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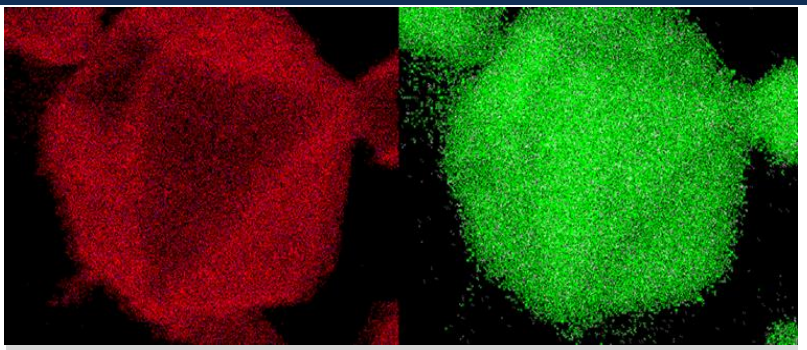

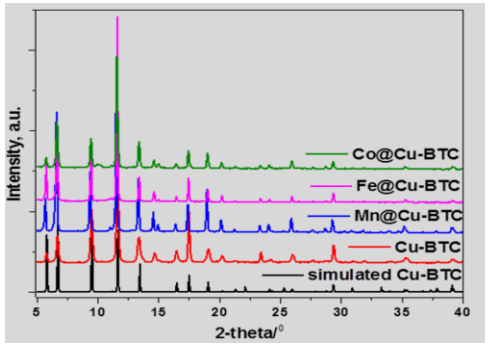

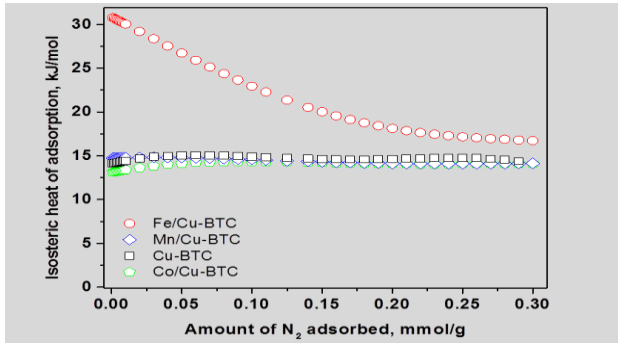

Efficient Air Separations with MOFs for CO_2 Capture via Oxy-fuel Combustion

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Sandia National Laboratories, Albuquerque, NM

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Materials for Carbon Capture
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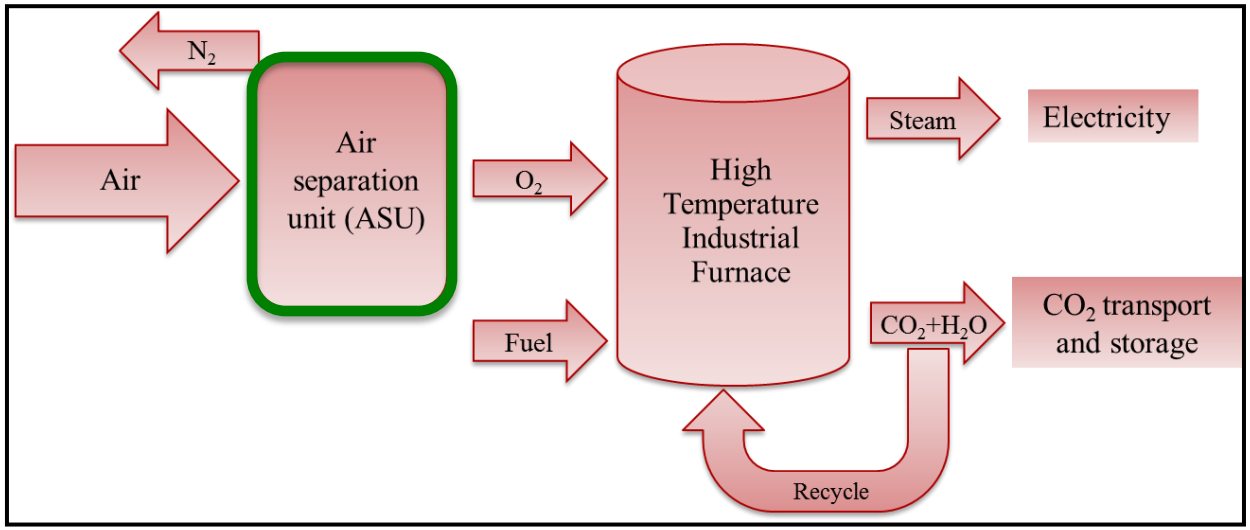
O_2/N_2 air separations with MOFs to increase efficiency of ASU



