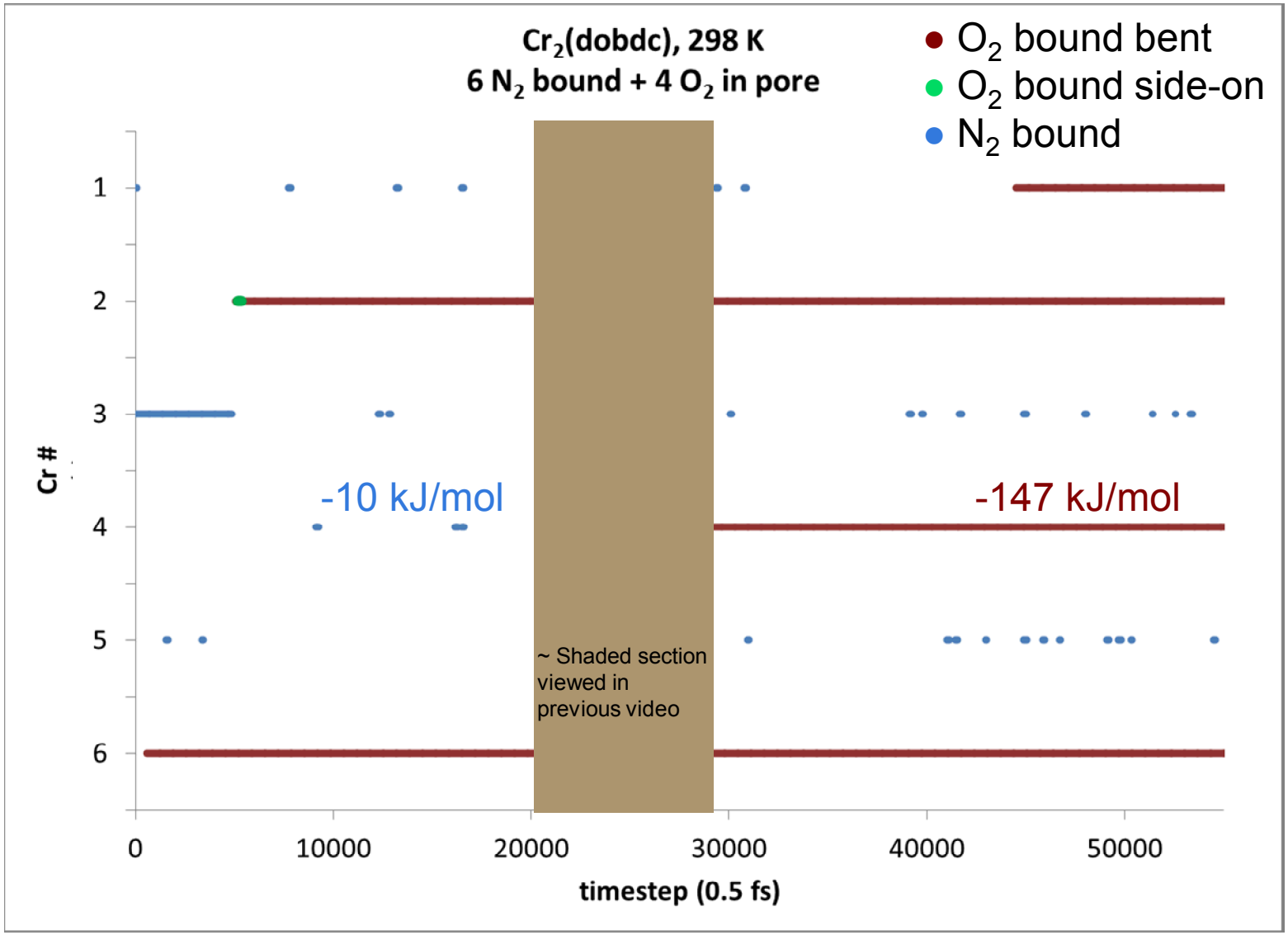
- $O_2$ slow to bind, but once on metal center, binding holds
- $N_2$ rapid bind and release from metal centers
- $O_2$ long term binding is consistently 'bent'
- Selective for $O_2$



*PCCP*, **2016**, 18, 11528

*tmnenof@sandia.gov*

# Gas Occupancy at Each Metal Site



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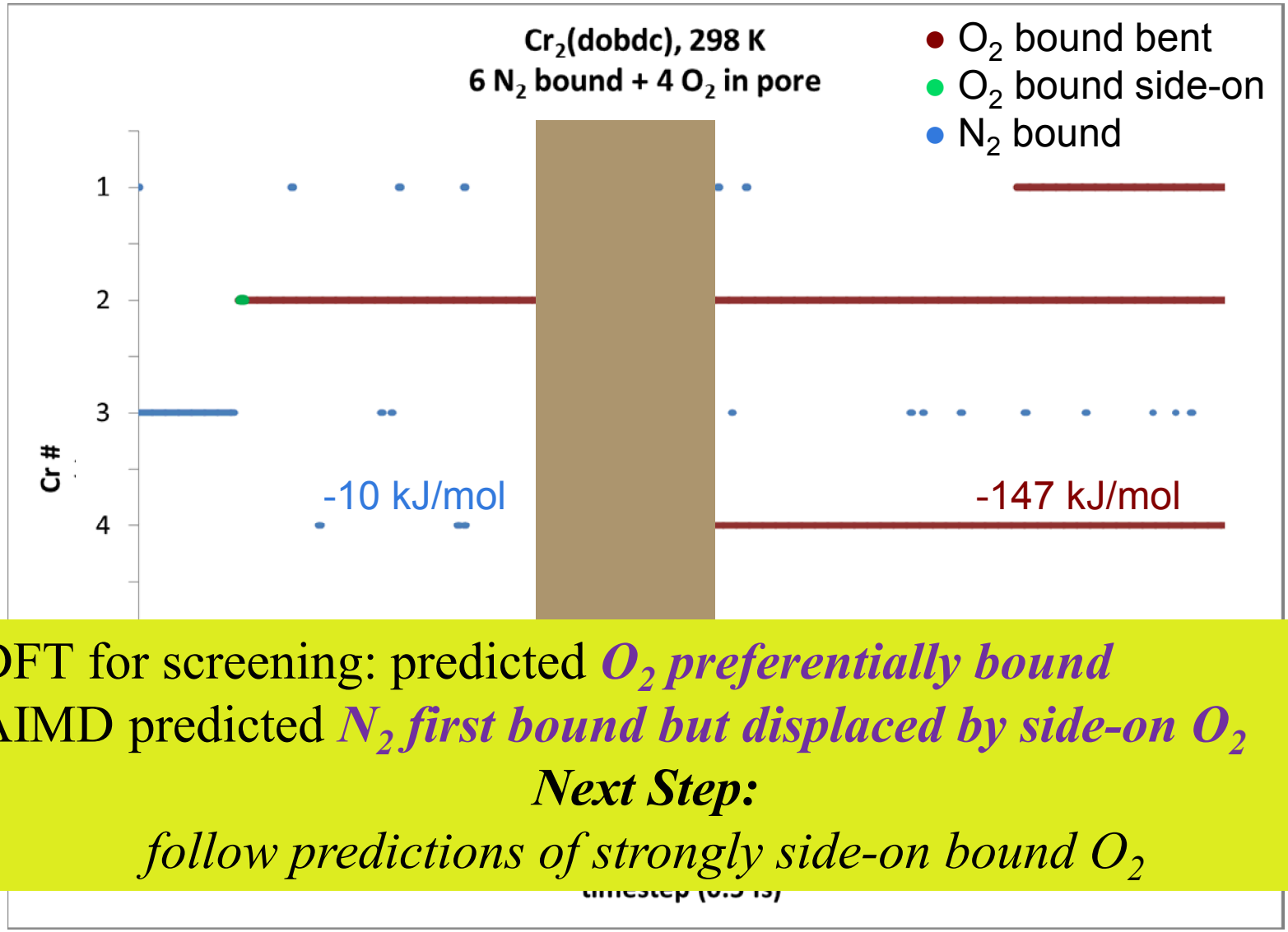
# Gas Occupancy at Each Metal Site




