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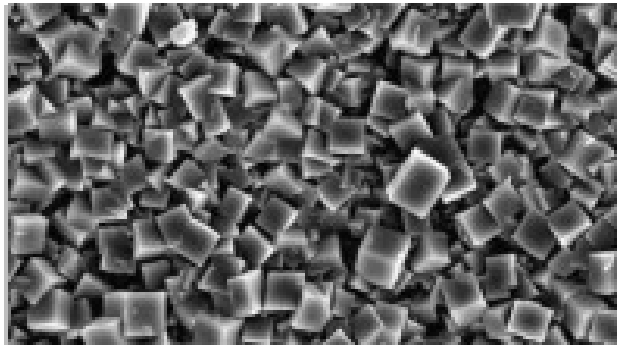

Metal-Organic Frameworks for Oxygen-Enrichment of Air: Insights from Molecular Simulation

Marie V. Parkes,* Jeffery A. Greathouse, Tina M. Nenoff

Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY | NNSA Nuclear Security Administration

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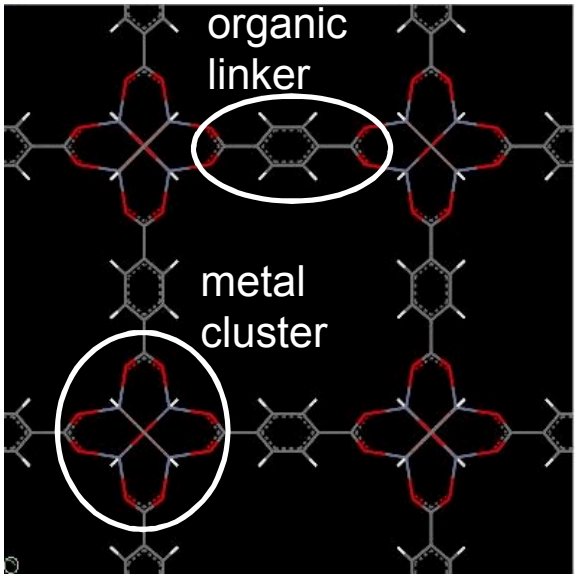
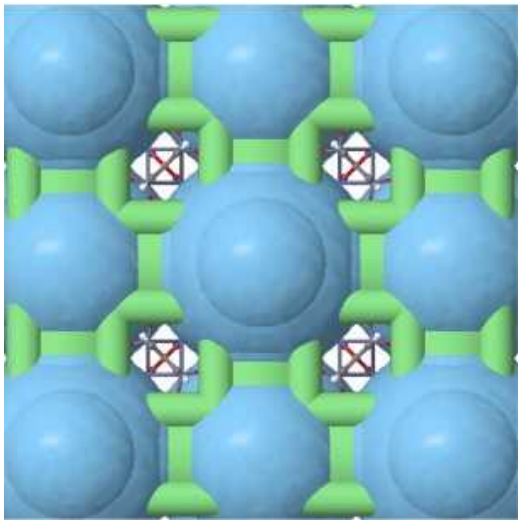
Metal-Organic Frameworks (MOFs)

- Porous solids made of an extended network of metal clusters coordinated to multidentate organic linkers
- Surface areas up to 5900 m^2g^{-1}
- "Crystalline sponges"





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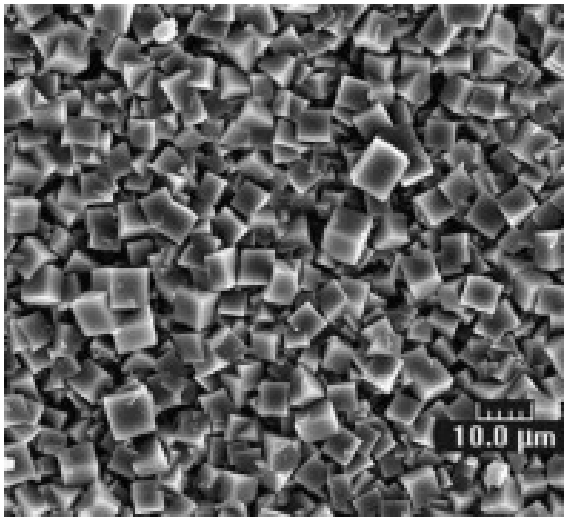

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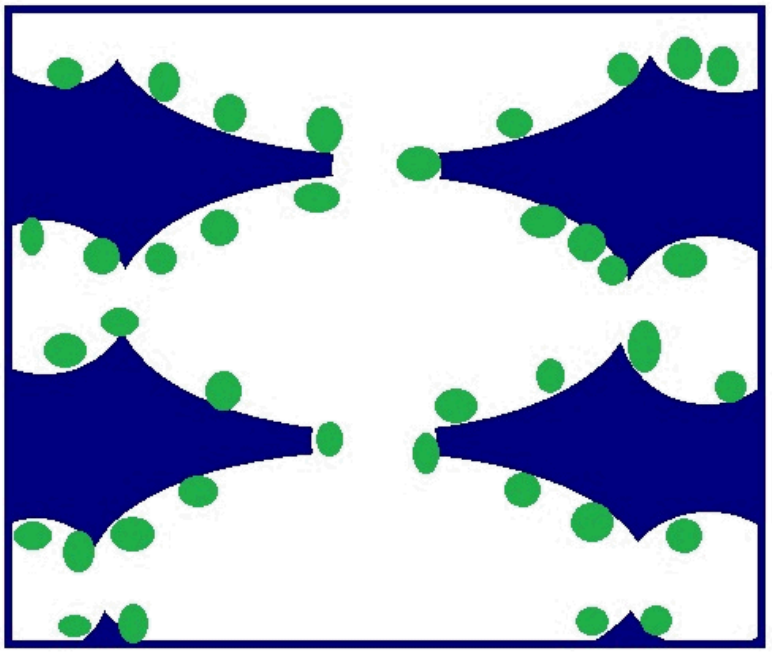
Separation of Gases in MOFs

