SAND2016-5724C

Exceptional service in the national interest

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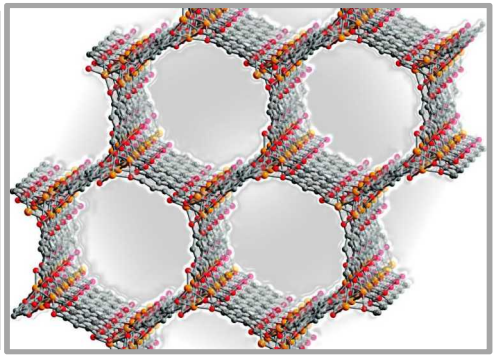
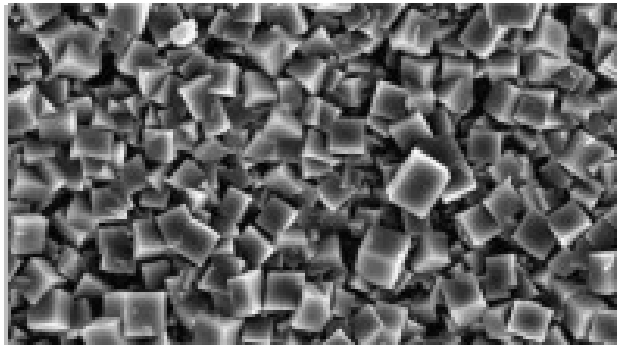



DFT Modeling of Metal-Organic Frameworks for Oxygen-Nitrogen Separation

Tina M. Nenoff,* Marie V. Parkes, Jeffery A. Greathouse, David Hart, Dorina Sava Gallis

Sandia National Laboratories, Albuquerque, NM USA

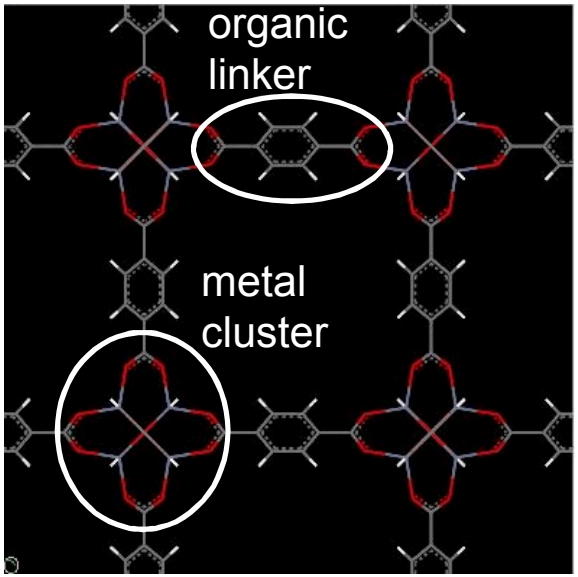
U.S. DEPARTMENT OF ENERGY

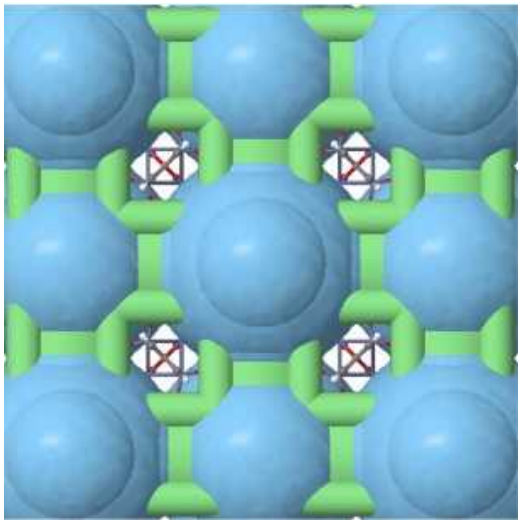
National Nuclear Security Administration

Funded by the Laboratory Directed Research and Development (LDRD) Program. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

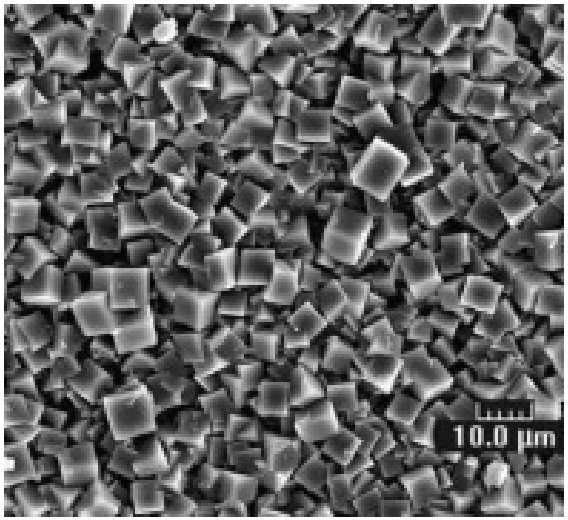
Metal-Organic Frameworks (MOFs)

- Porous solids made of an extended network of metal clusters coordinated to multidentate organic linkers
- Surface areas up to 6000 m^2g^{-1}
- "Crystalline sponges"





MMM. 2013, 165, 32-39



MMM, 2009, 123, 100-106.

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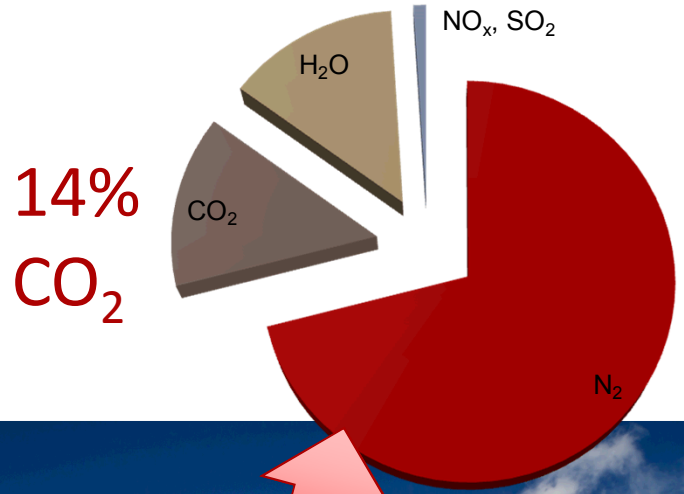
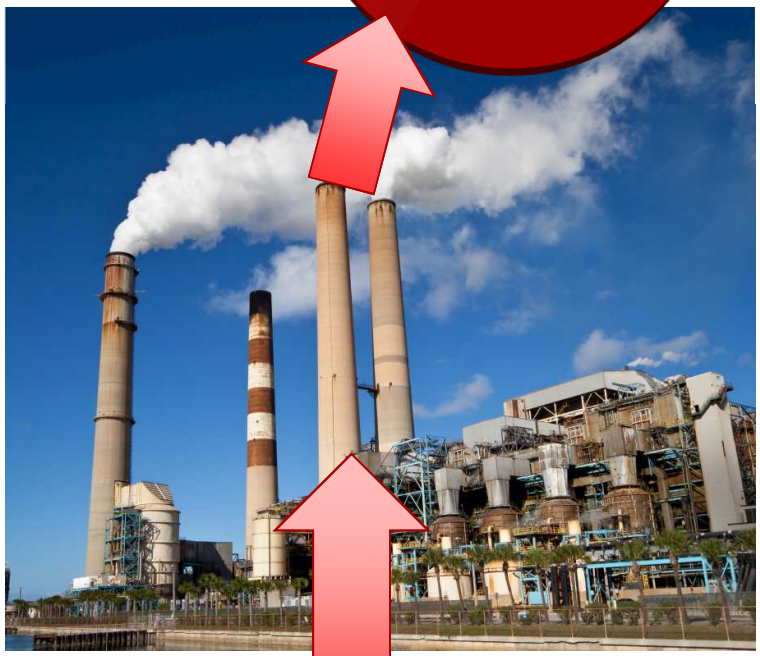
Oxyfuel for Cleaner Power Plants

- Coal-burning power plants major source of carbon dioxide emissions
- Interest in capturing CO_2 emissions

What comes out depends on what goes in!



14% CO_2



Air (78% N_2, 21% O_2)

ock photo from www.shutterstock.com.