DFT for screening: predicted ***$O_2$ preferentially bound***

AIMD predicted ***$N_2$ first bound but displaced by side-on $O_2$***

***Next Step:***

*follow predictions of strongly side-on bound $O_2$*



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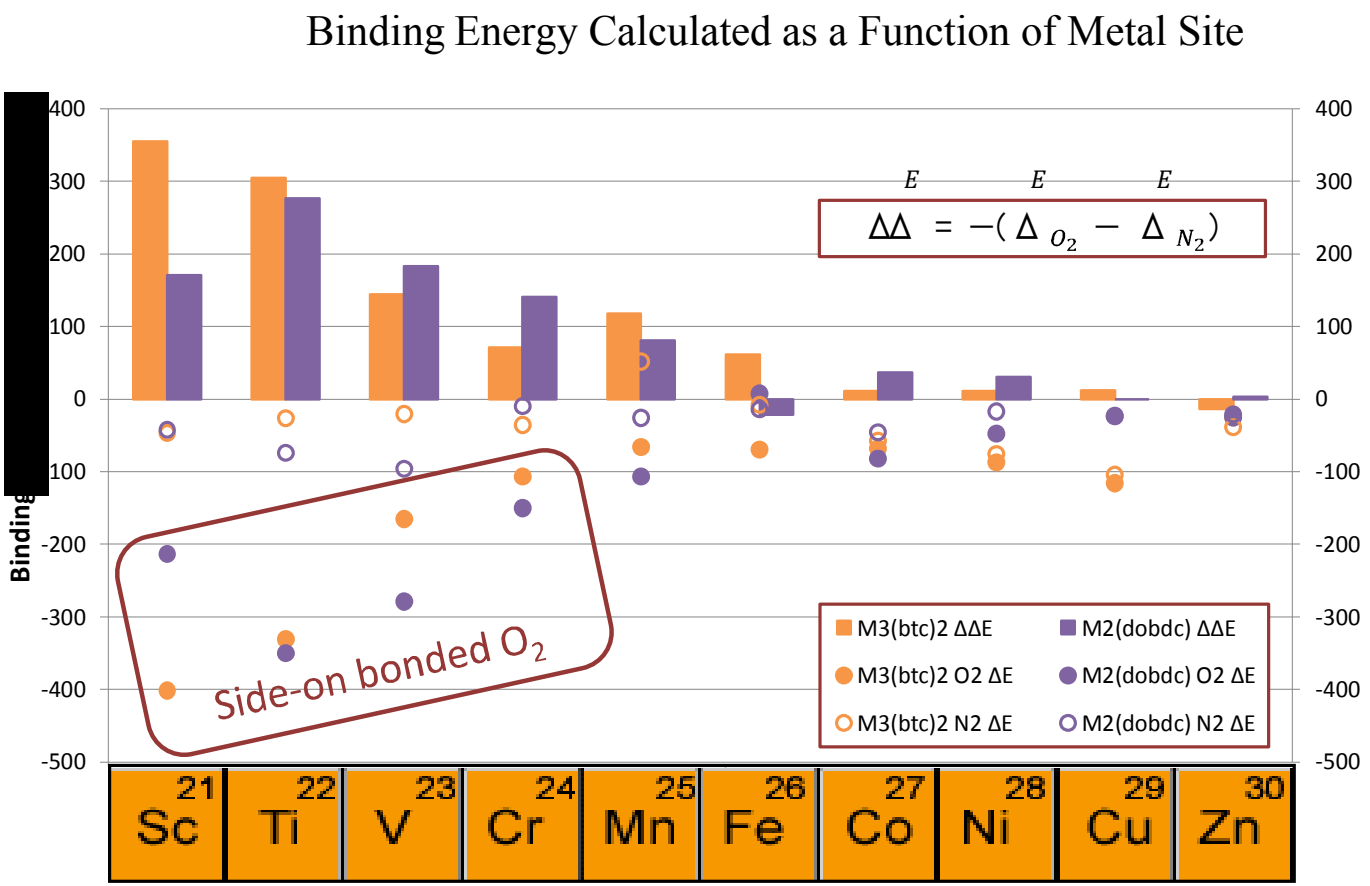
# Use of Strongest *Side-On Binding* Predictions






*J. Phys Chem C*, **2015**, *119*, 6556.