- 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

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Integrated modeling and materials development approach

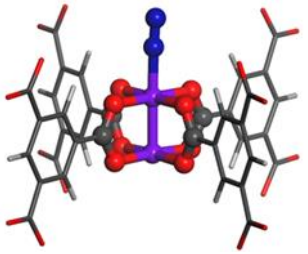
- MOFs with coordinatively unsaturated metal centers are promising materials for O_2/N_2 separations
- Two prototypical MOFs from this category, $Cr_2(BTC)_3$ (*J. Am. Chem. Soc.* **2010**, *132*, 7856) and $Fe_2(DOBDC)$ (*J. Am. Chem. Soc.* **2011,** *133*, 14814) show preferential adsorption of O_2 over N_2

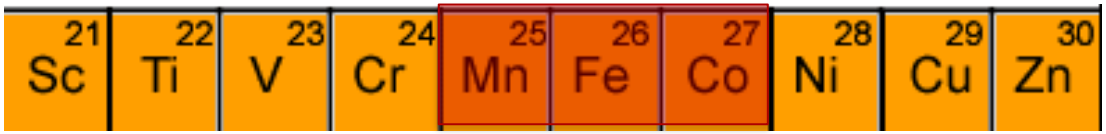
Predictive molecular modeling

- Previous studies have used quantum mechanics to estimate binding energies of small molecules on metal sites in MOFs (*Chemical Science* **2013,** *4*, 3544-3556)
- Plane wave DFT calculations were performed on periodic structures in the Vienna Ab initio Simulation Package (VASP)
- Static binding energies for O_2 and N_2 were calculated at 0 K
- Binding geometries for side-on and bent O_2 and bent and linear geometries for N_2 were evaluated for first row transition metals

Materials development

- Guided by the modeling results, experiments were first directed at the *synthesis of the most feasible analogs of known materials*
- Metal ion postsynthetic exchange (PSE) or postsynthetic ion metathesis (PSIM) pursued, recently demonstrated to access materials difficult to obtain via conventional routes (*J. Am. Chem. Soc.* **2012**, *134*, 18082−18088)





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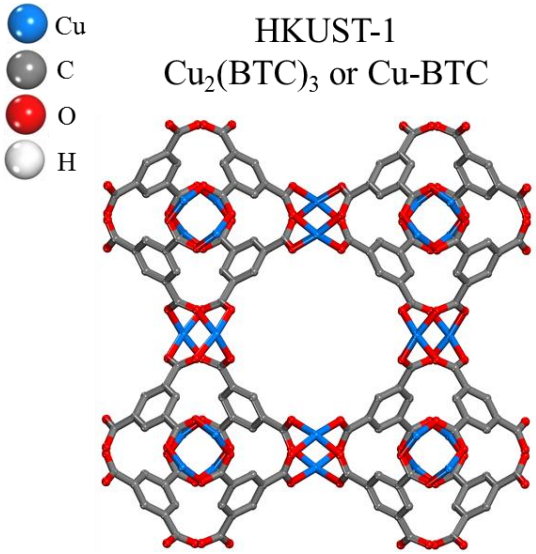
Targeted synthesis of porous Mn-, Fe- and Co- analogues of Cu-BTC