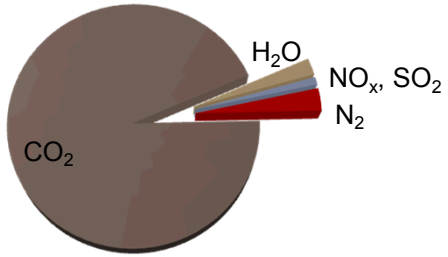
Hu, Y. CO_2 Capture from Oxy-Fuel Combustion Power Plants. Licentiate Thesis, KTH Royal Institute of Technology, Stockholm, Sweden, 2011

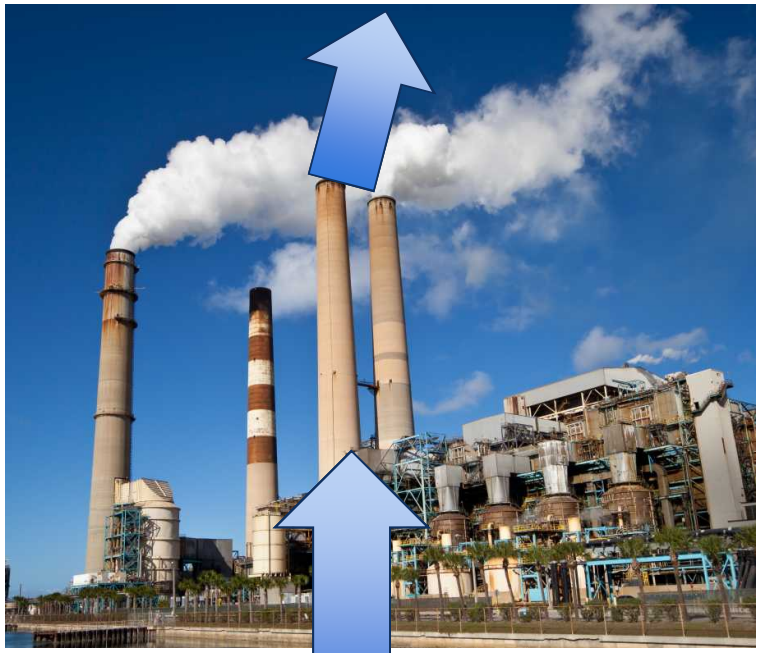
Oxyfuel for Cleaner Power Plants

- Oxyfuel advantages
  - 75% reduction in flue gas volume
  - Decreased NO_x emissions
  - Greater thermal efficiency
  - More energy efficient (not using energy to heat N_2)
  - Easier to capture CO_2

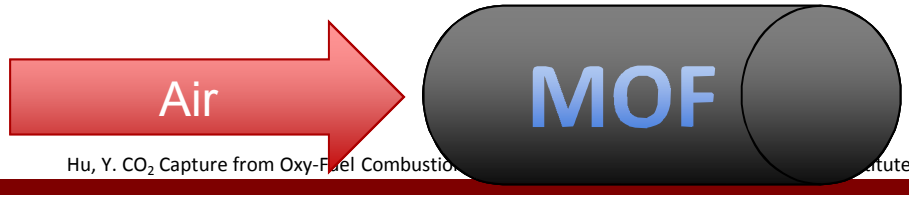
- Goal: MOFs for O_2 separation
  - Alternative to energy-intensive cryogenic separation

94% CO_2





ock photo from www.shutterstock.com.



Hu, Y. CO_2 Capture from Oxy-Fuel Combustio itute of Technology, Stockholm, Sweden, 2011

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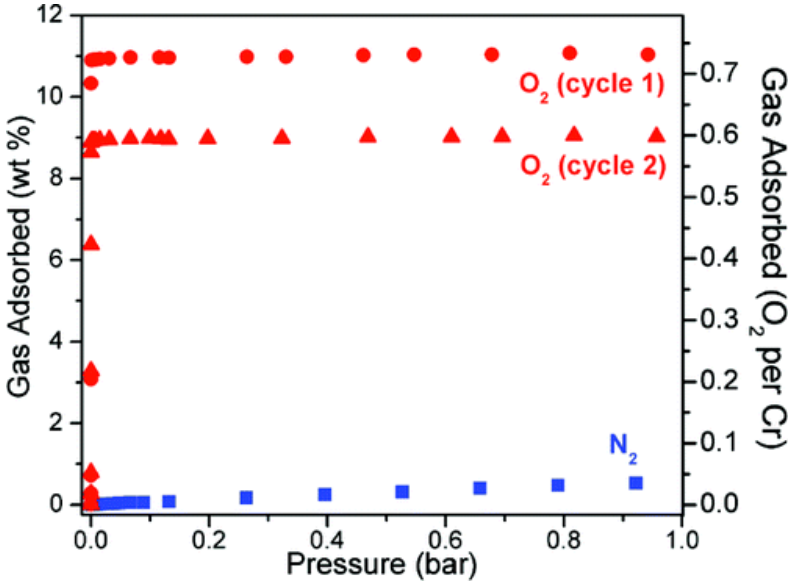
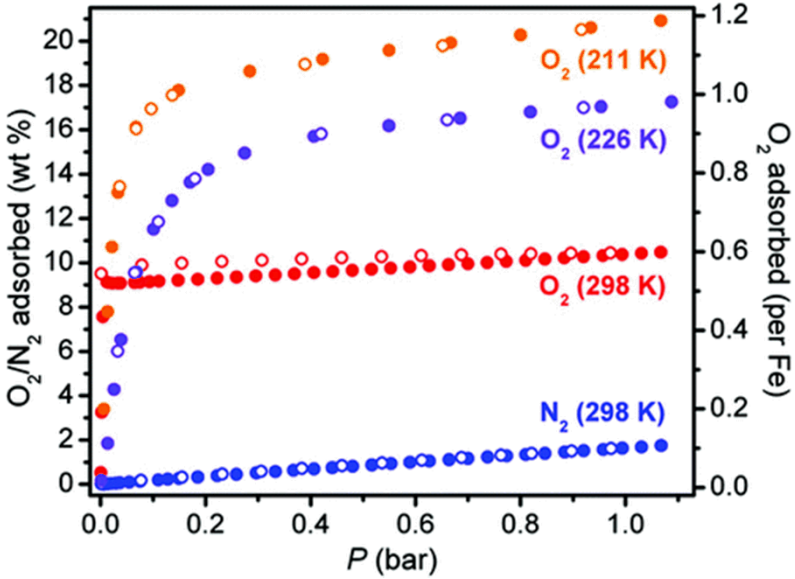
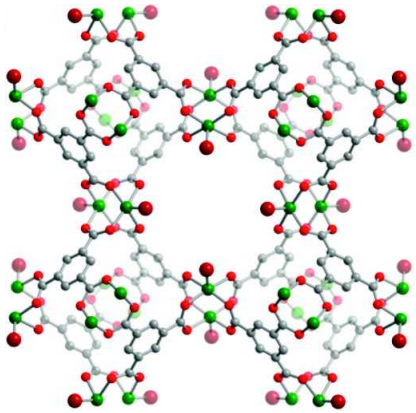
Literature MOFs Separate O_2/N_2



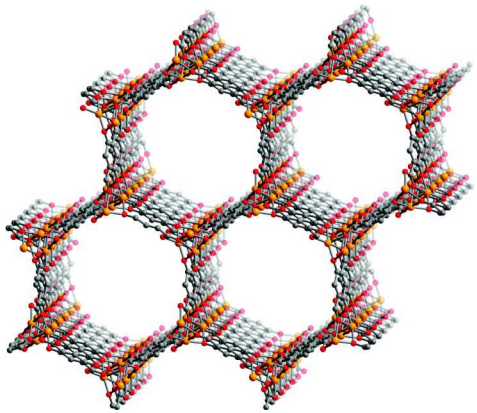


$Cr_3(btc)_2$



Long, J. R., et.al., *J. Am. Chem. Soc.* **2010**, *132*, 7856.