*tmnenof@sandia.gov*

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

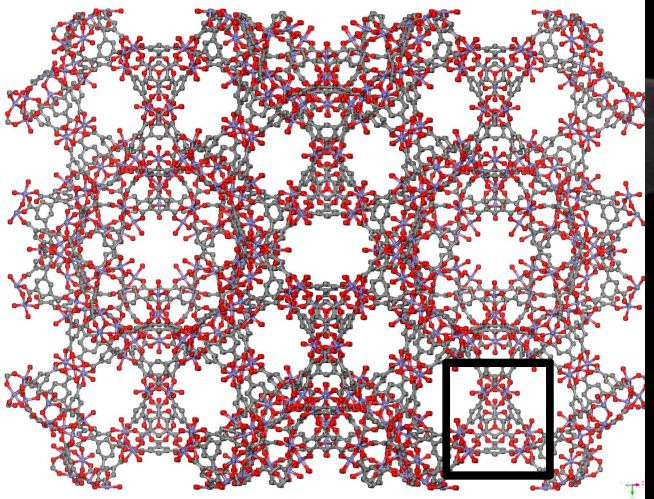
*US provisional Patent filed 2016*

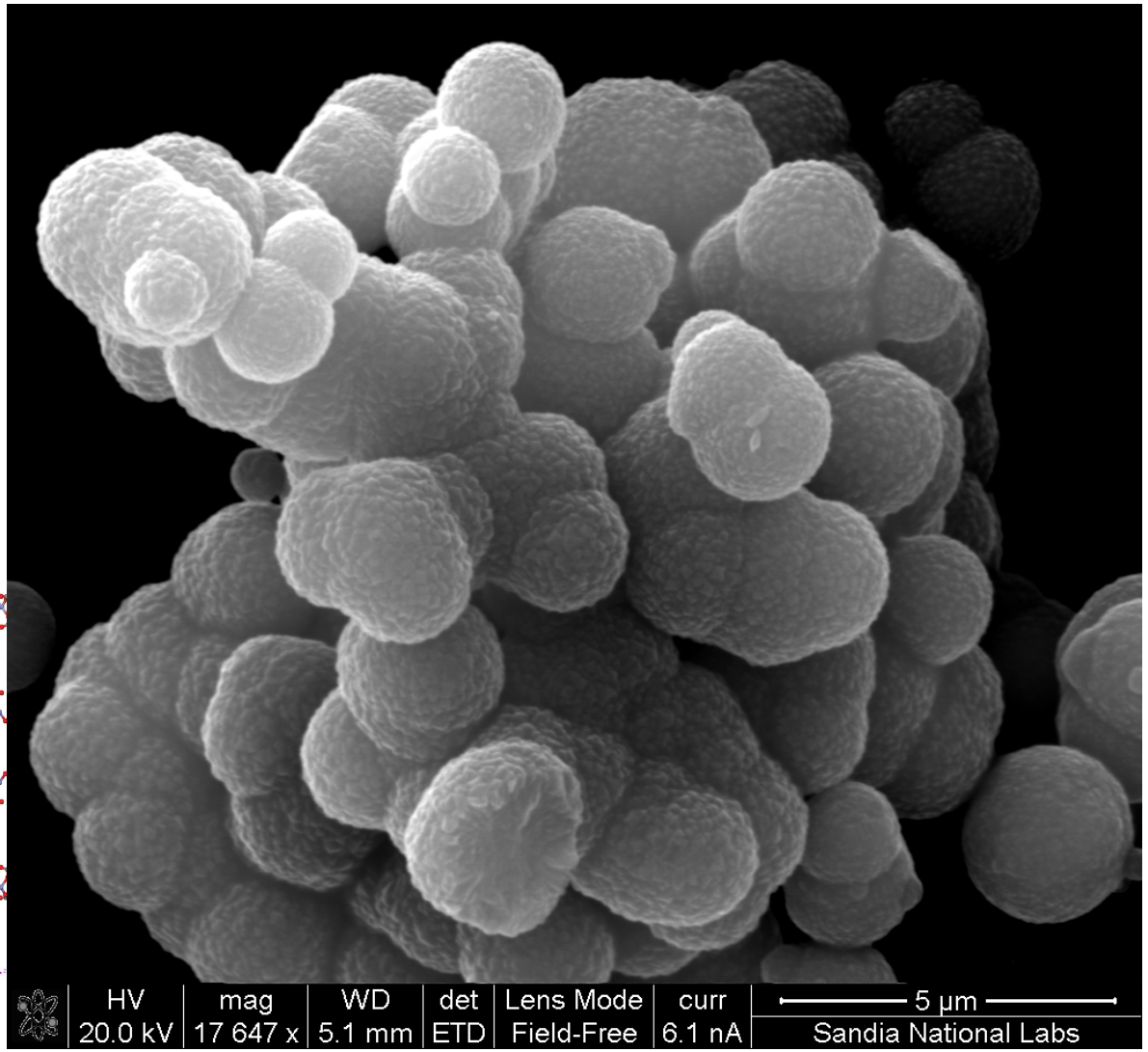
## Sc-MIL-100

***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



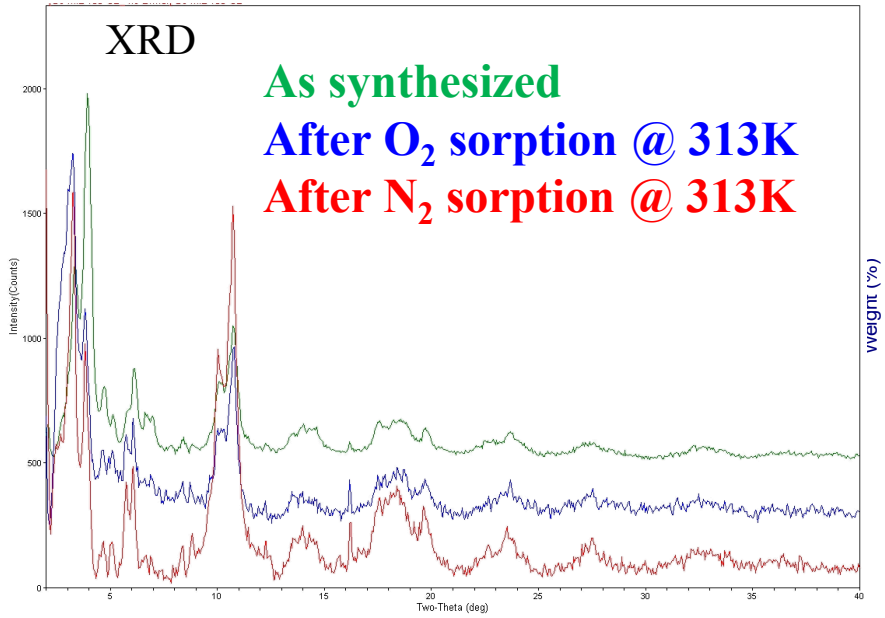


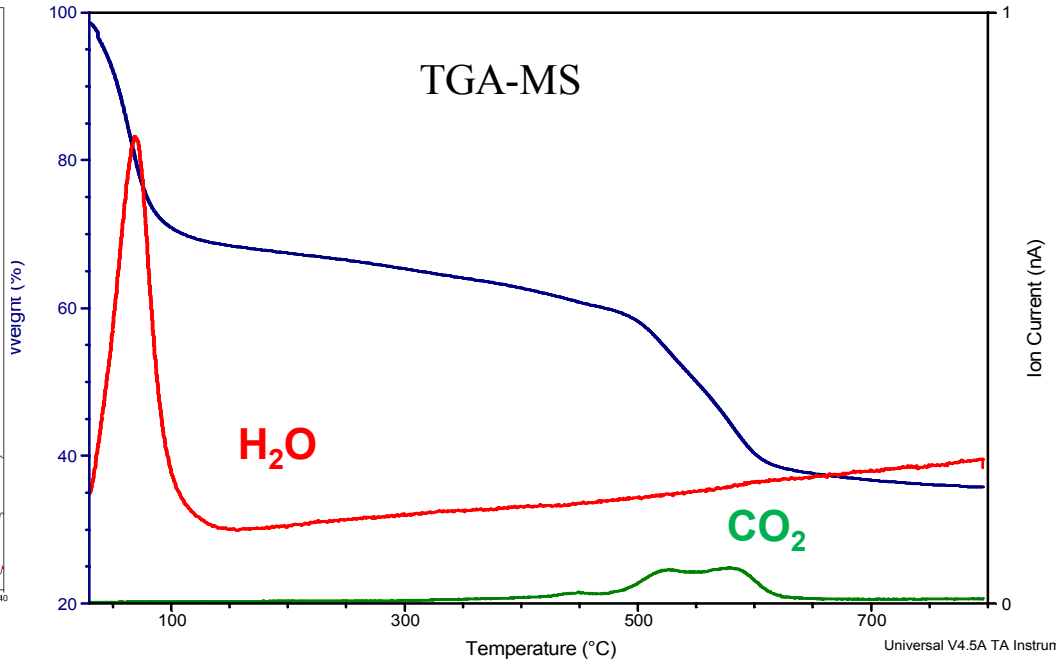


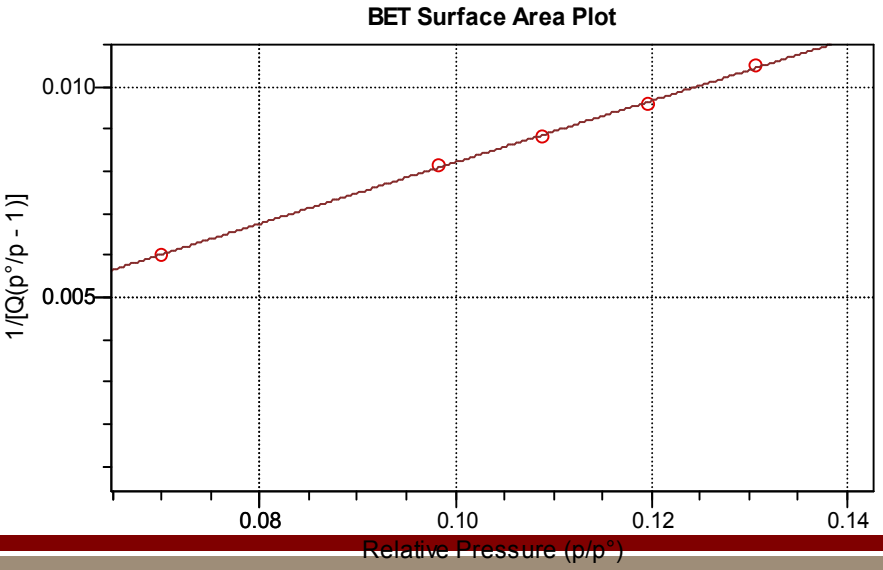

Sava Gallis, D. F., Greathouse, J.A.; Rodriguez, M.A.; Parkes, M.V.; Chapman, K.W.; Nenoff, T.M. *Chem. Mater*. **2016**, 28(10), 3327-3336 .