Diffusion of noble gases in MOFs

Adsorption of oxygen and nitrogen



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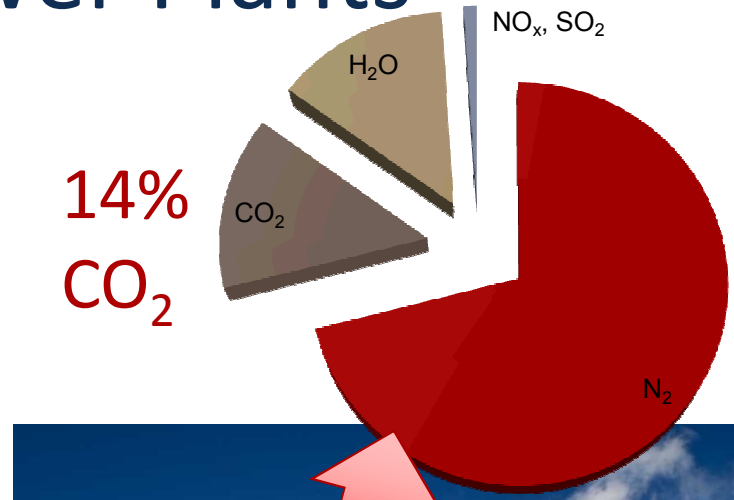
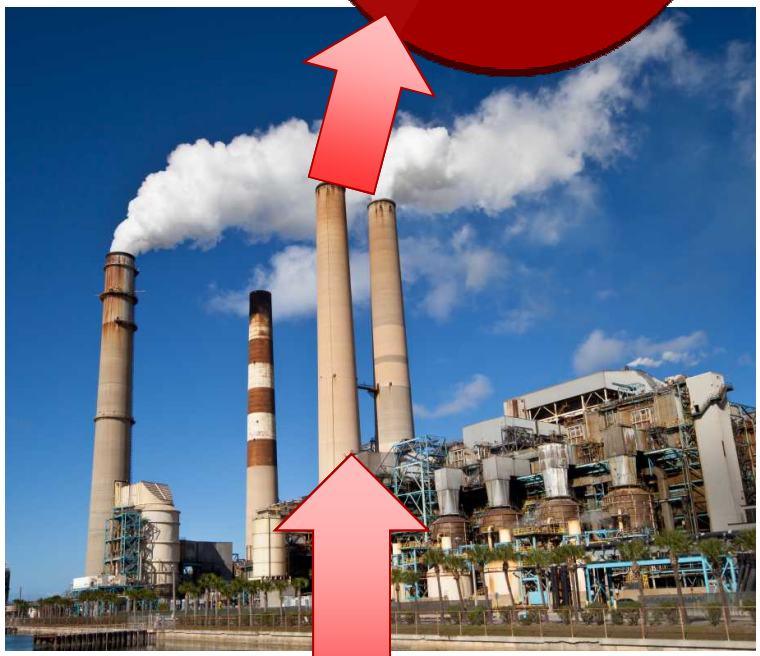
Oxyfuel for Cleaner Power Plants

- 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



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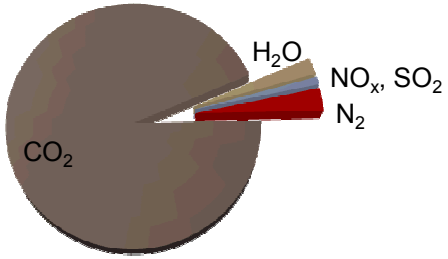
Air (78% N_2, 21% O_2)

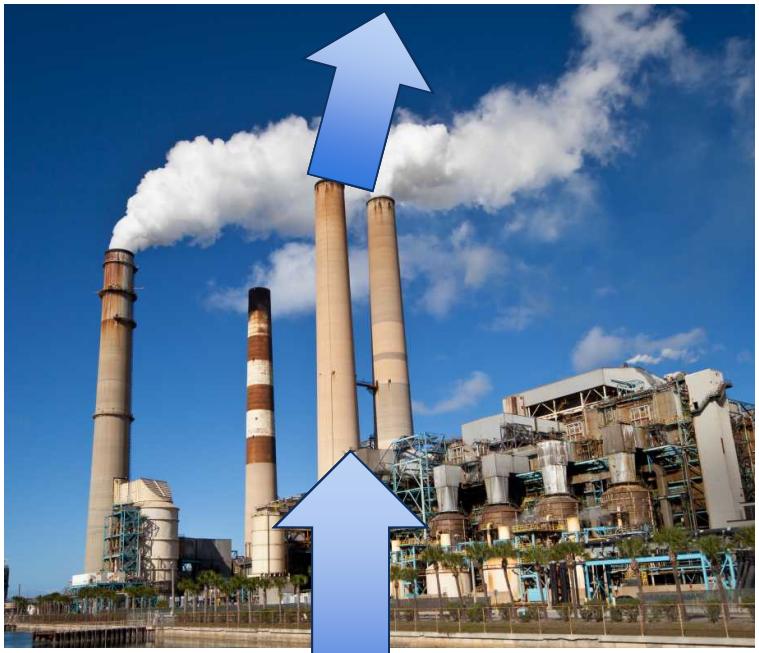
Hu, Y. CO_2 Capture from Oxy-Fuel Combustion Power Plants. Licentiate Thesis, KTH Royal Institute of Technology, Stockholm, Sweden, 2011