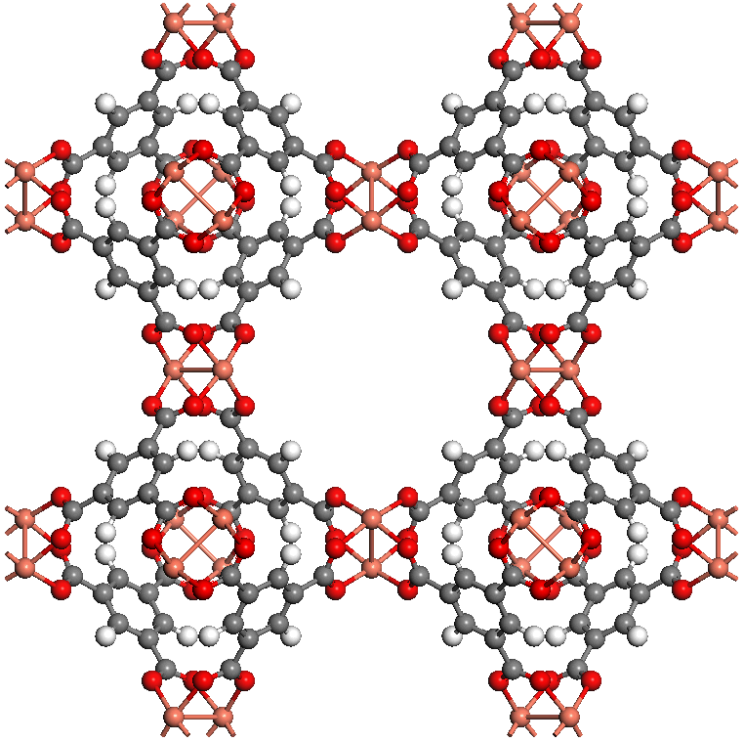
$Fe_2(dobdc)$



Long, J. R. et.al, *J. Am. Chem. Soc.* **2011**, *133*, 14814

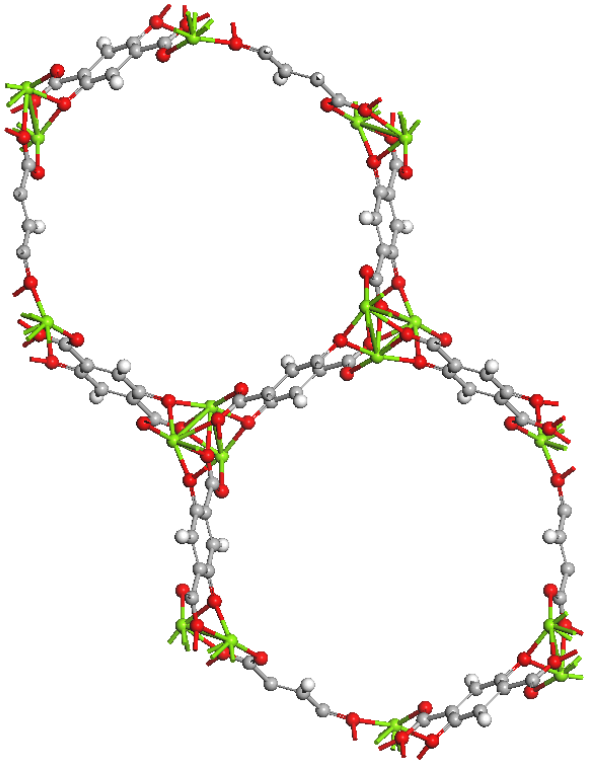
MOFs for O_2/N_2 Separation

$Cr_3(btc)_2$



Cages: 6.9 Å, 11.1 Å, 13.2 Å
Windows: 4.1 Å, 6.9 Å

$Fe_2(dobdc)$



Channels: 10.8 Å

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

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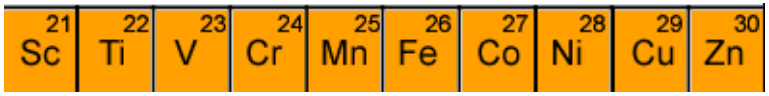
DFT Calculations

Vienna *ab initio* simulation package (VASP)

- MOF
  - $M_3(btc)_2$ analogs
  - $M_2(dobdc)$analogs
- Metals



- Gas (one molecule per primitive cell)
  - O_2
  - N_2

- Plane wave DFT geometry optimizations, periodic structure
- PBE density functional with dispersion correction (PBE-D2), PAW potentials for core electrons
- Spin polarization

$$E_{binding} = E_{MOF+O_2} - \left(E_{MOF} + E_{O_2}\right)$$

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

O_2, N_2 Binding Energies (ΔE), $\Delta\Delta E = \Delta E_{N2} - \Delta E_{O2}$

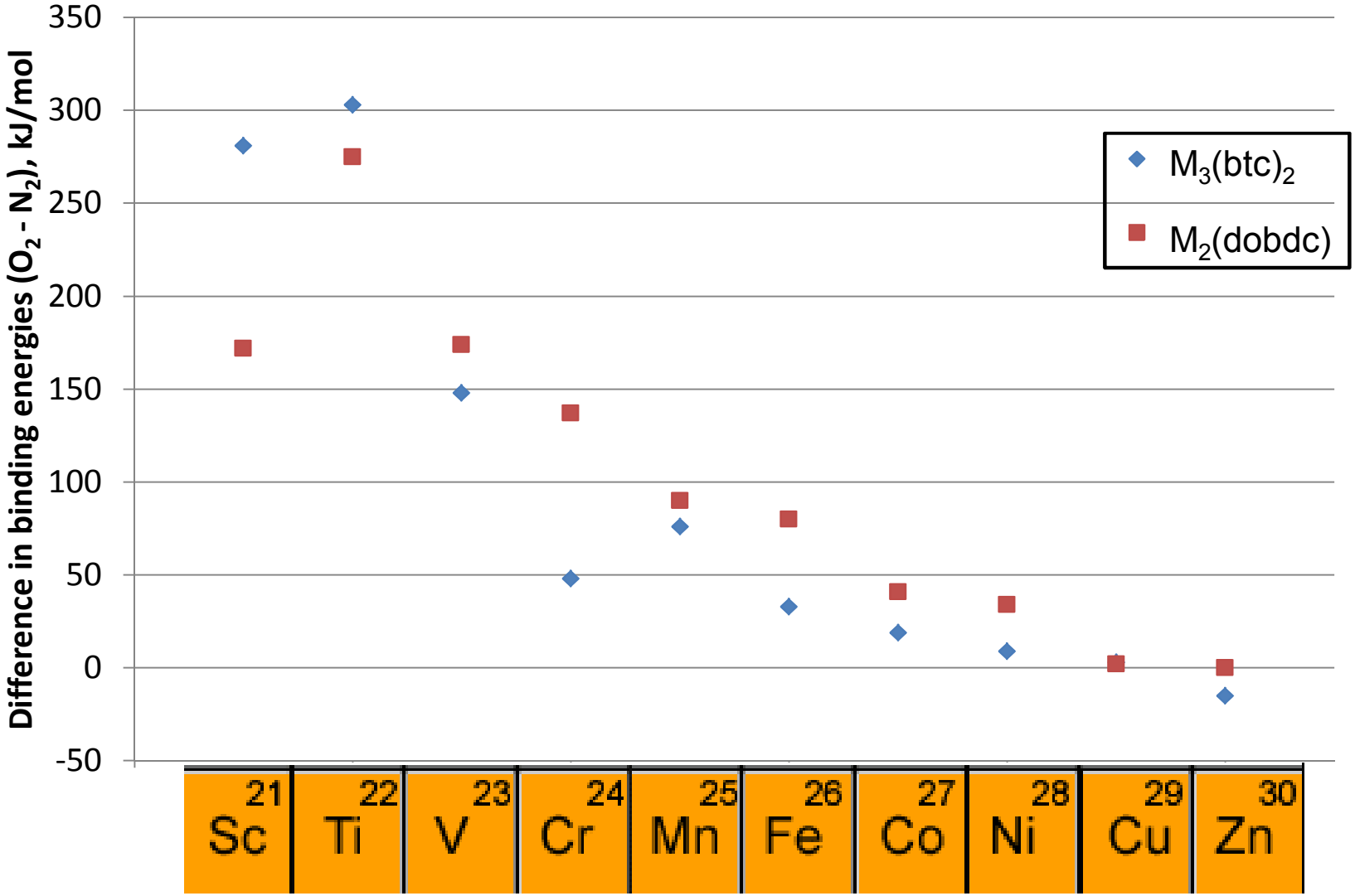
metal	$M_3(btc)_2$ binding energy (kJ/mol)			$M_2(dobdc)$ binding energy (kJ/mol)		
	O_2	N_2	ΔΔE	O_2	N_2	ΔΔE
Sc	-328	-46	281	-215	-43	172
Ti	-329	-26	303	-354	-79	275
V	-158	-10	148	-264	-90	174
Cr	-100	-52*	48	-147	-10	137
Mn	-264	-188	76	-116	-26	90
Fe	-45	-12	33	-88	-7	80
Co	-81	-62	19	-83	-41	41
Ni	-53	-44	9	-79	-46	34
Cu	-103	-100	3	-31	-29*	2
Zn	-22	-38	-15	-21	-21	0