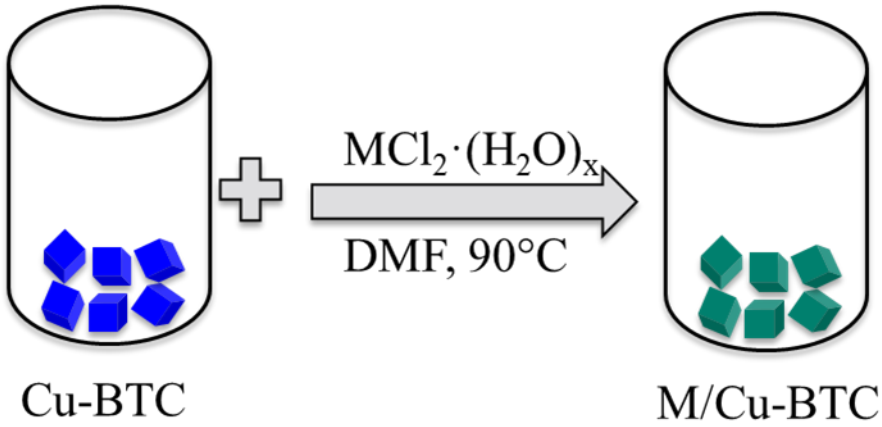
- Porous analogues of Cu-BTC include: Cr, Mo, Ru, Ni (the Ru and Ni have much lower than expected surface areas, 1000-1100 m^2/g)

- Porphyrin-templated Mn-, Fe- and Co- Cu-BTC analogues known, however no measurable accessible porosity (*J. Am. Chem. Soc.* **2012**, *134*, 928−933)



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

Postsynthetic metal ion exchange



M= Mn, Fe, Co

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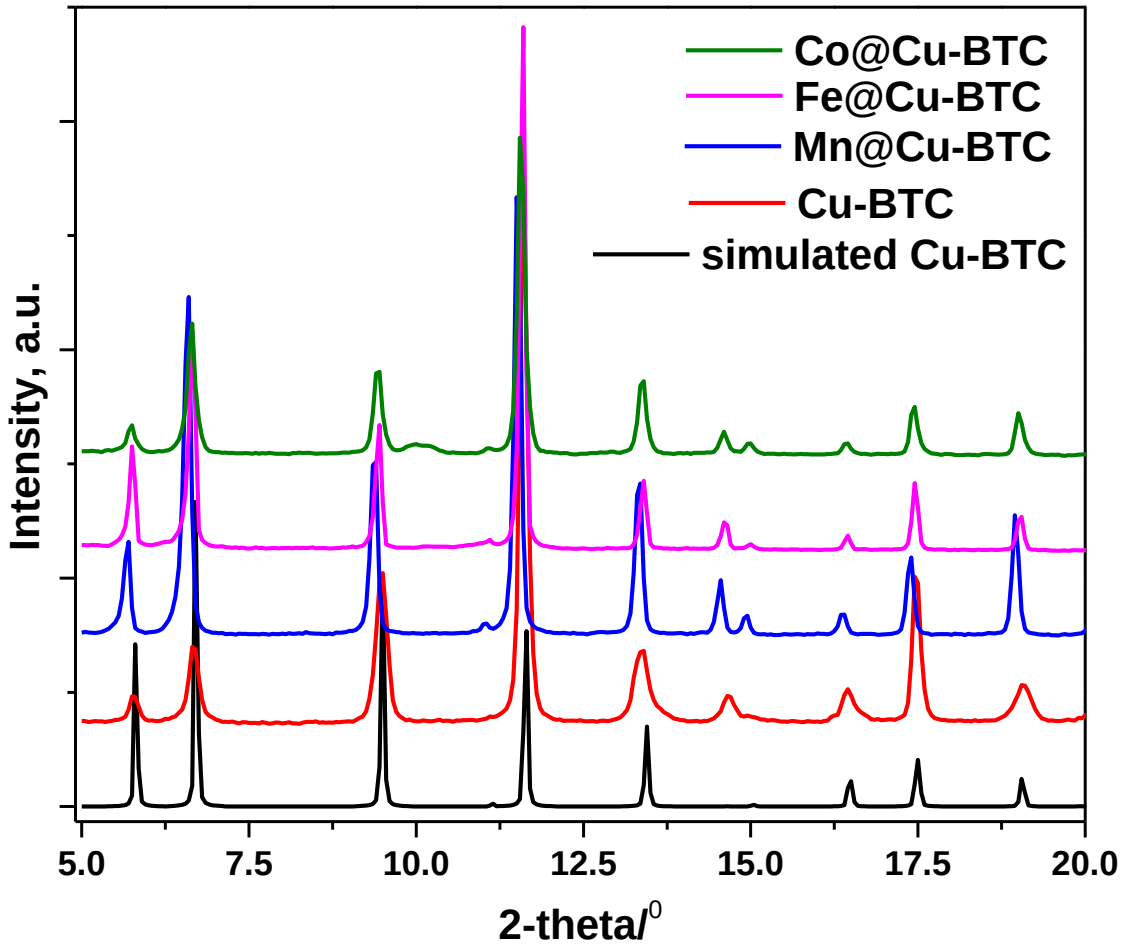
Confirmation of in-framework metal substitution as indicated by unit cell expansion