*tmnenof@sandia.gov*

# Sc-MIL-100: Stable MOF framework over Wide Temp Range and Exposure to Variety of Gases




BET surface area:
1321.7194 ± 24.4623 m²/g

High Surface Area with Accessible Metal Centers



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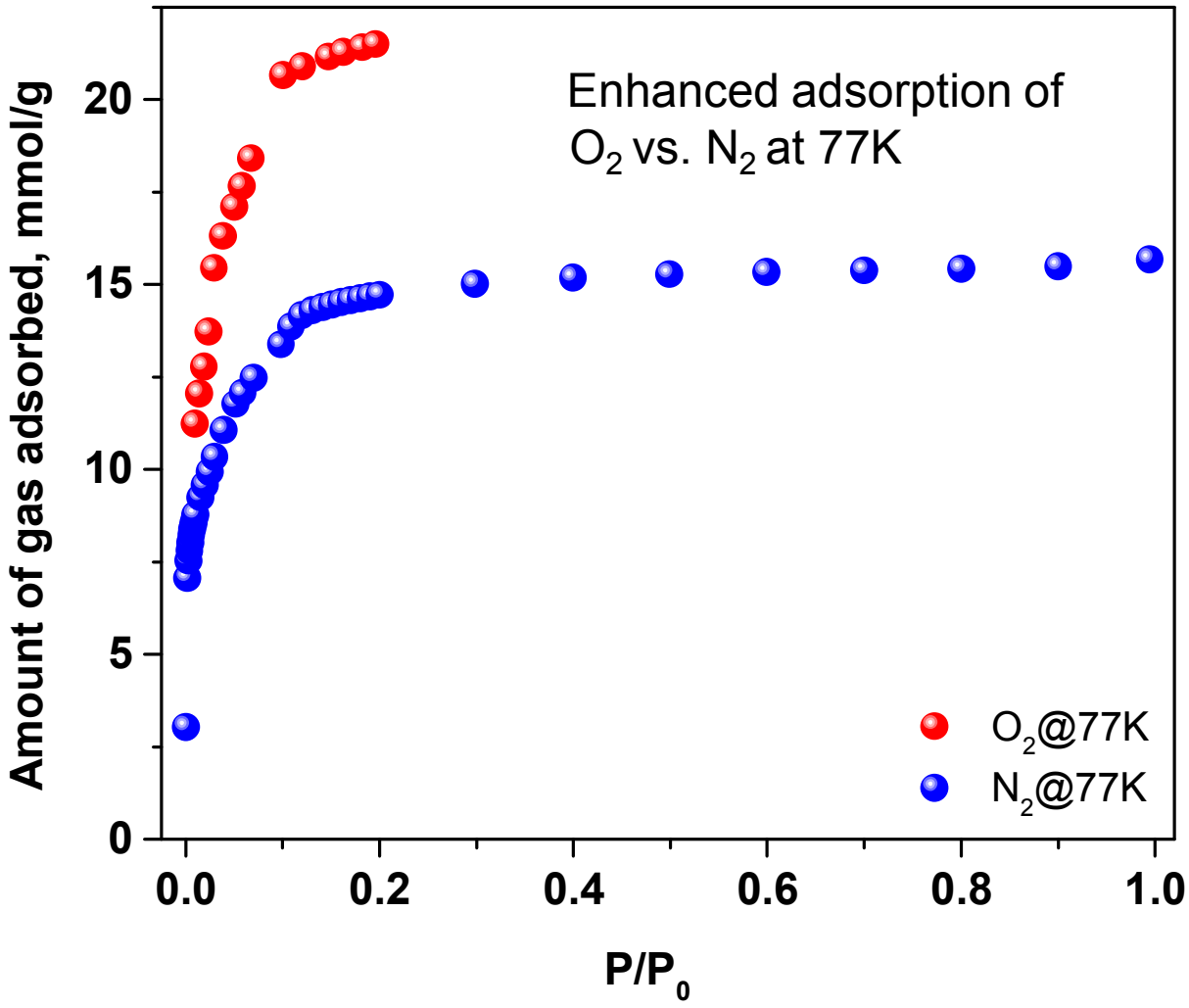
# Sc-MIL-100: Metal-Center has a role at 77K




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



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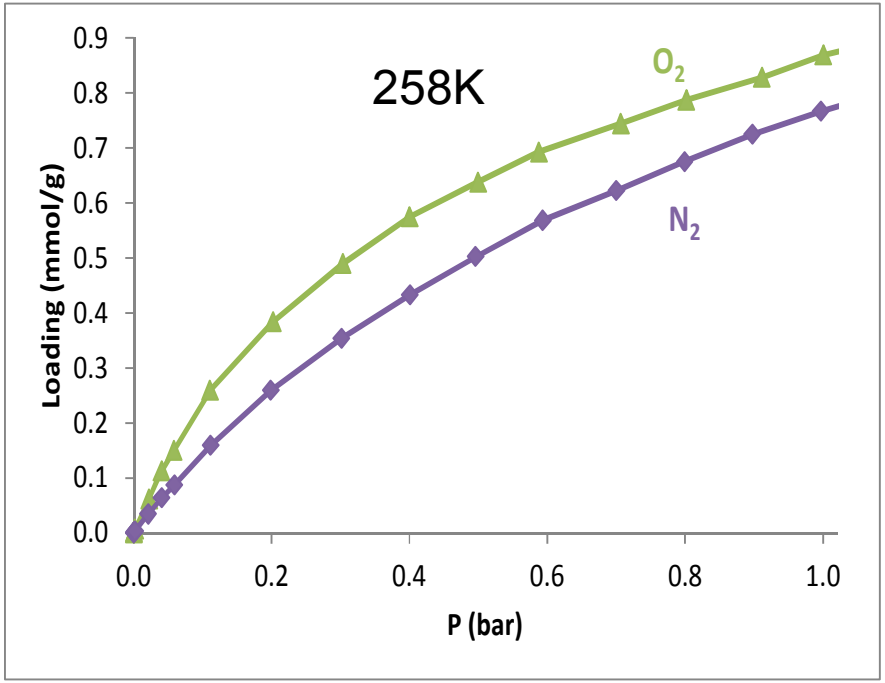
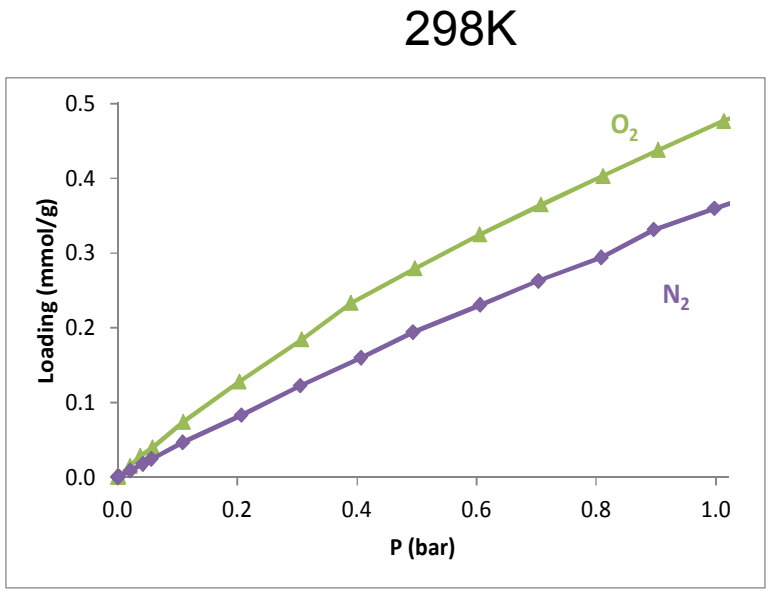
# Sc-MIL-100: GCMC Isotherm Calculations at 258K and 298K