* Gas atoms not adsorbed on metal

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

Tina M. Nenoff, tmnenof@sandia.gov

Difference in Binding Energies (=ΔΔE)



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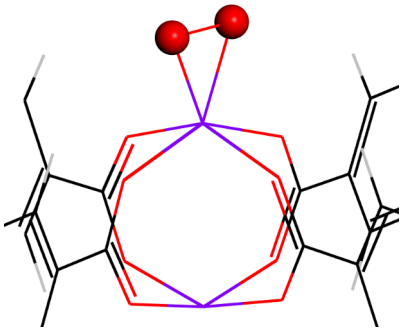
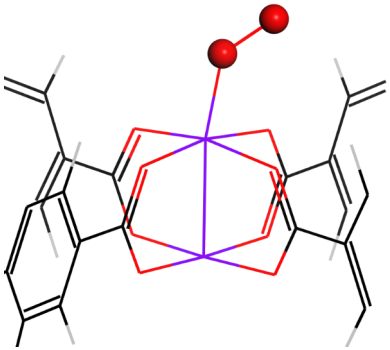
O_2 and N_2 Binding Modes

O_2

- Side-on

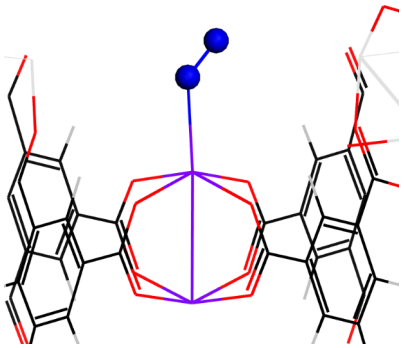


- Bent

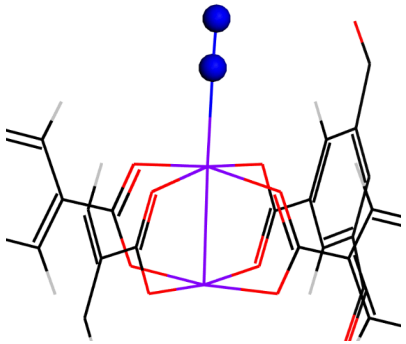


N_2

- Bent



- Linear



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O_2, N_2 Binding Energies (ΔE): Highlighting M-MOFs easily made by metal center ion exchange

metal	$M_3(btc)_2$ binding energy (kJ/mol)			$M_2(dobdc)$ binding energy (kJ/mol)		
	O_2	N_2	ΔΔE	O_2	N_2	ΔΔE
Sc	-328	-46	281	-215	-43	172
Ti	-329	-26	303	-354	-79	275
V	-158	-10	148	-264	-90	174
Cr	-100	-52*	48	-147	-10	137
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Co	-81	-62	19	-83	-41	41
Ni	-53	-44	9	-79	-46	34
Cu	-103	-100	3	-31	-29*	2
Zn	-22	-38	-15	-21	-21	0

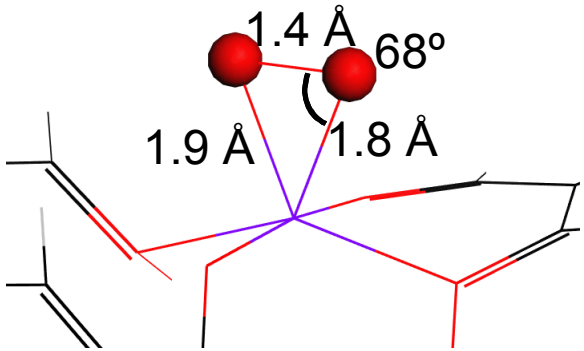
* Gas atoms not adsorbed on metal

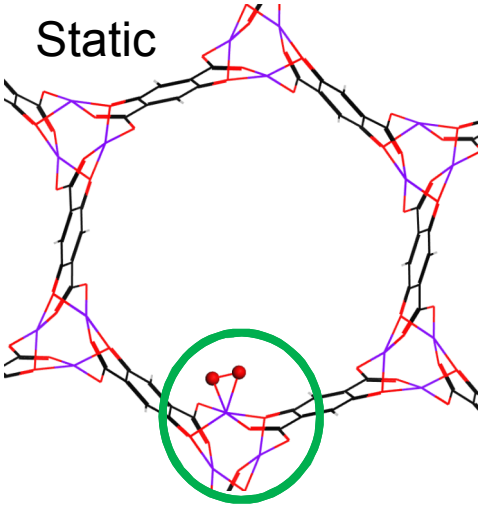
J. Phys. Chem. C **2015**, *119*, 6556.

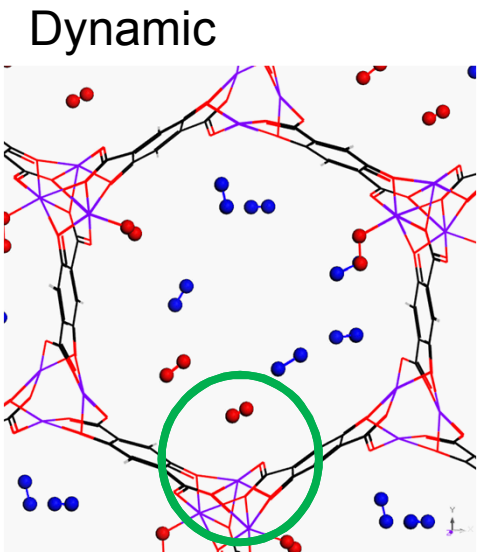
Tina M. Nenoff, tmnenof@sandia.gov

Minimum Energy Binding Mode

O_2 binding to Cr_2(dobdc)



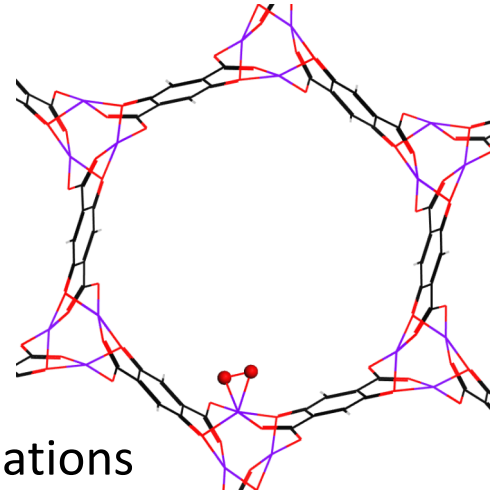




- Side-on bonded, but not showing thermal bent geometry at dynamic binding
- -147 kJ/mol
- *Static configuration*
- *0 K*

Minimum-energy configuration doesn't tell the whole story! "Snap Shot", no thermal effect

AIMD Calculations



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

- Temperatures
  - 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.