Oxyfuel for Cleaner Power Plants

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

94% CO_2





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

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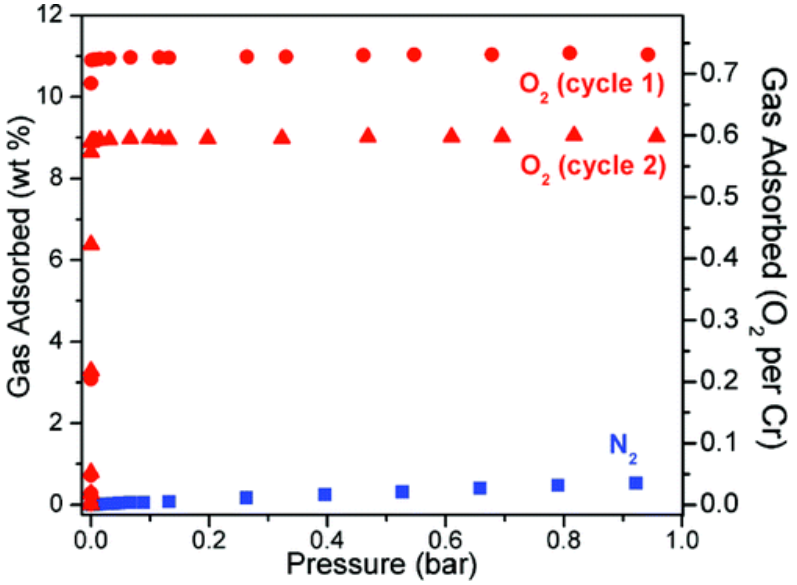
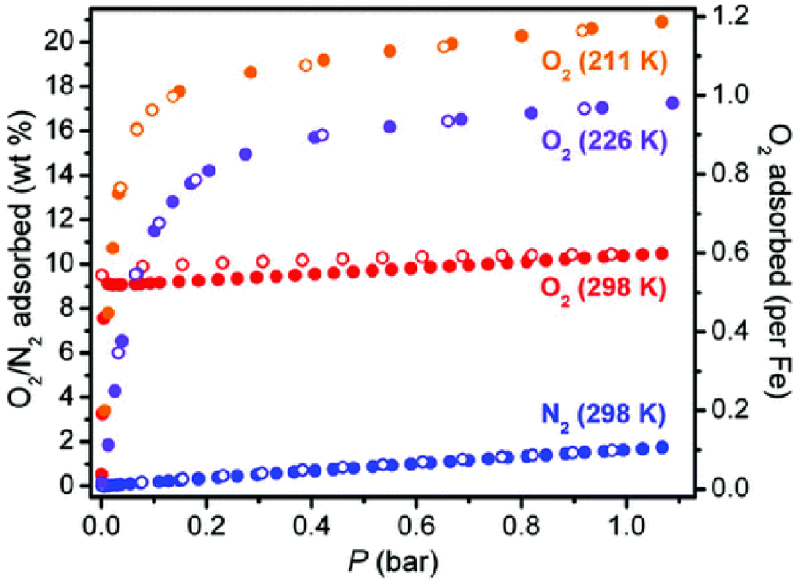
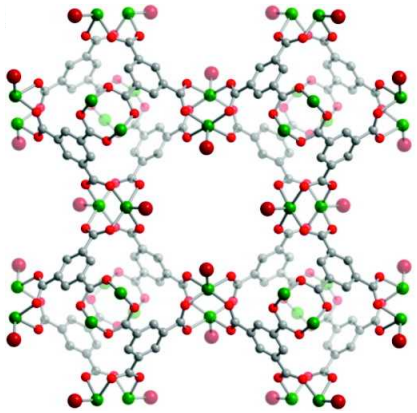
Known MOFs Separate O_2/N_2