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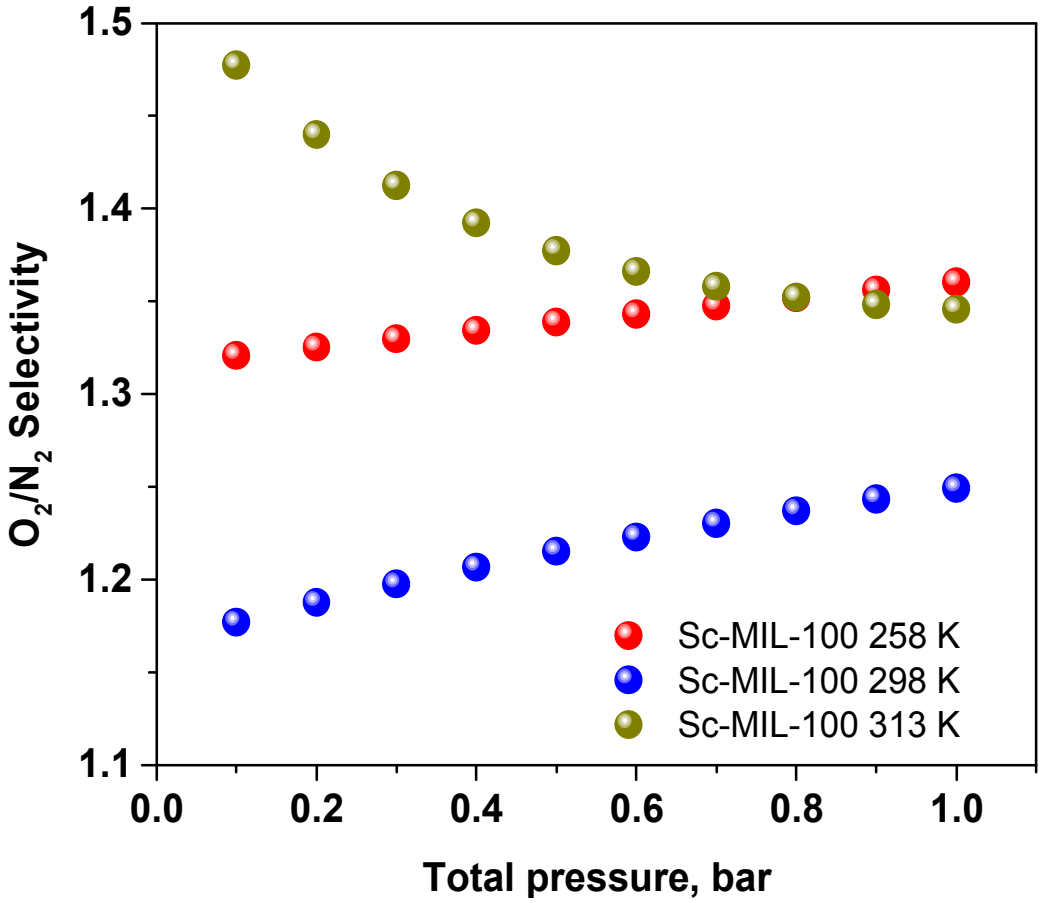
# Simulations of Competitive Gas Adsorption: based on GCMC data, 298K




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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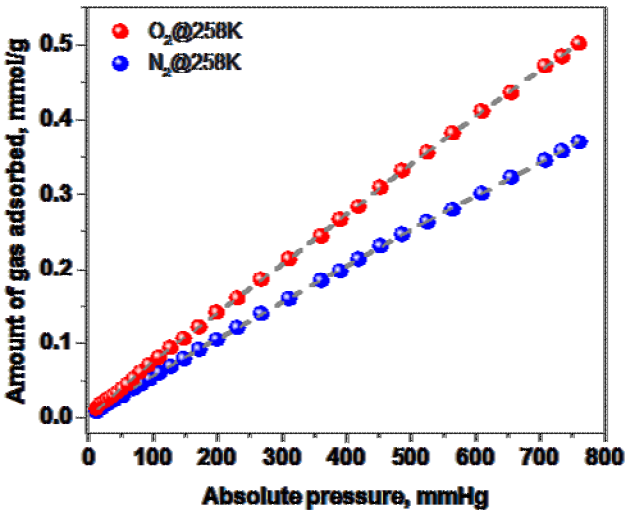
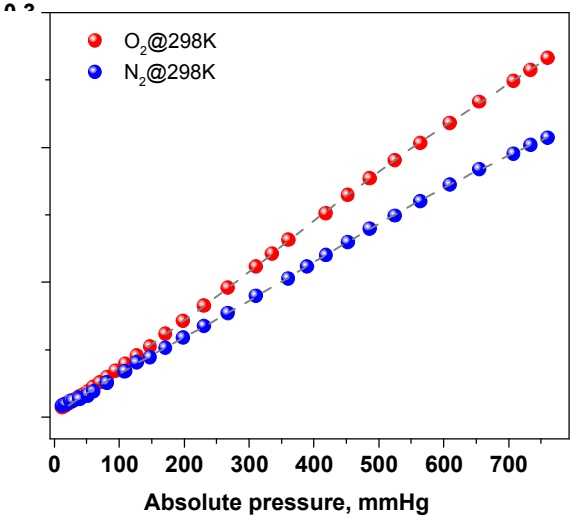
Fit using the virial eq.