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Initial Gas Positions From Static DFT

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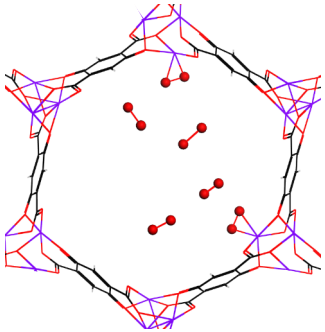
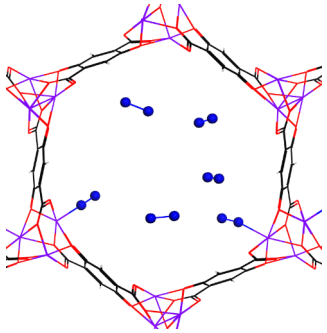
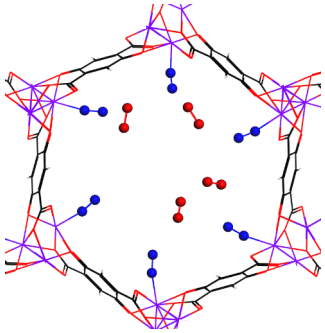
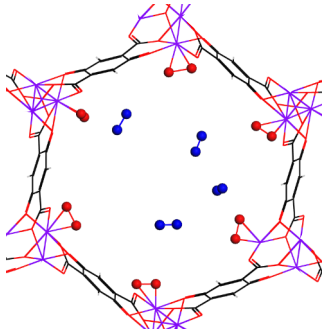
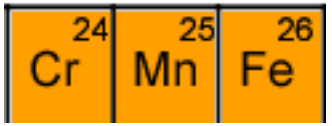
Guests	2 O_2 bound 4 O_2 unbound	2 N_2 bound 4 N_2 unbound
Single component		
Mixed gas Competitive binding		
	6 N_2 bound 4 O_2 unbound	6 O_2 bound 4 N_2 unbound