	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

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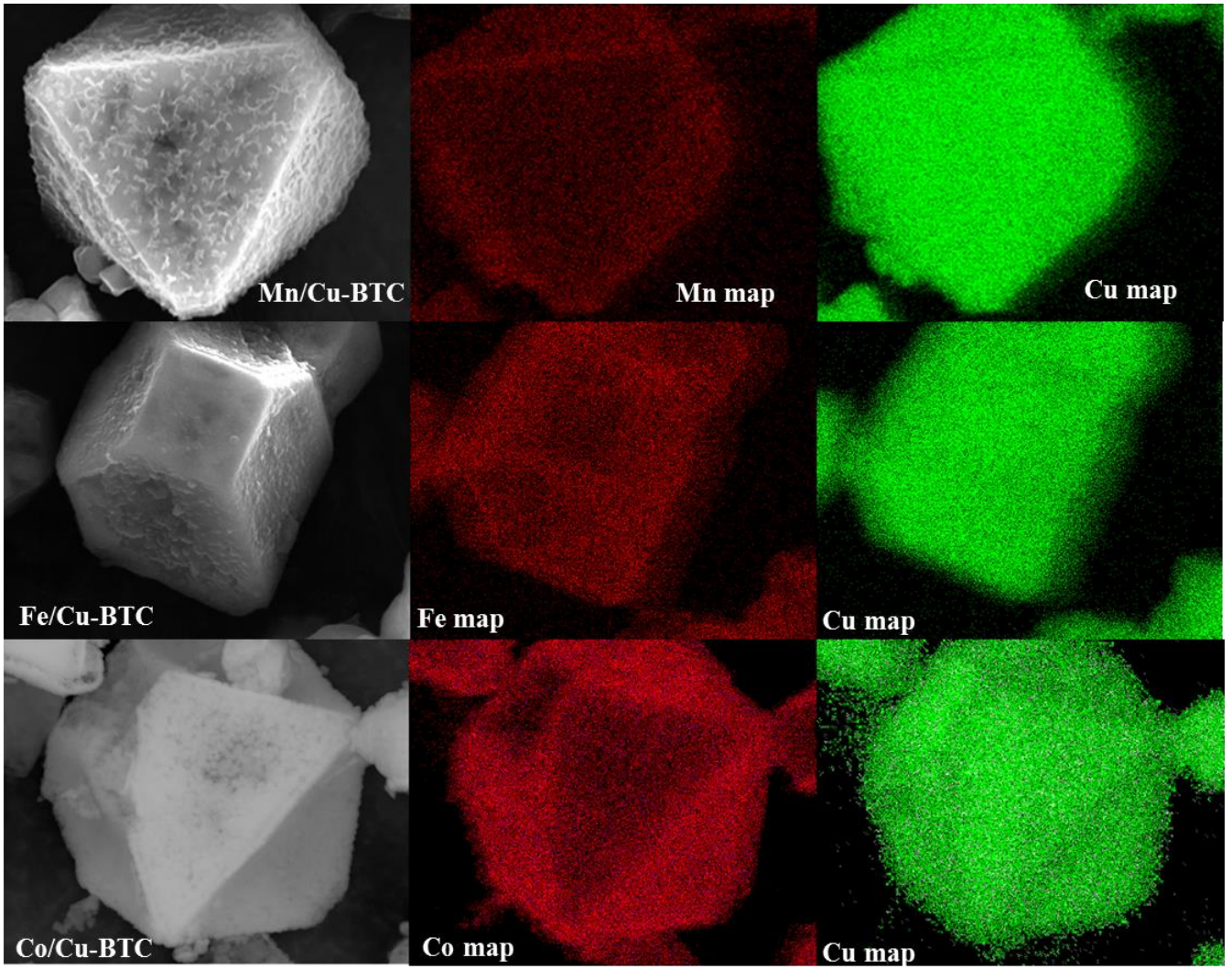
Metal substitution further confirmed by SEM-EDS



SEM-EDS mapping shows homogeneous dispersions of the substituted metals in the Cu-BTC matrix