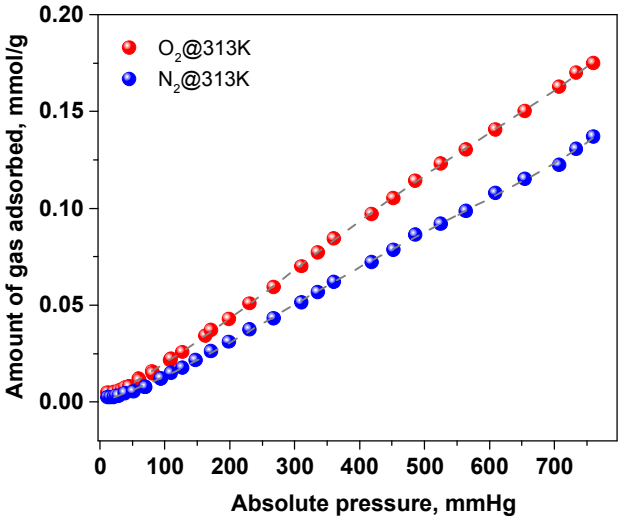
$O_2$ vs. $N_2$ @**258K**




$O_2$ vs. $N_2$ @**298K**




$O_2$ vs. $N_2$ @**313K**




Isotherm trends mimic those predicted by GCMC



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

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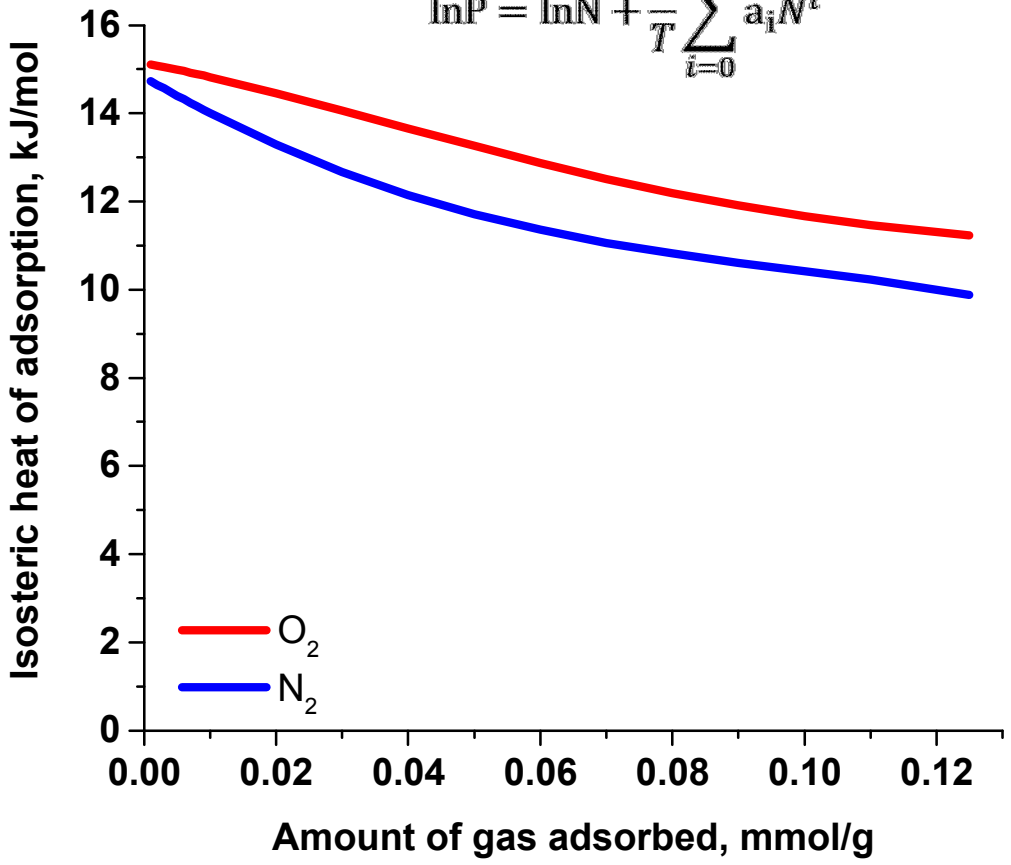
Qst derived from 258K, 298K and 313 K
Independent Virial Fit HOA

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



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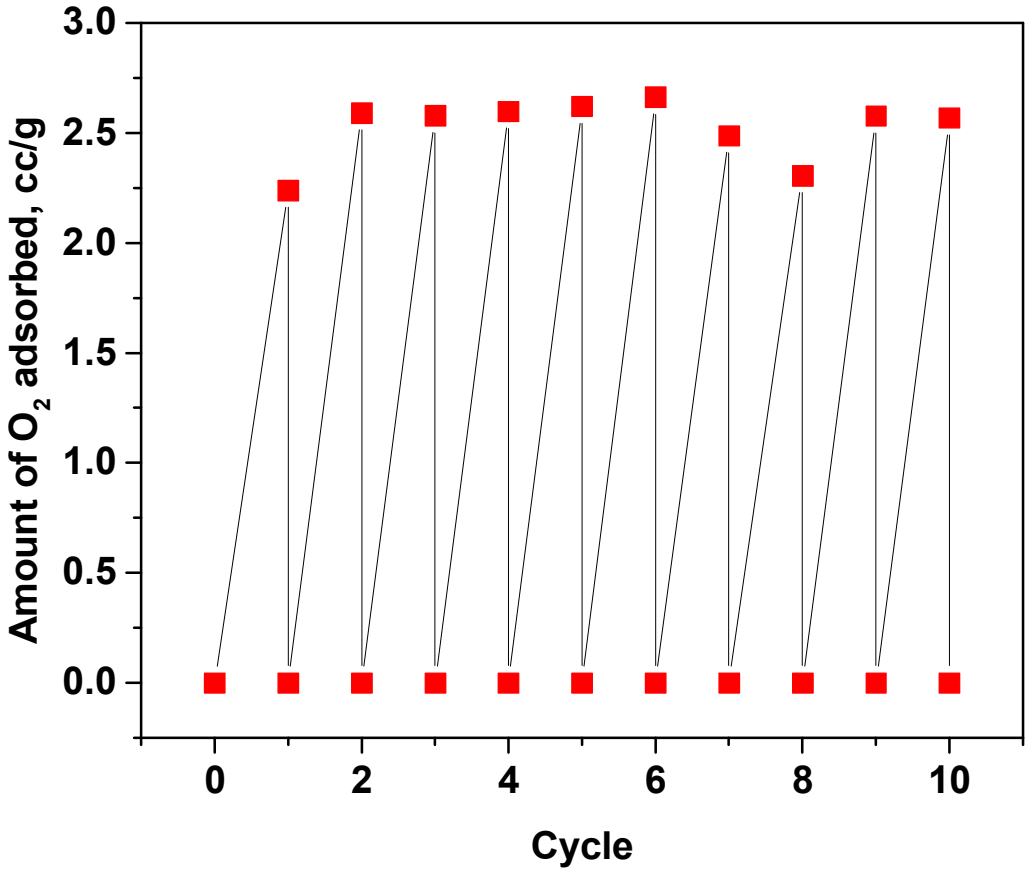
# Sc-MIL-100 Performance:
## $O_2$ adsorption & Desorption over 10 cycles, 298 K, 1 atm




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





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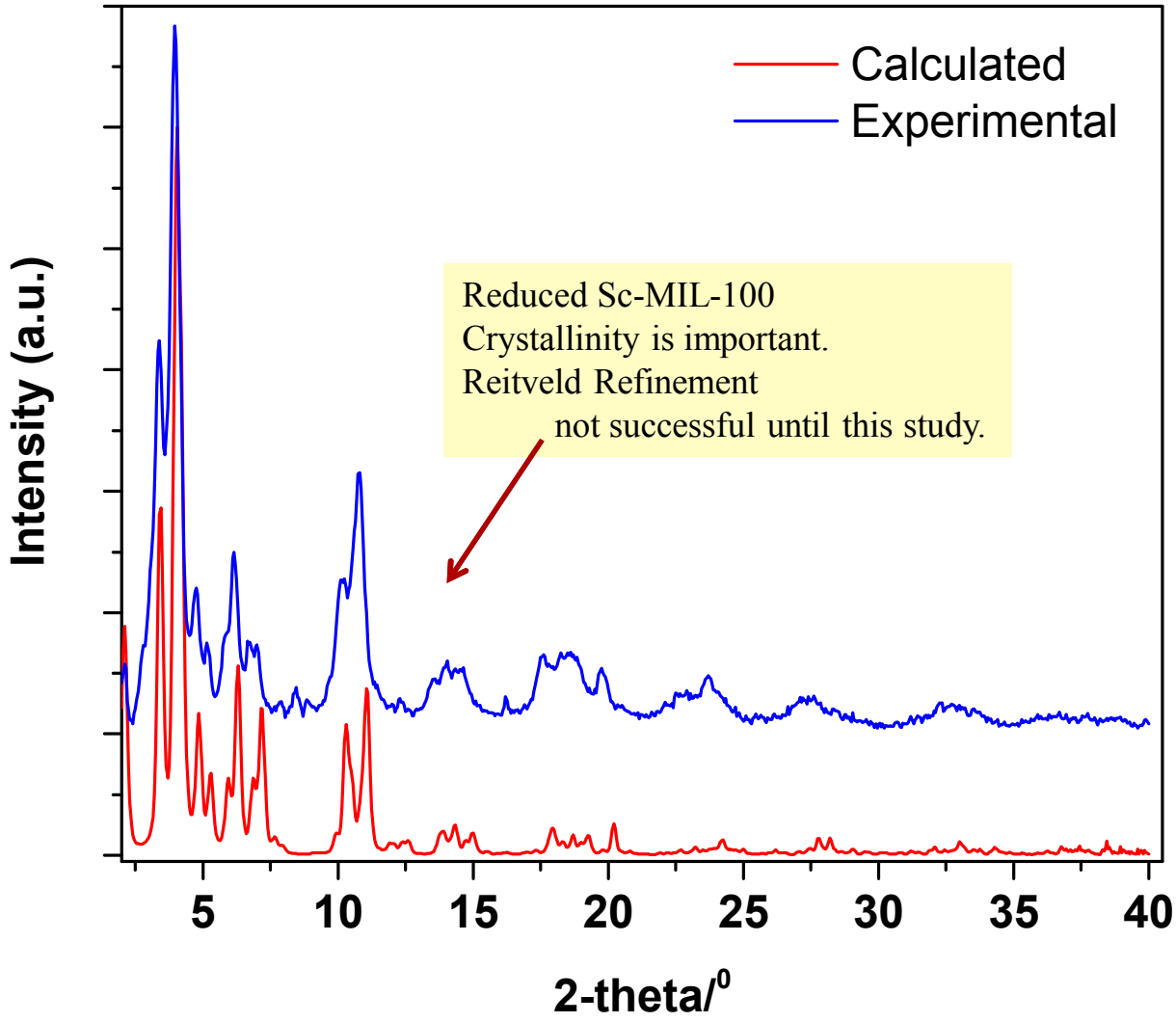
# Structure-Property Relationship Understanding of Sc-MIL-100 Oxygen Selectivity