Temperatures

201 K
258 K
298 K

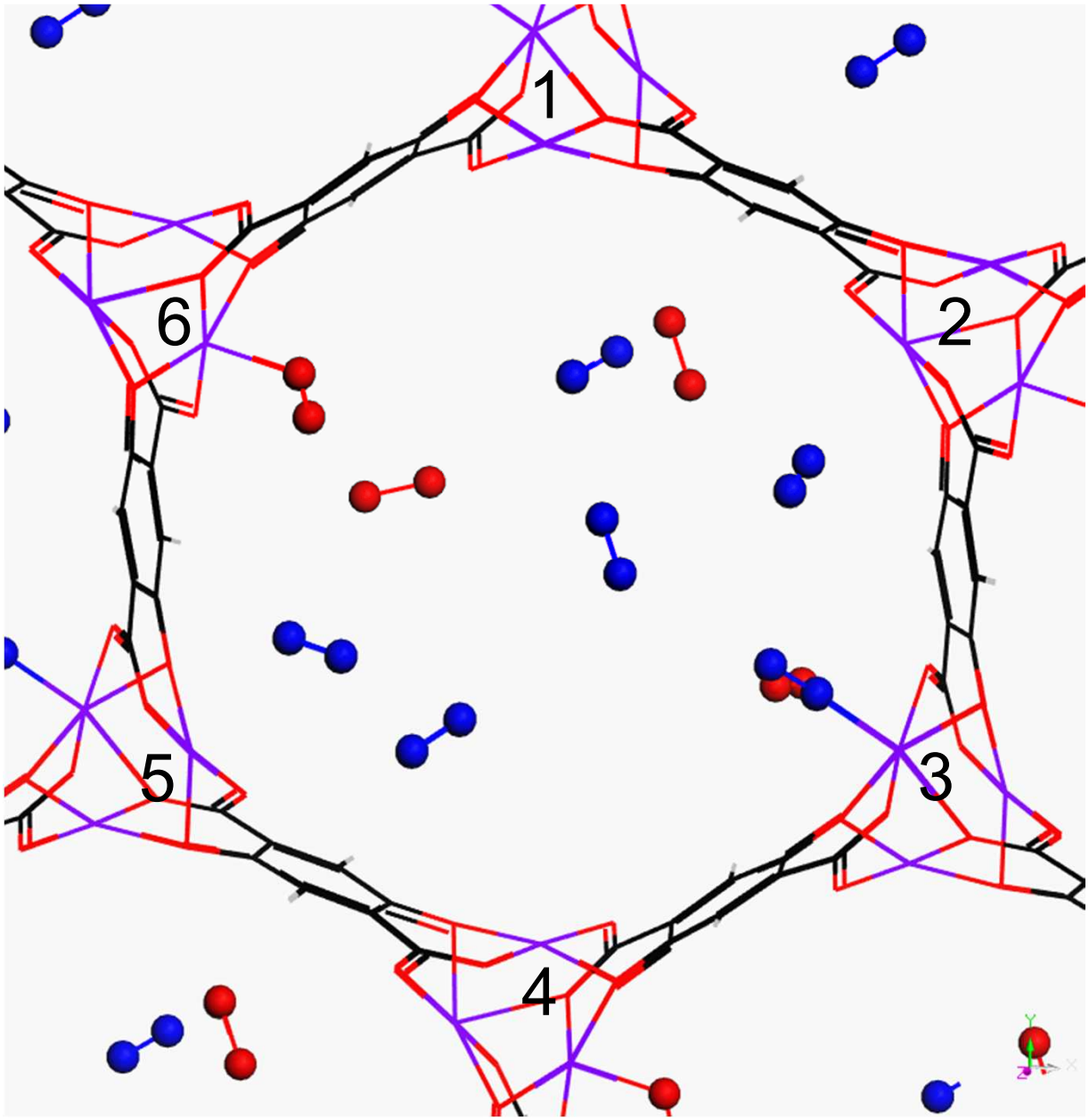
Metals



Red Sky Supercomputer
36 Simulations

3,800 processor-days each

http://hpc.sandia.gov/



Cr_2(dobdc)
6 N_2 + 4 O_2
298 K

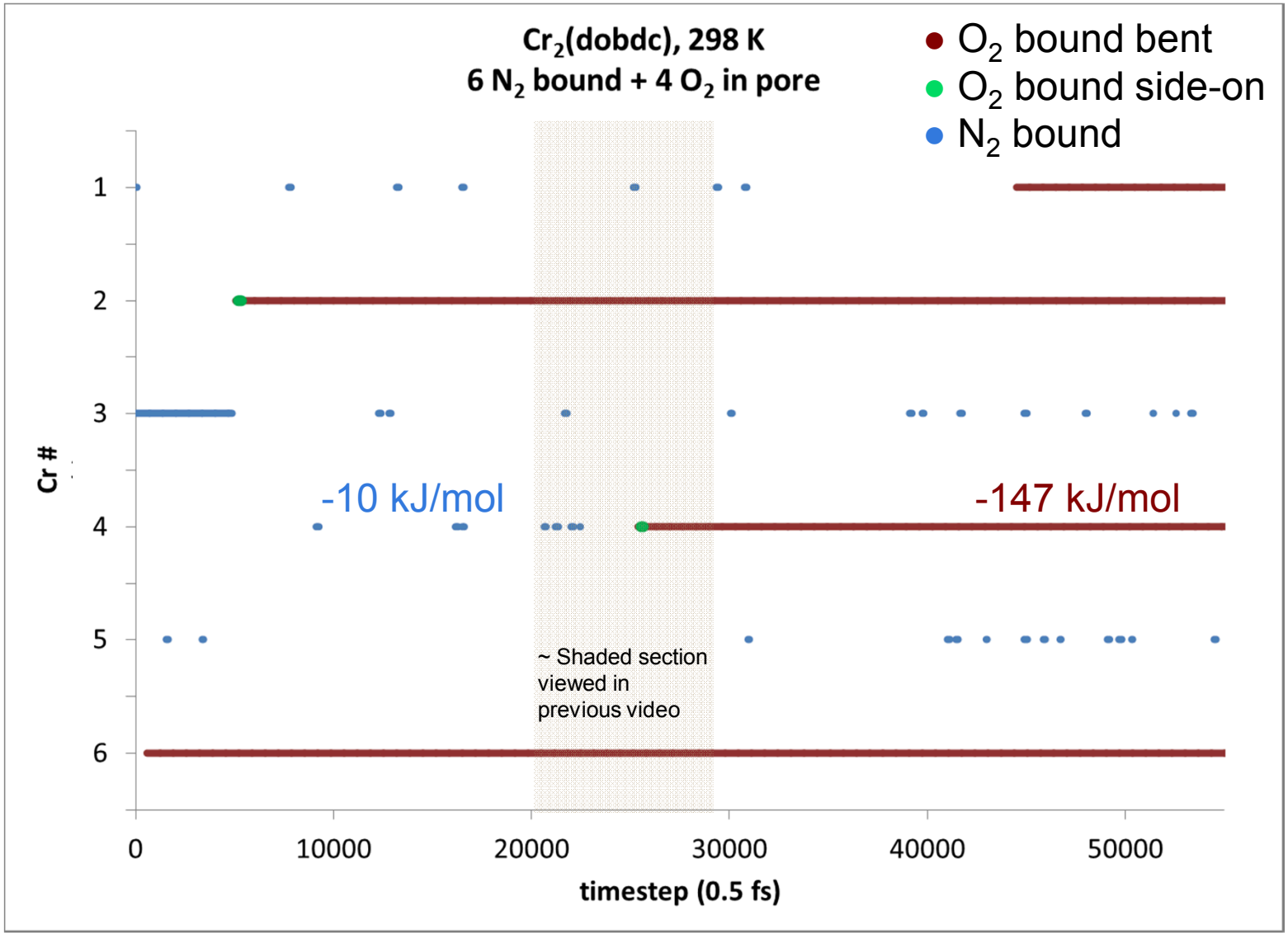
NVT
Time 2 ps – 15 ps

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

Gas Occupancy at Each Metal Site



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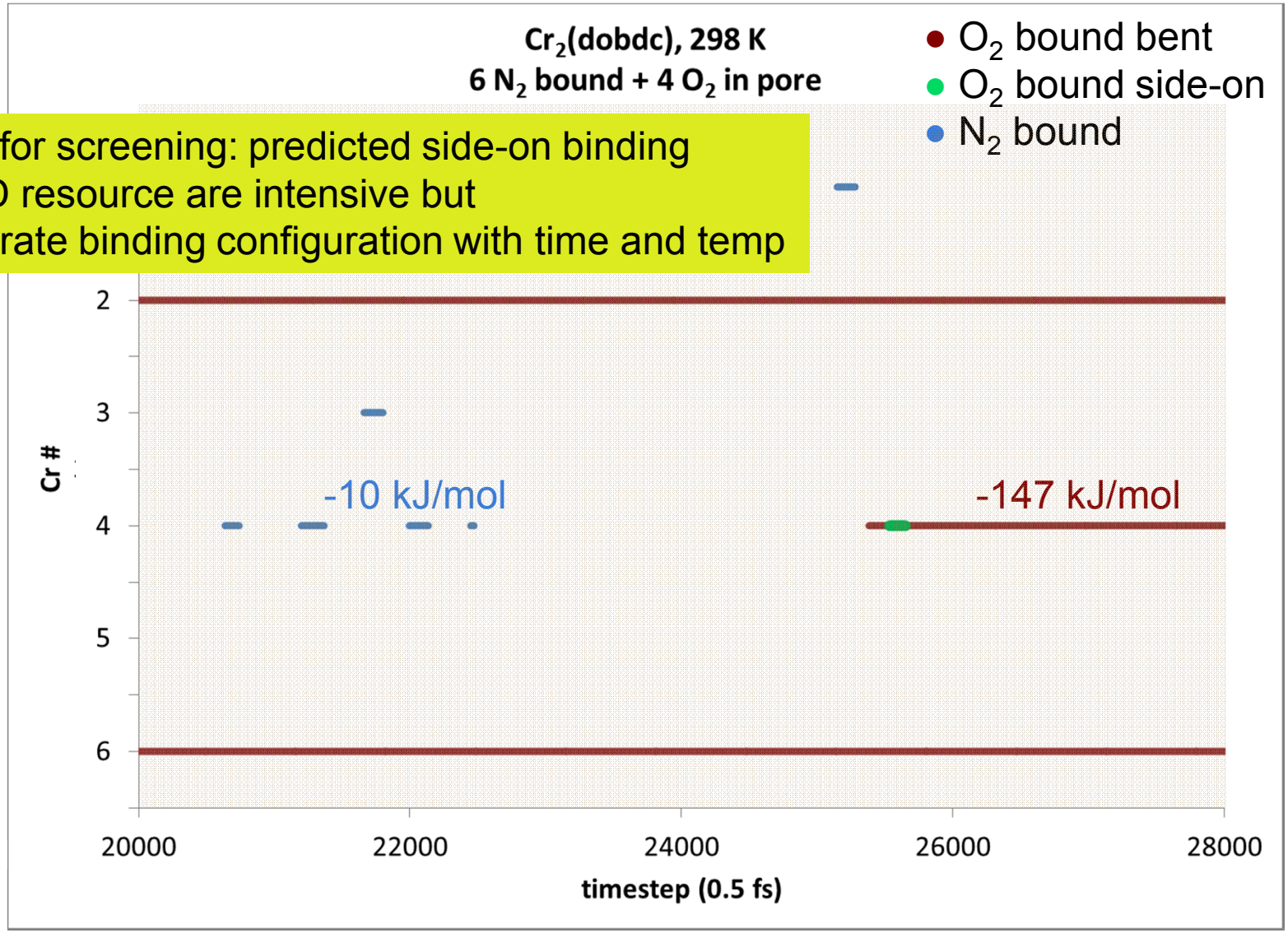
Gas Occupancy at Each Metal Site:
previous slide shaded area



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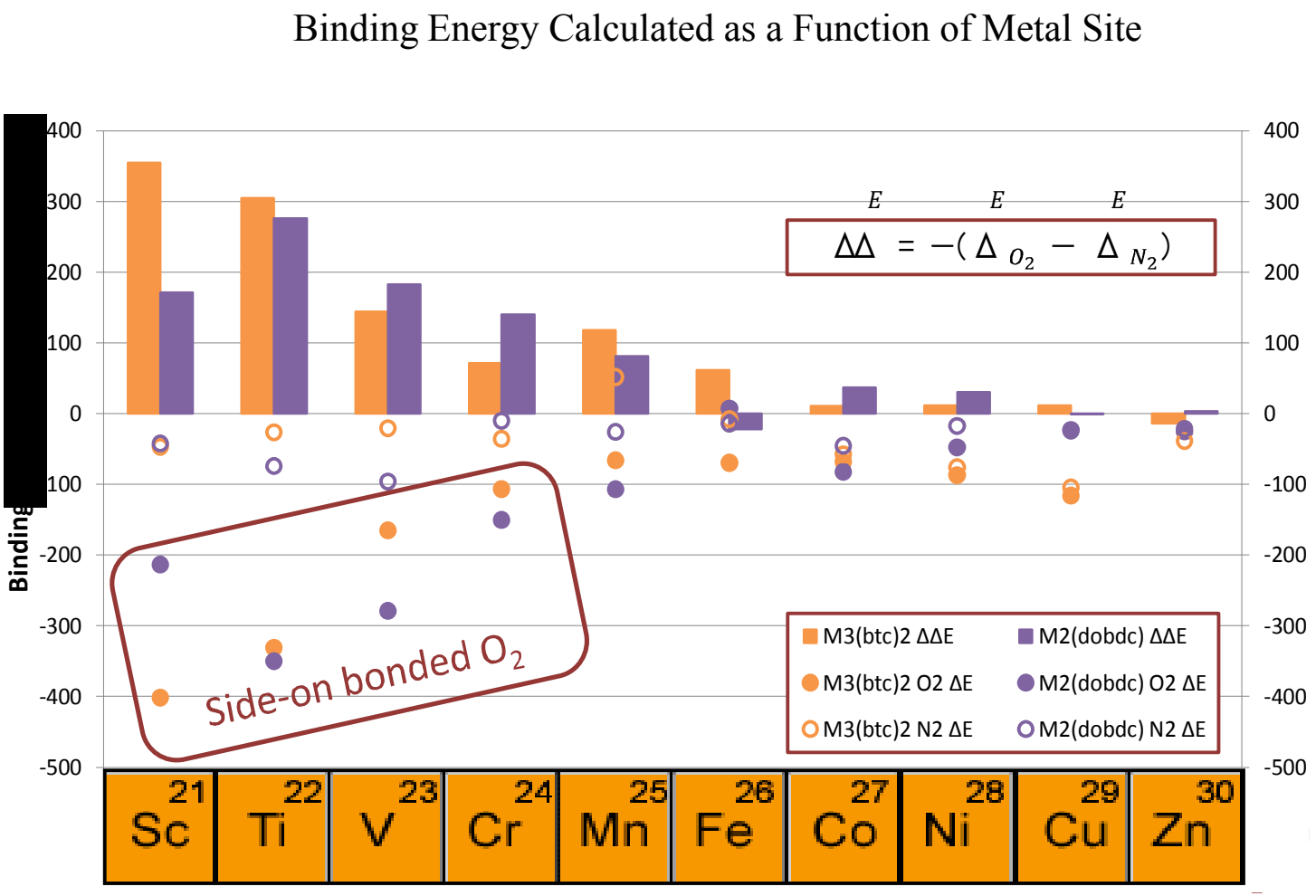
Study of Early Transition Metal MOFs for O_2 Selectivity



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Sc-MIL-100 for O_2 Selectivity