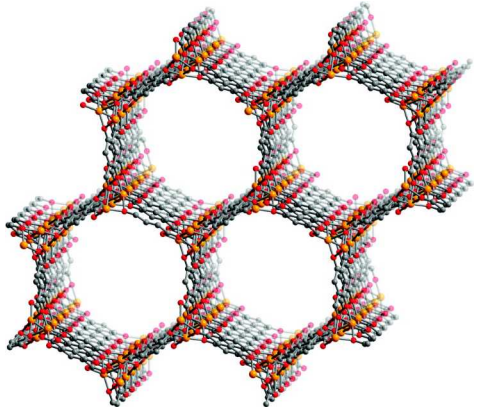




(Cr)HKUST-1



(Fe)MOF-74



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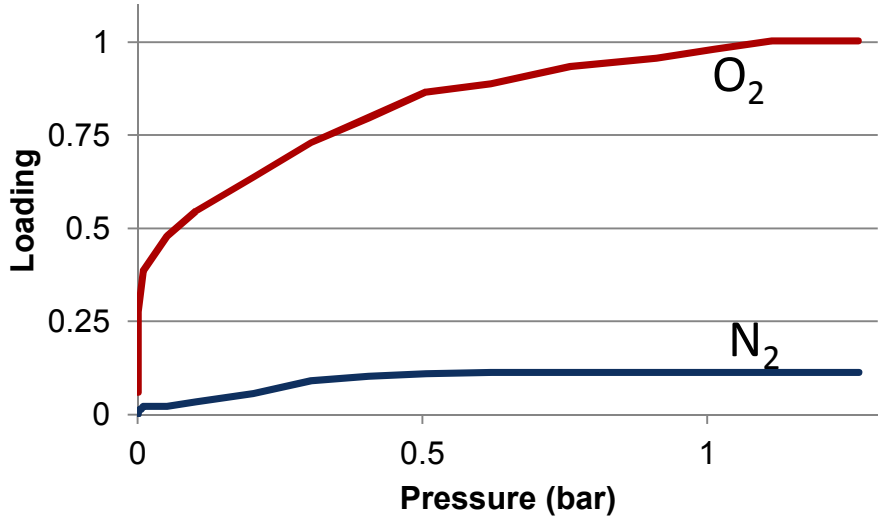
MOFs for O_2/N_2 Separation

Air → MOF → 95% O_2

- Clean crystal structures — 2855
- Initial screening based on known properties — 554
- Screening based on O_2/N_2 Henry's constants — 75
  Sarkisov, L. *J. Phys. Chem. C* **2012**, *116*, 3025-3033.
- Classical modeling of uptake with standard force fields — 0



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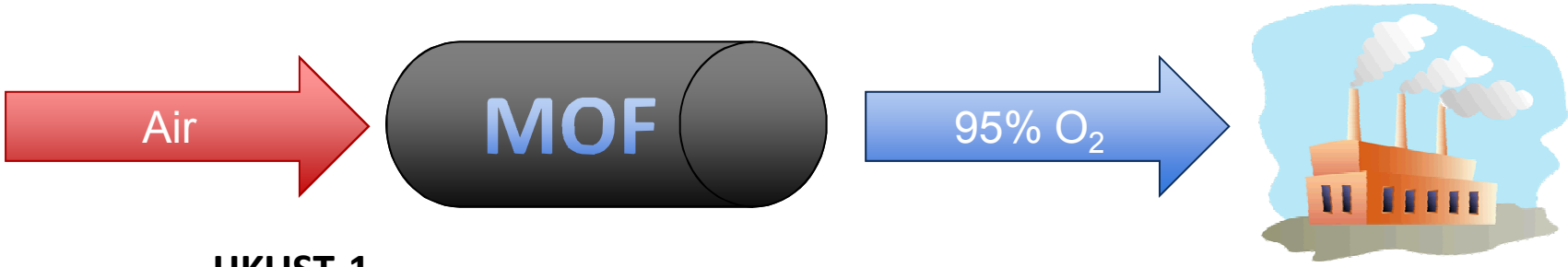
MOFs for O_2/N_2 Separation



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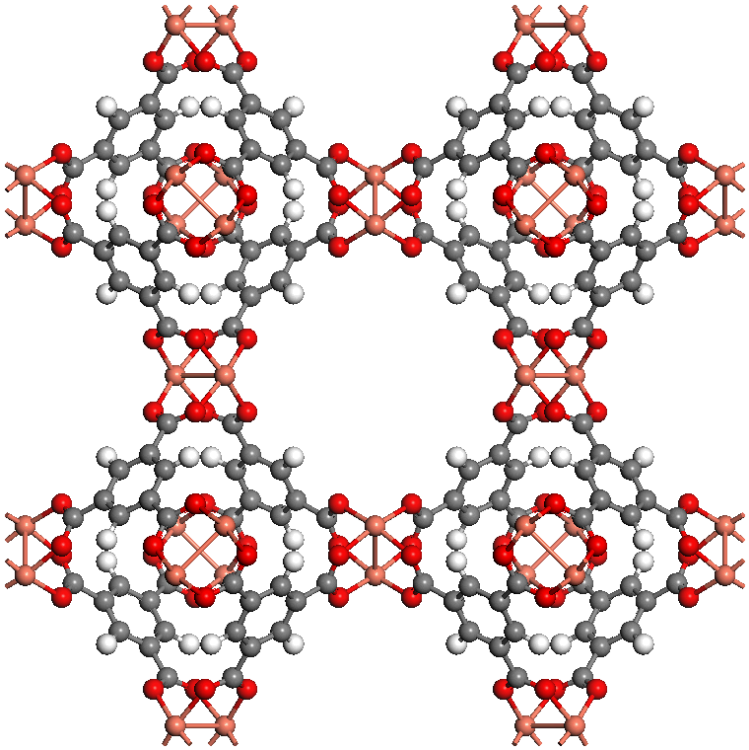