High Energy Synchrotron X-ray, APS/ANL






*Chem. Mater.* **2016**, 28(10), 3327.

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# 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)***.

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

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**
**Beamline 11-ID-B**



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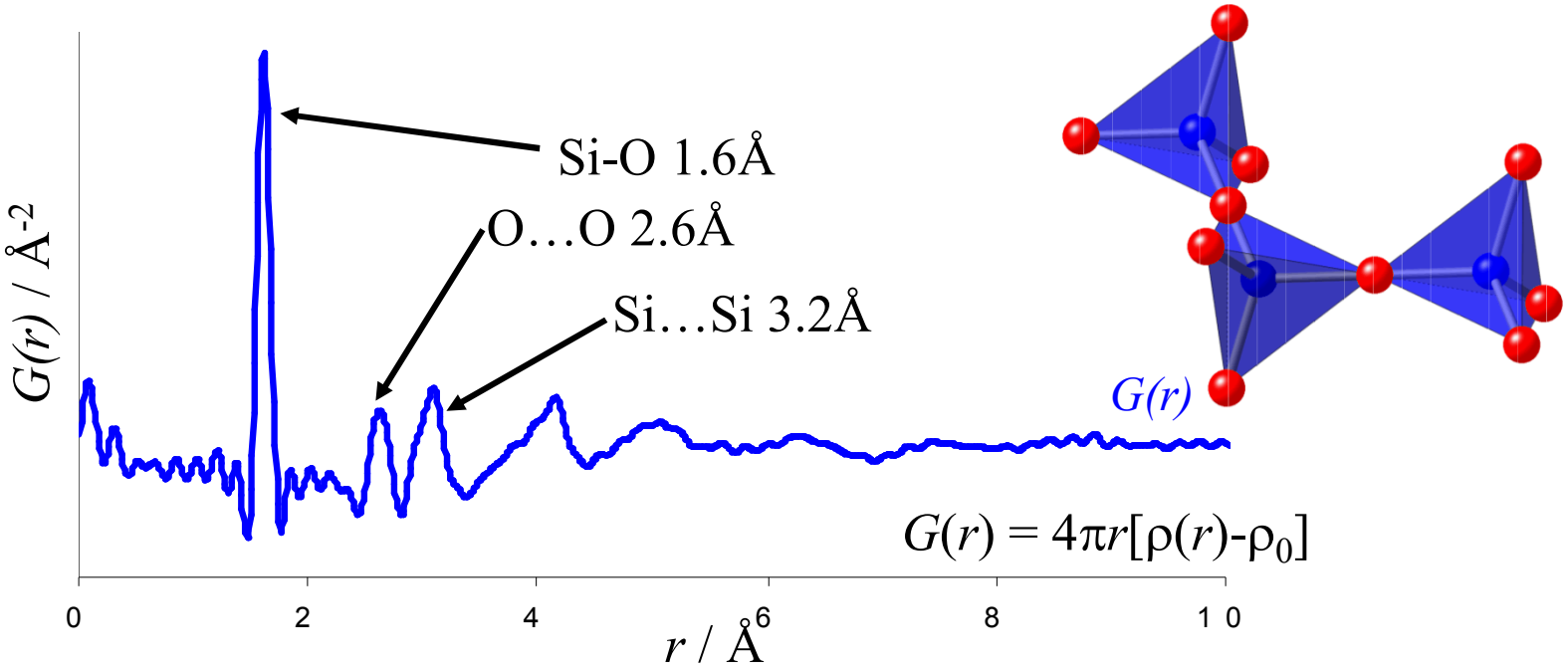
# PDF: Insight Into Short Range Structural Order
## eg., Amorphous $SiO_2$ (Glass)

*- 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 using Differential (d)- PDF

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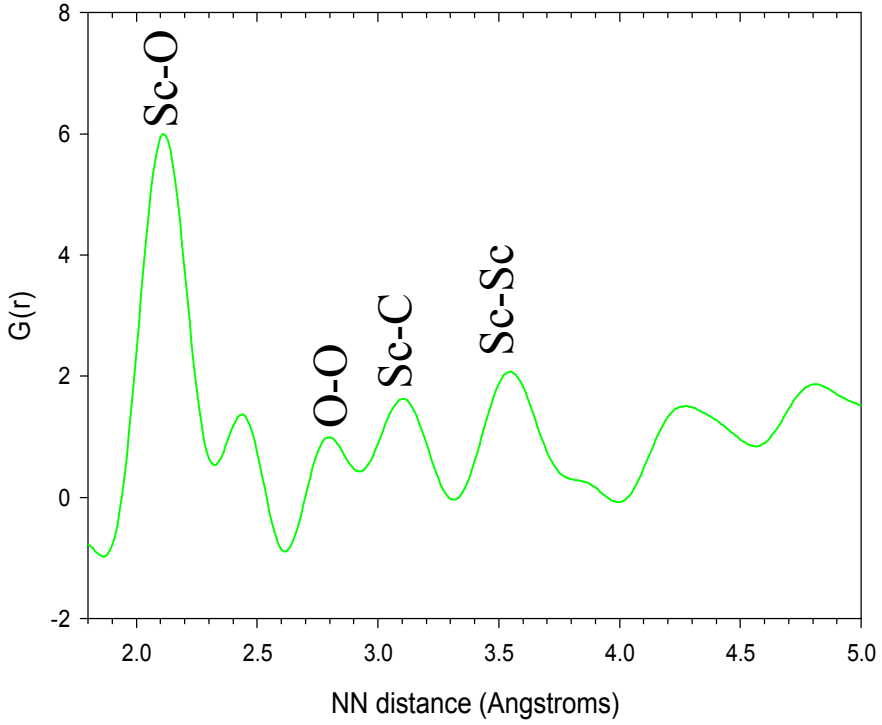
d-Pair Distribution Function (d-PDF)




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($\mu_3$) or M-O (carboxylate)), suggests **M-O-M angle of 113°** << 120° of a planer trimer