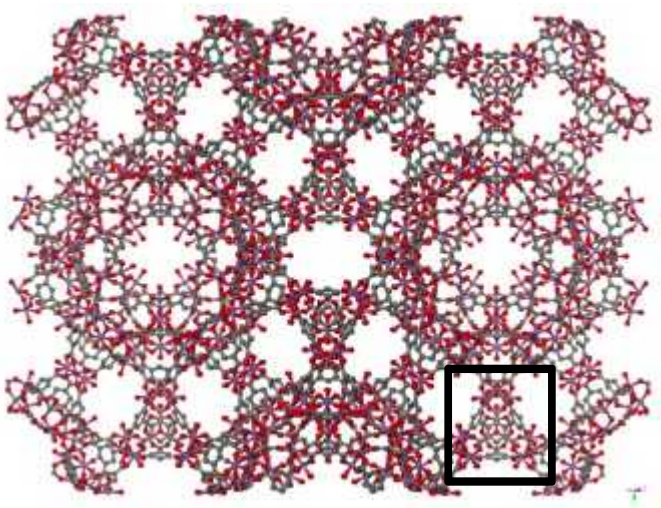
Sandia National Laboratories

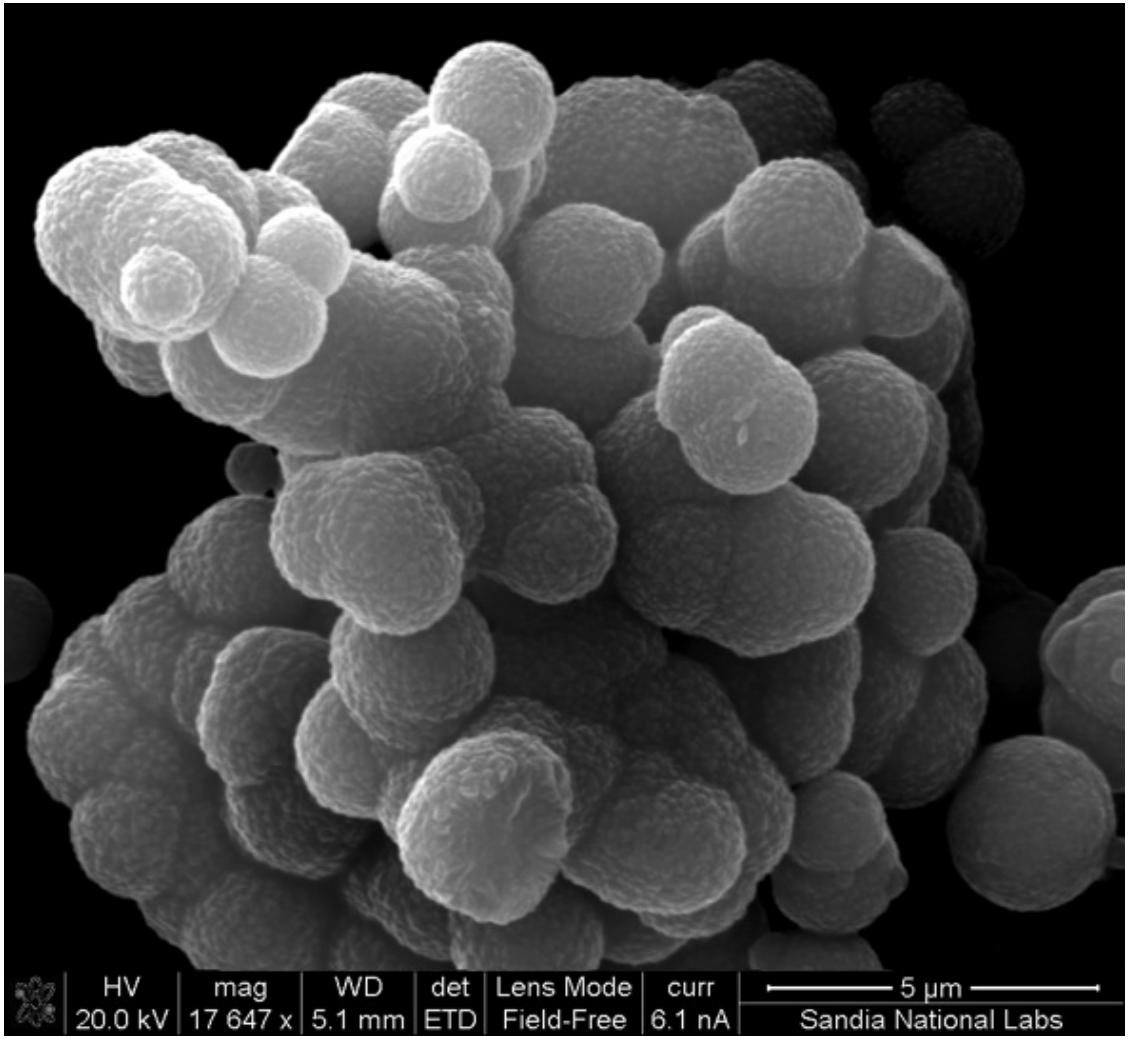
Sc/BTC/DMF/HCl

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.

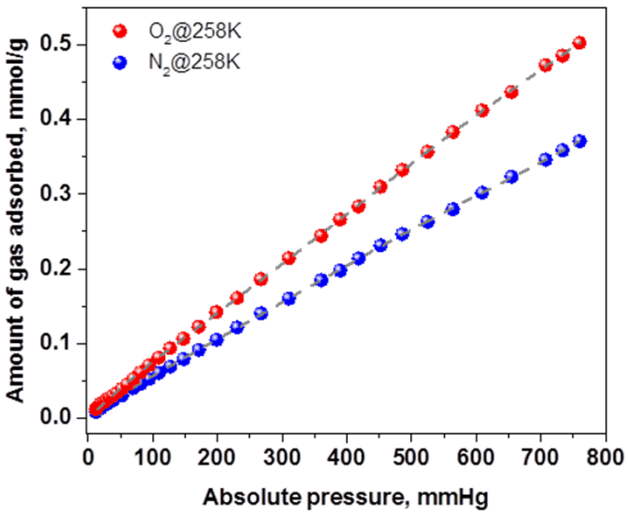
US Provisional Patent 2015

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

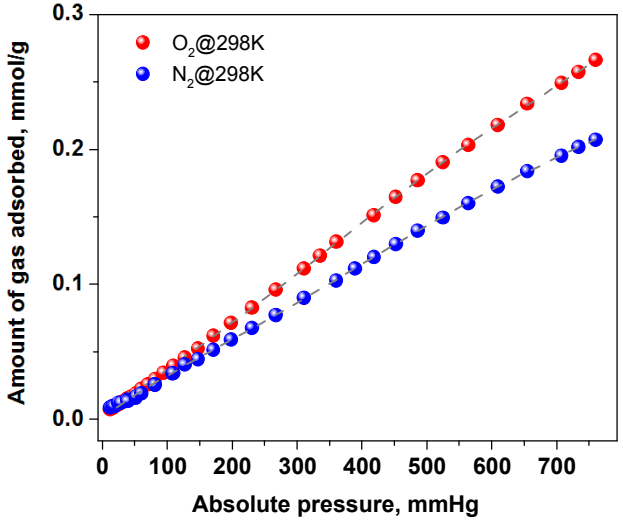
Sandia National Laboratories

Fit using the virial eq.