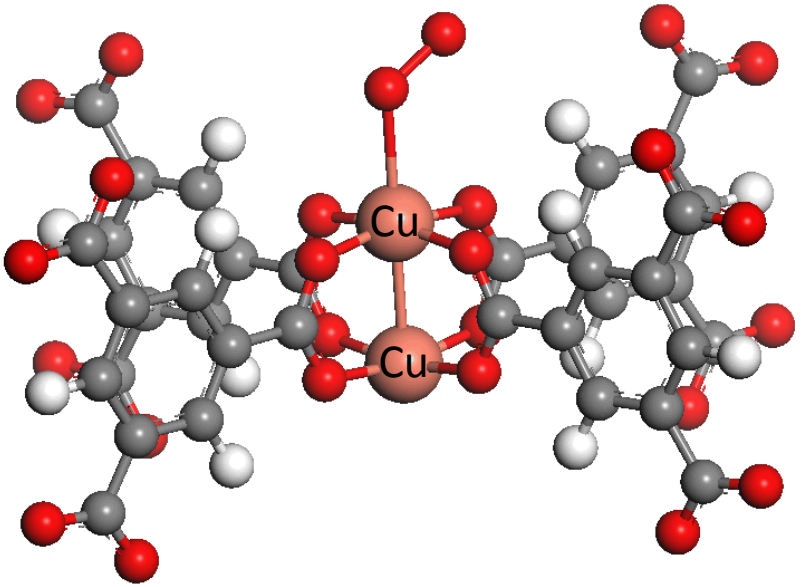

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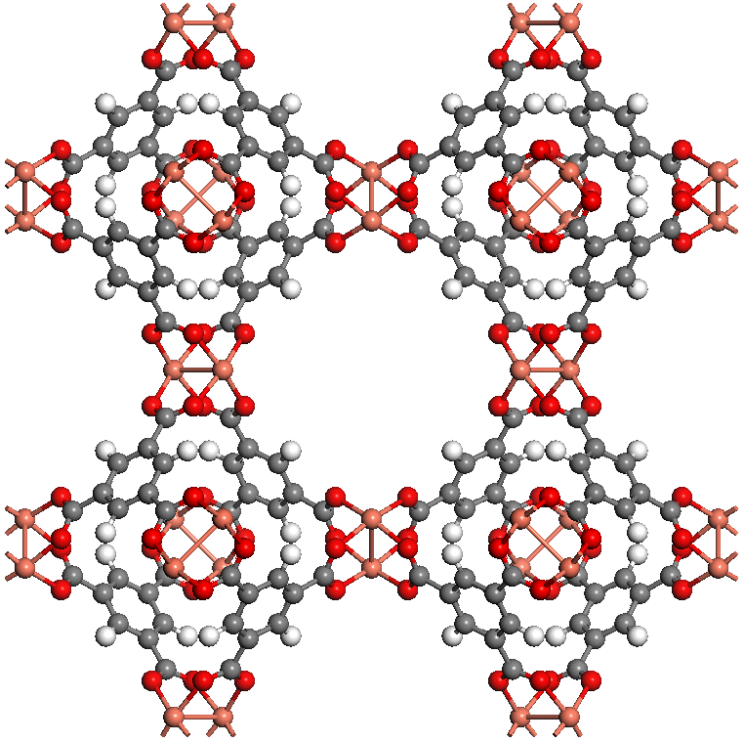
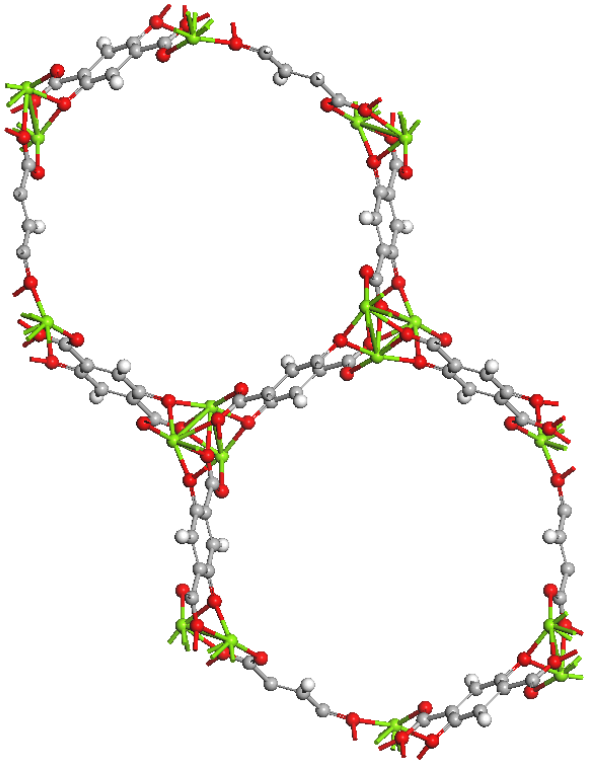
MOFs for O_2/N_2 Separation

HKUST-1



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

MOF-74



Pores: 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
  - HKUST-1 analogs
  - MOF-74 analogs
- Metals

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

- Gas (one molecule per simulation 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

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

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O_2, N_2 Binding Energies (ΔE)

metal	HKUST-1 binding energy (kJ/mol)			MOF-74 binding energy (kJ/mol)		
	O_2	N_2	ΔΔE	O_2	N_2	ΔΔE
Sc	-401	-47	354	-251	-41	210
Ti	-329	-24	305	-255	-74	181
V	-127	-20	107	-229	-96	133
Cr	-106	-41*	65	-132	-11	121
Mn	(failed)	-11		-106	-26*	80
Fe	-66	-14	52	-52*	-15*	37
Co	-67	-57	10	-81	-45	36
Ni	-54	-50	4	-85	-17*	68
Cu	-85	-104	-19	-60	-18*	42
Zn	-24	-38	-14	-24	-21*	3