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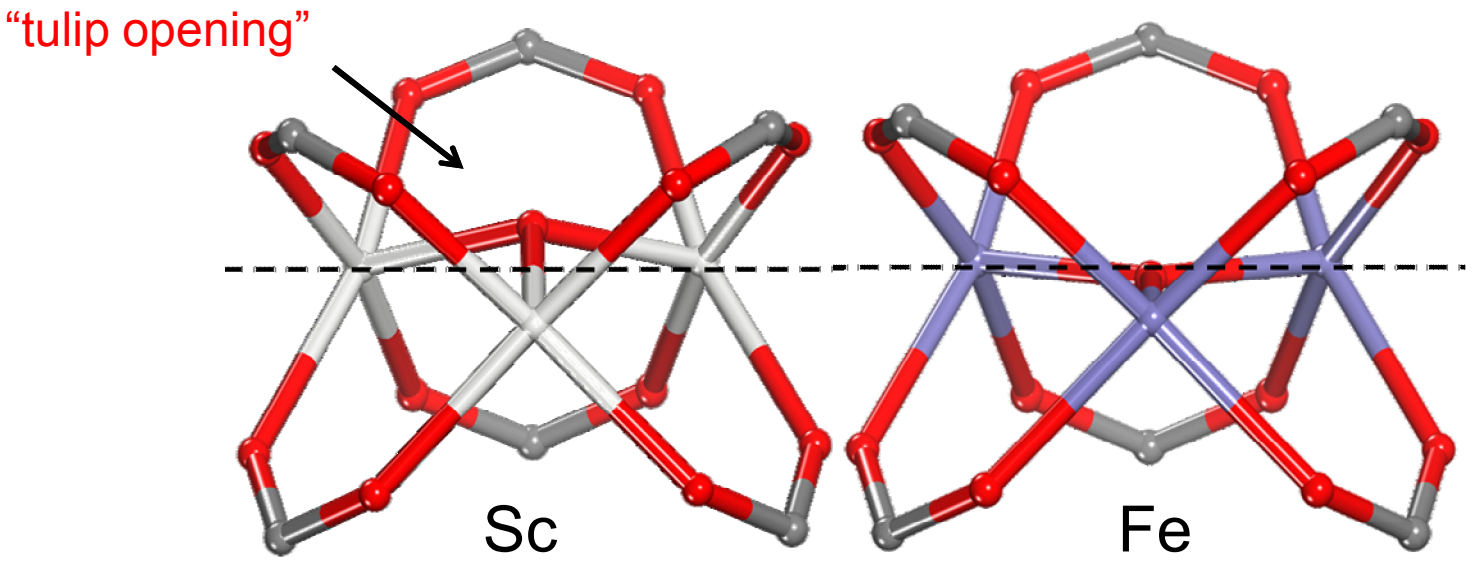
# Sc-MIL-100: Structure-Property relationship evaluated. Preferred $O_2$ sorption – Large Sc Distorts Cluster

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%



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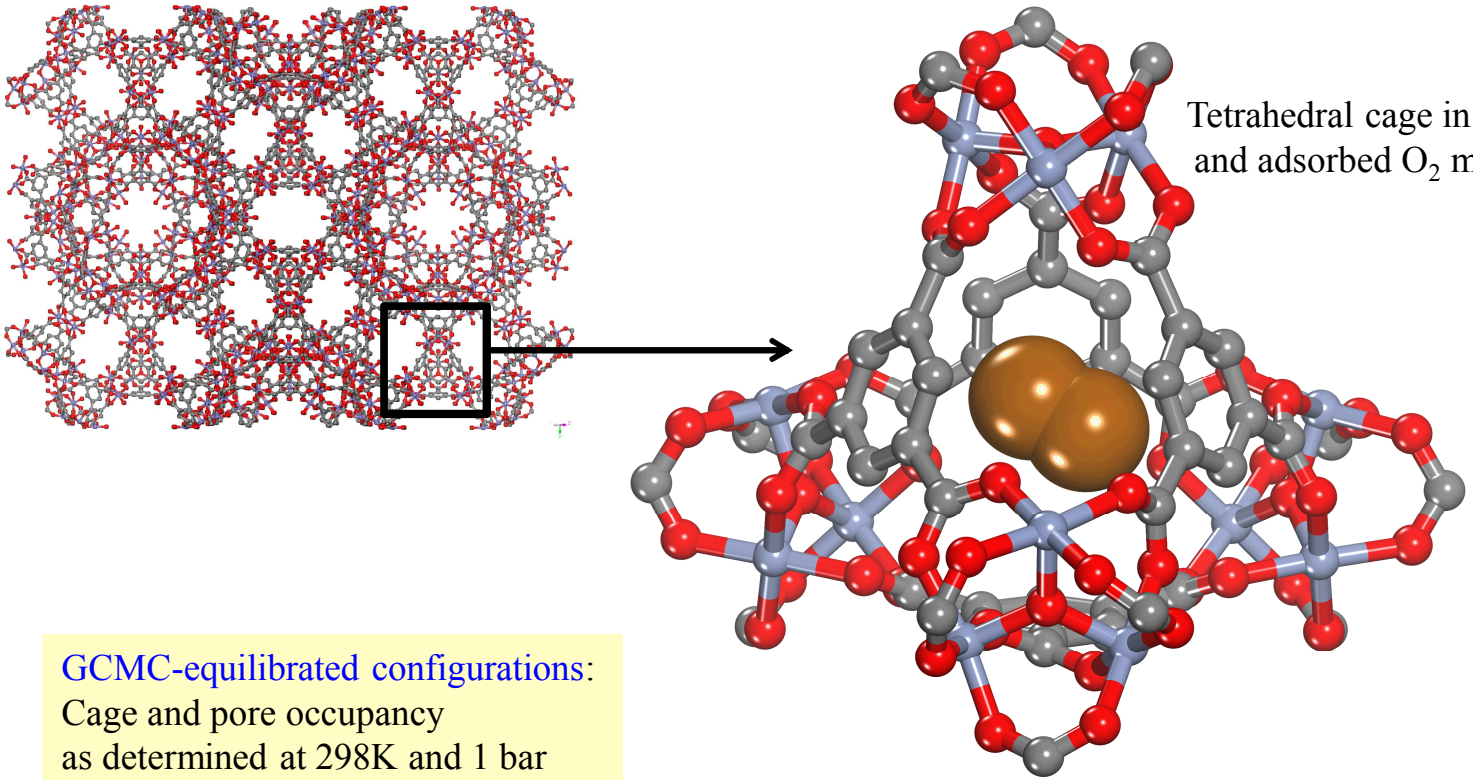
# Sc-MIL-100: Probable Sc-O binding sites



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 |



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# Conclusions

- Multidisciplinary teaming allows for in-depth understanding of materials structure-properties

- The collaborative use of DFT and AIMD enabled the prediction and understanding of metals needed in MOFs for selective gas binding

- **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.

- Modeling pointed us toward Sc based MOFs for $O_2$ preferential adsorption, chemistry, crystallography, & gas testing explained why the material worked well.

- On-going Research:
  *Techno-economic Analysis Model* for ion exchange resins in silica removal from Industrial Water Recycle and
  *Burner Design* to Oxyfuel combustion applications
  *Novel MOFs* designed for Fission Gas Separations



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# Questions? / Thank you

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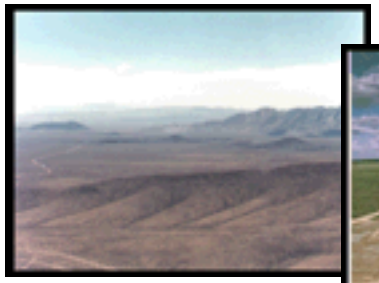
Sandia National Laboratories' Sites

Albuquerque, New Mexico

Kauai Test Facility
Hawaii

Tonopah Test
Range,
Nevada

Livermore,California



Yucca Mountain
Nevada

WIPP,
New Mexico

Pantex, Texas



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