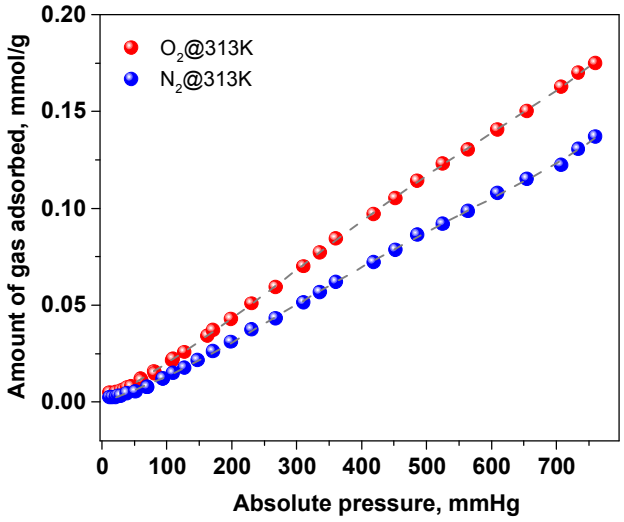
O_2 vs. N_2 @**258K**



O_2 vs. N_2 @**298K**

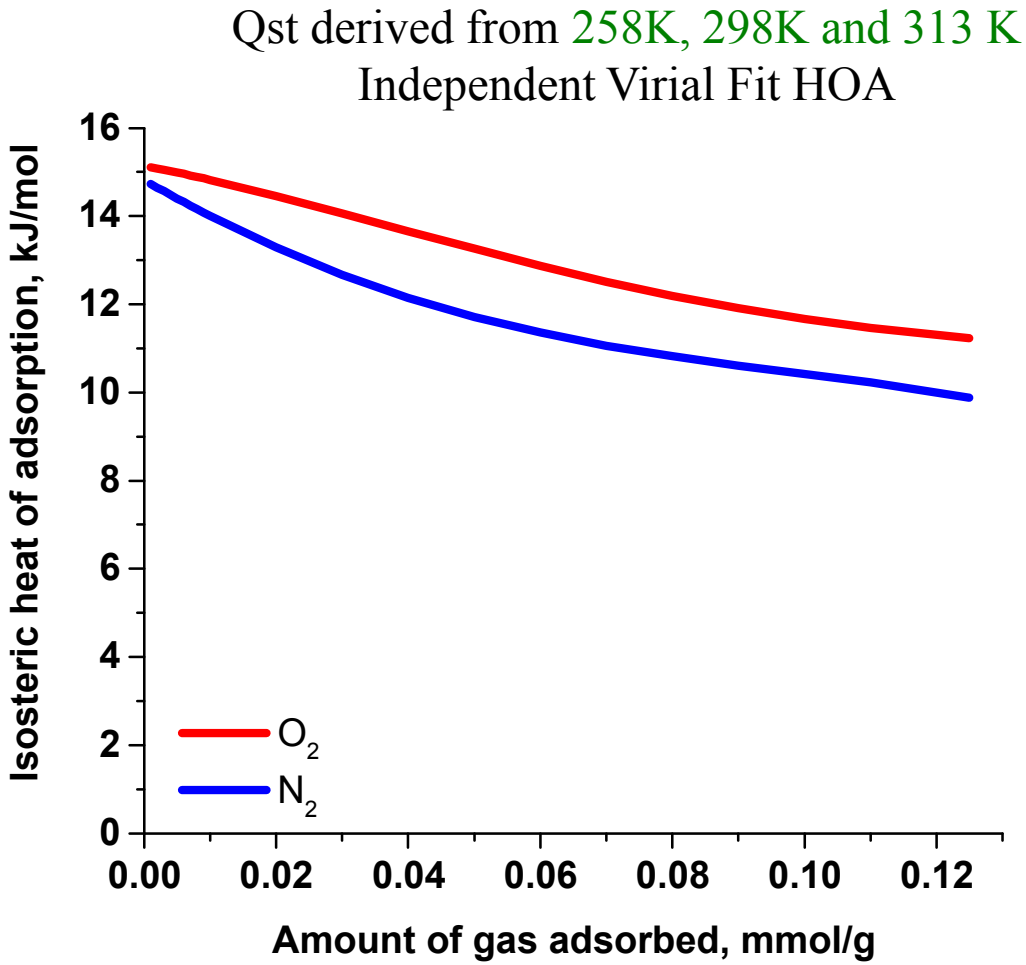


O_2 vs. N_2 @**313K**



Isotherm trends mimic those predicted by GCMC

Isosteric heat of Adsorption (kJ/mol)
Higher binding energy for O_2 vs N_2



US provisional Patent 2015

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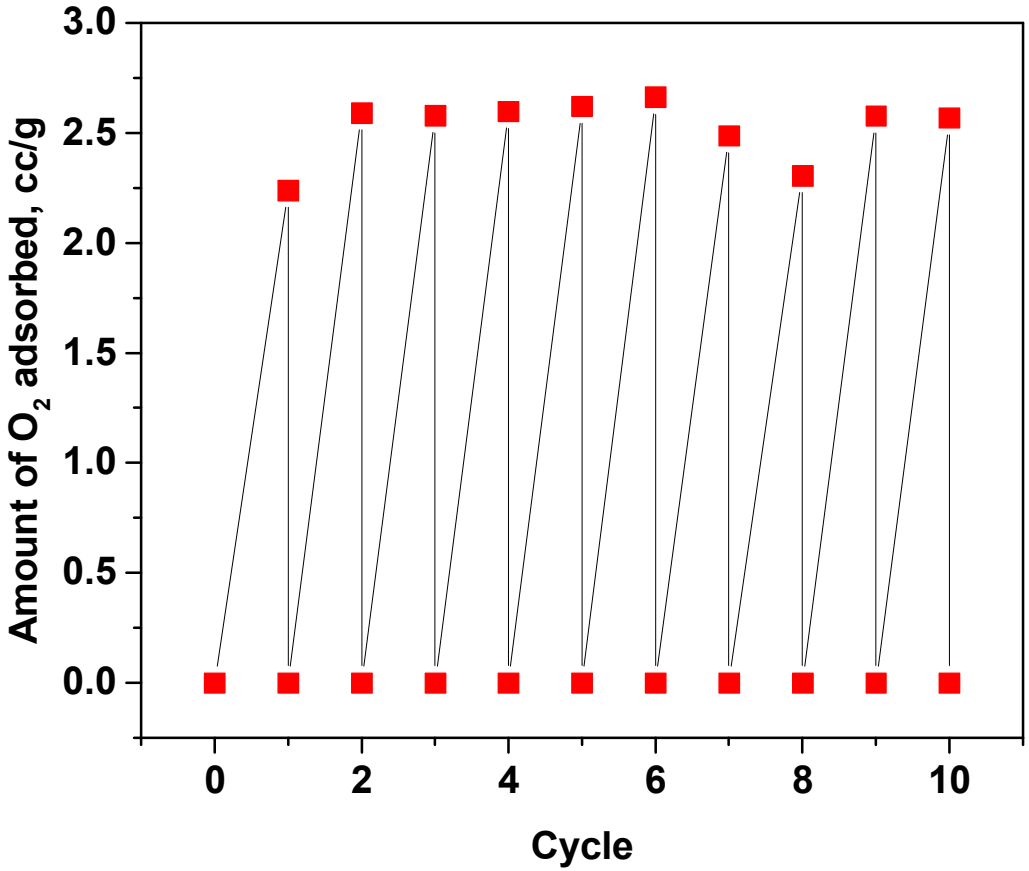
O_2 Adsorption and Desorption over 10 cycles, 298K, 1 atm



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US provisional Patent 2015

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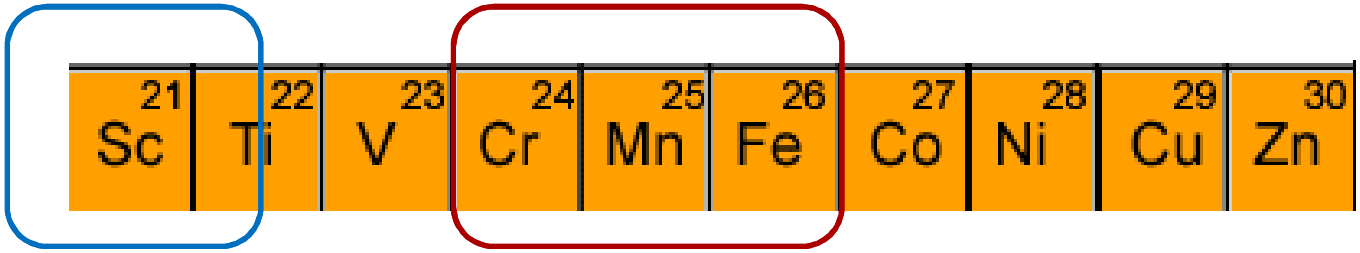
Conclusions



- Metal matters!
  - Mid transition metal trends are consistent in two different MOF frameworks
- Focus on mid transition metals
  - Easy to synthesize
  - Mild yet preferential O_2 binding
- Novel use of AIMD
  - Use AIMD to obtain more insights into mechanism of binding
- Differences in O_2/N_2 binding to metal sites
  - O_2 binds and sticks
  - N_2 binds on-off

- Early Transition Metals: Open MIL-100 framework, Sc shows optimum binding for O_2

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Thank You

Sandia National Laboratories

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