* Gas atom not adsorbed on metal

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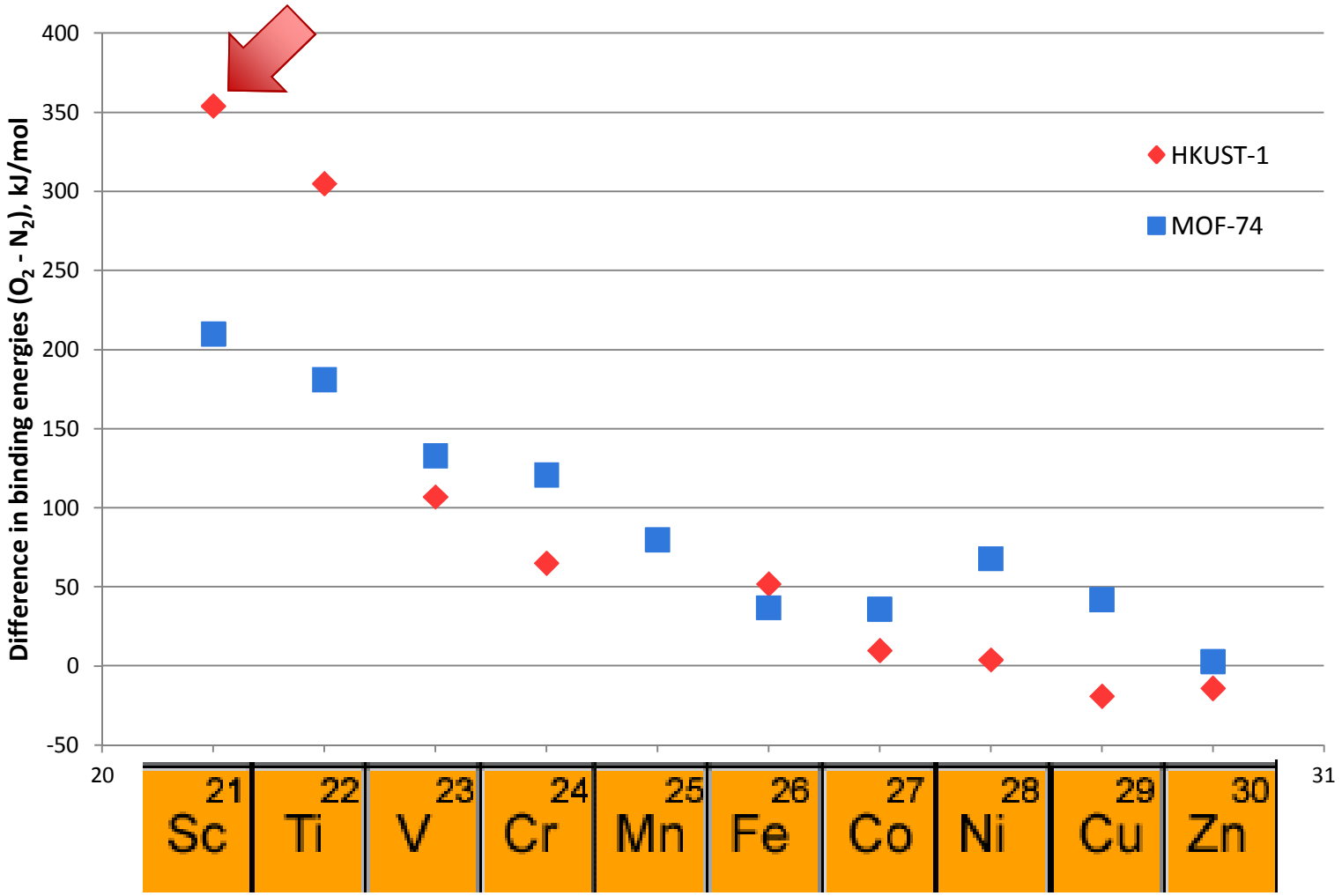
Difference in Binding Energies (ΔΔE)



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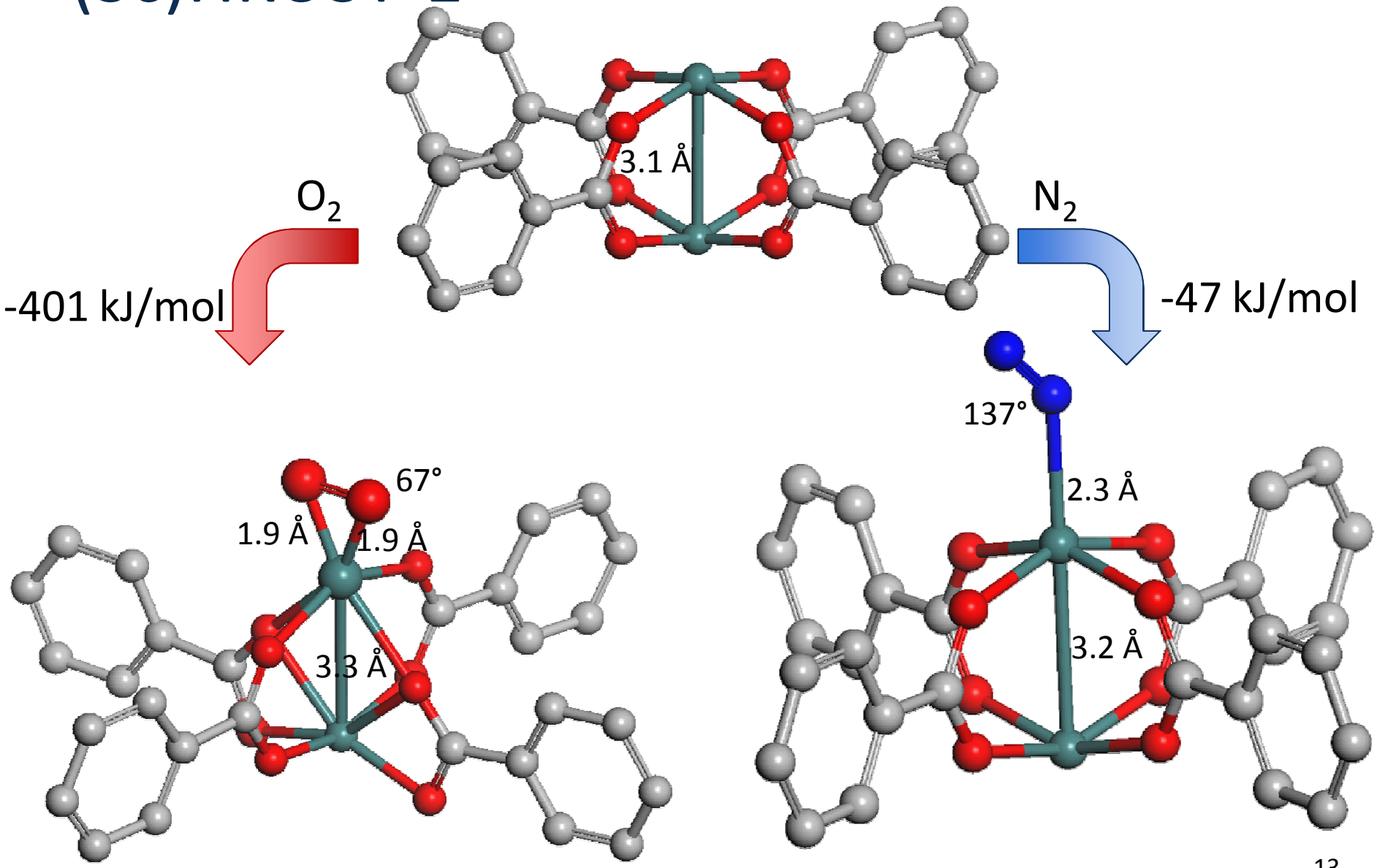
(Sc)HKUST-1