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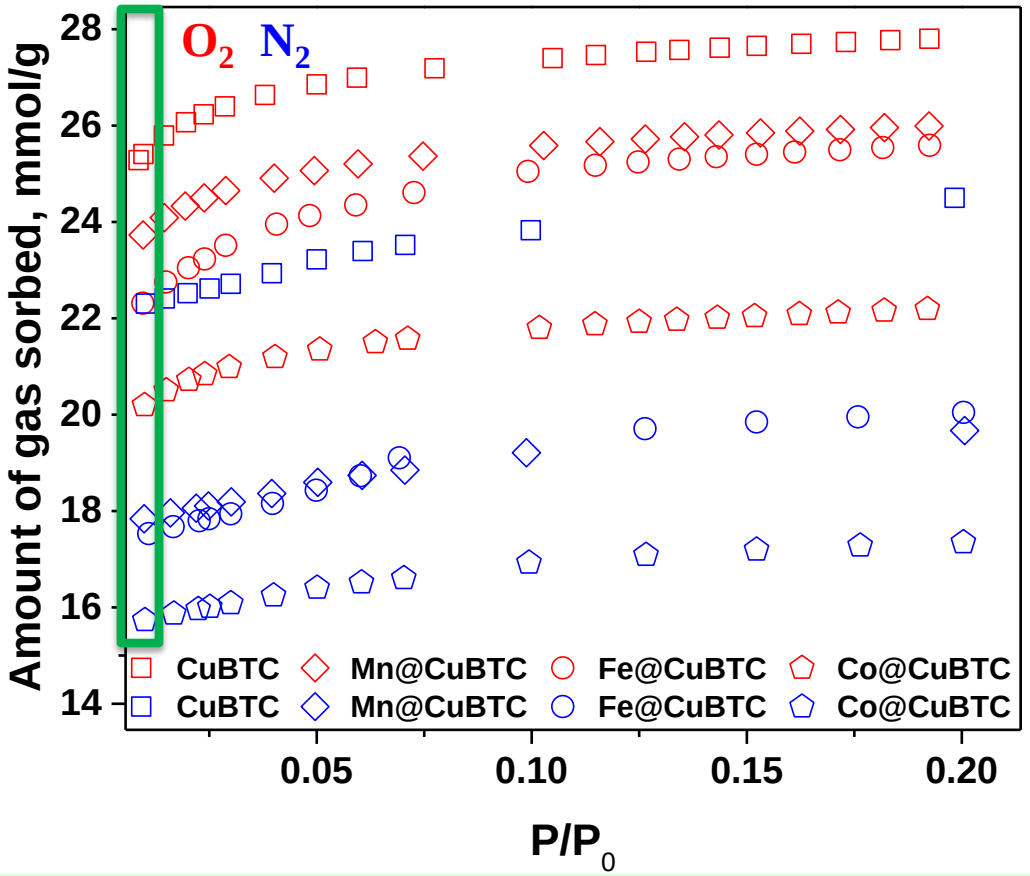
Excellent DFT and experiment correlation at low temperature and low pressure