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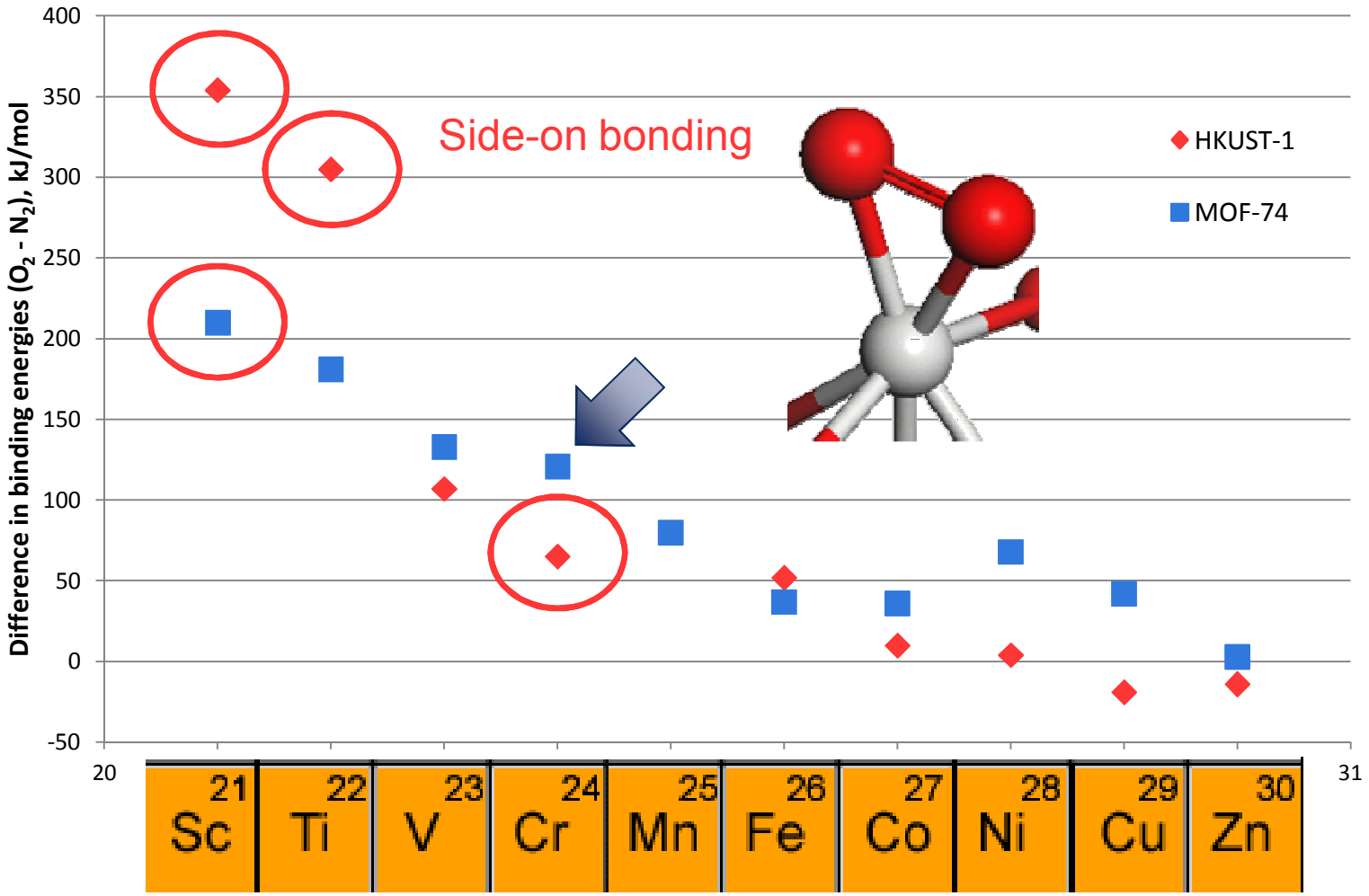
Difference in Binding Energies (ΔΔE)



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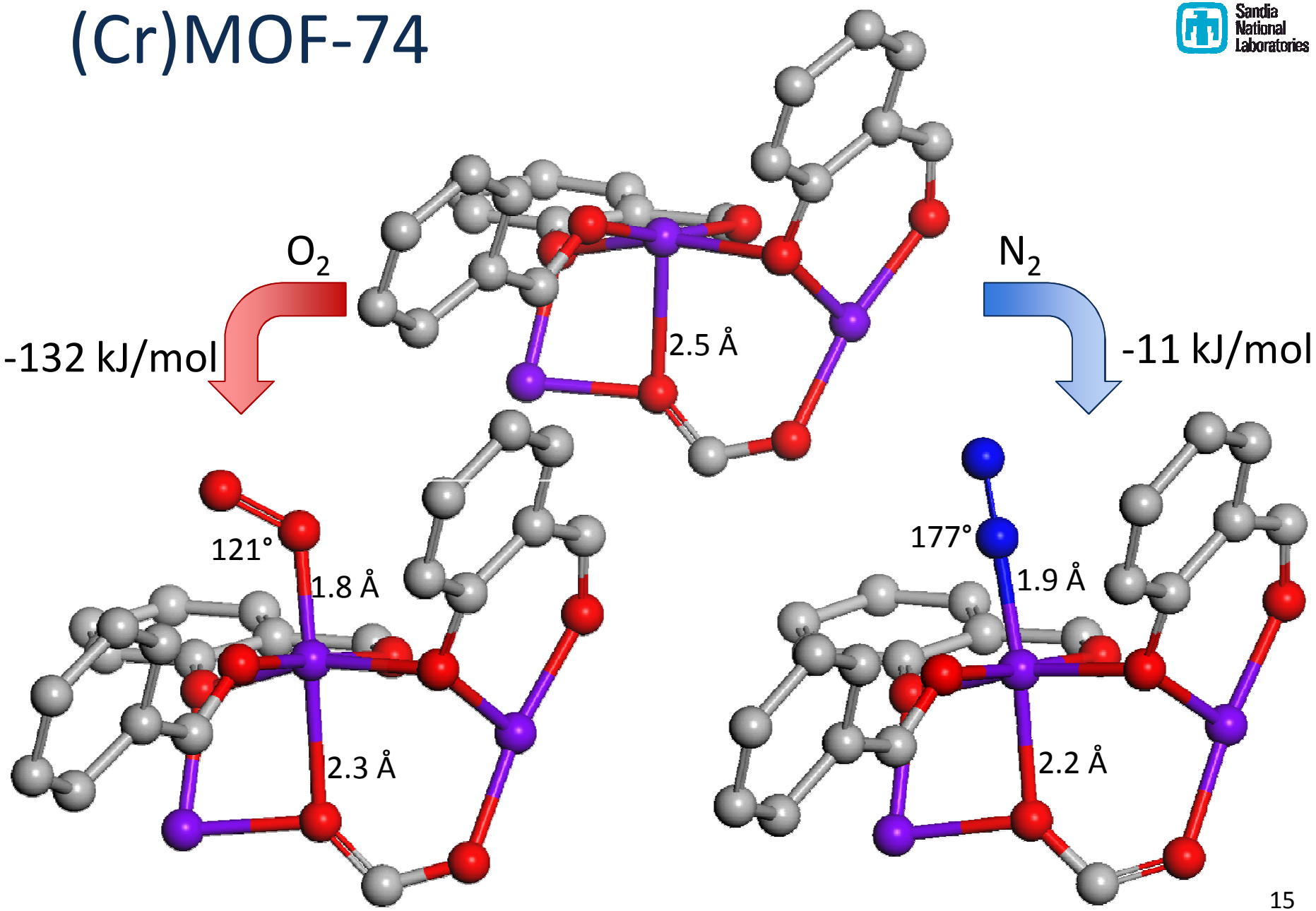
(Cr)MOF-74



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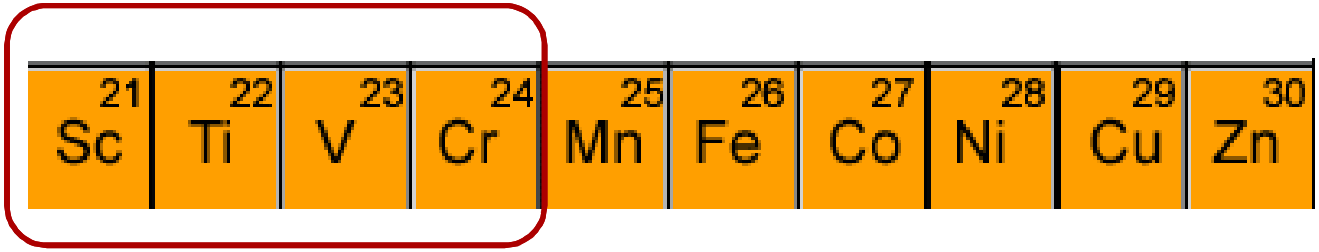
Conclusions



- Metal matters!
  - Trend consistent in two MOFs
  - Focus on early transition metals
- Other metals
  - First-row vs second-row transition metals?
  - Main group metals?
  - Alkaline earth metals?
- Develop force fields
  - Classical simulations to model O_2 and N_2 adsorption
- Synthesis, apply to separation of air for oxyfuel production

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Acknowledgments

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