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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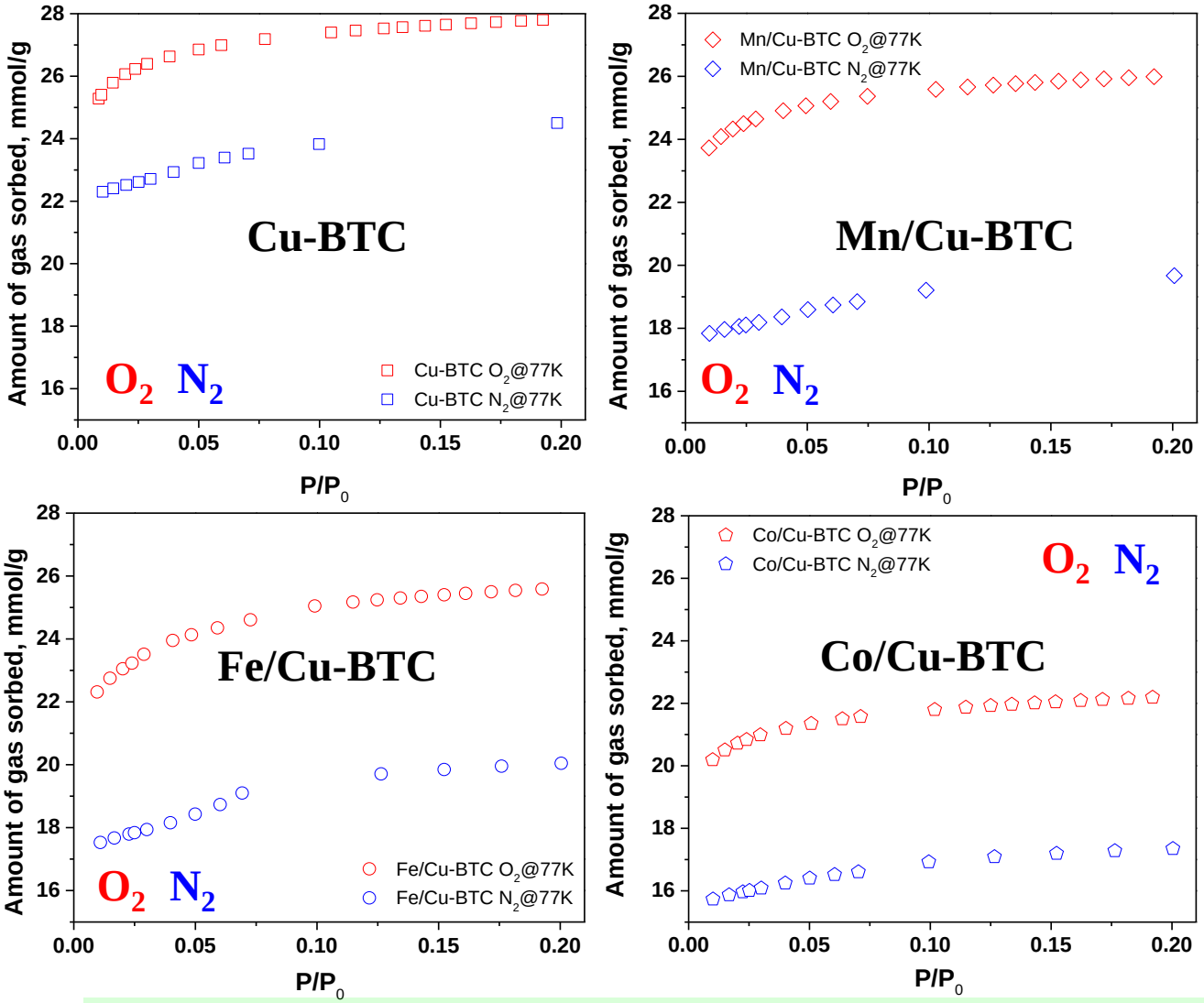
77 K: all samples have higher O_2 loadings over N_2



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

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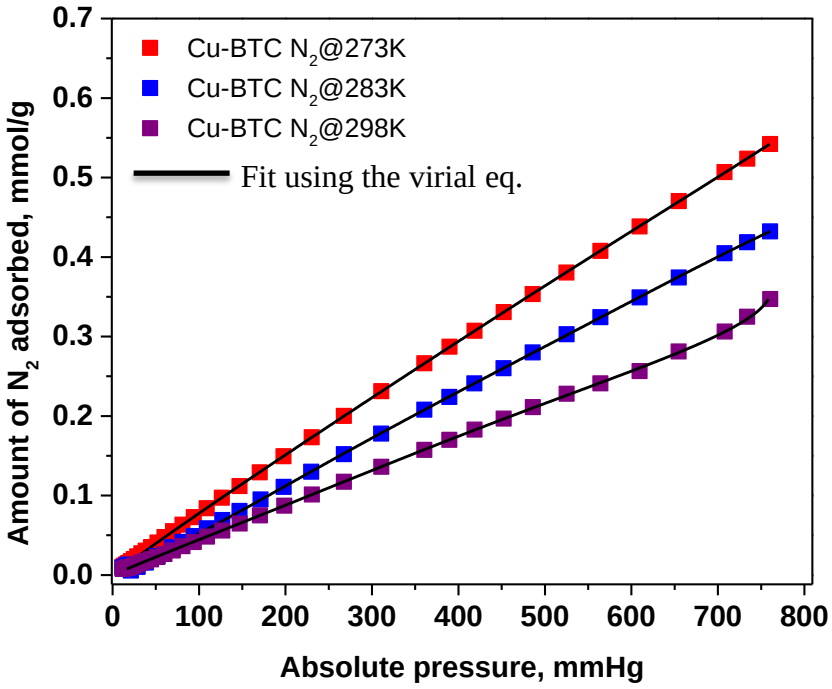
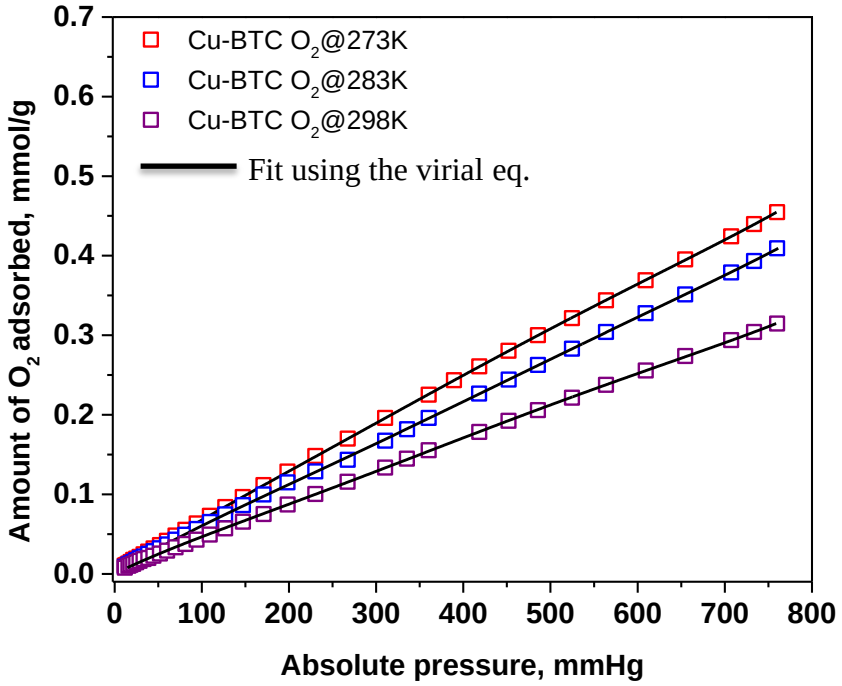
273-298 K: as temperature increases, O_2 loadings decrease with respect to N_2

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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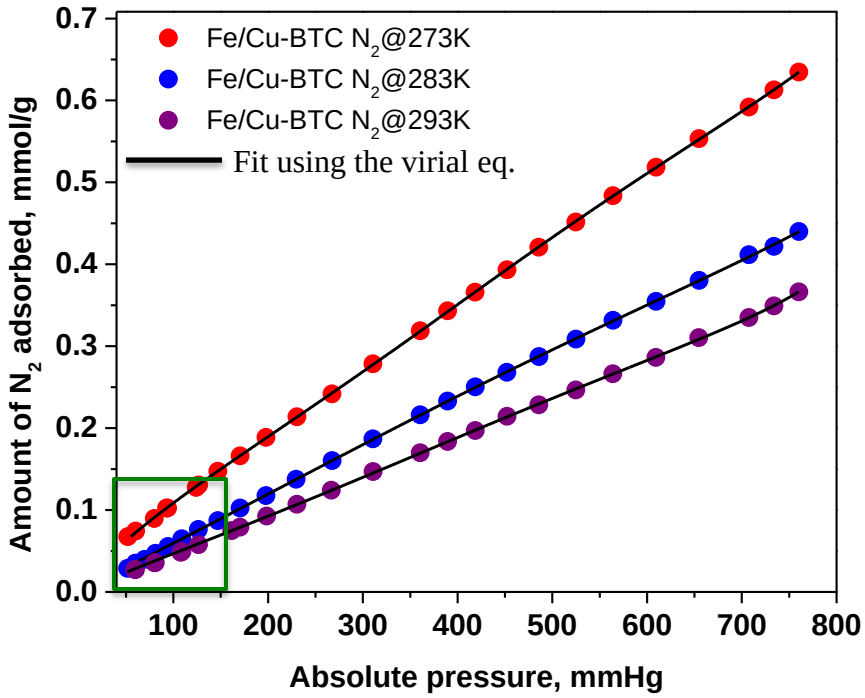
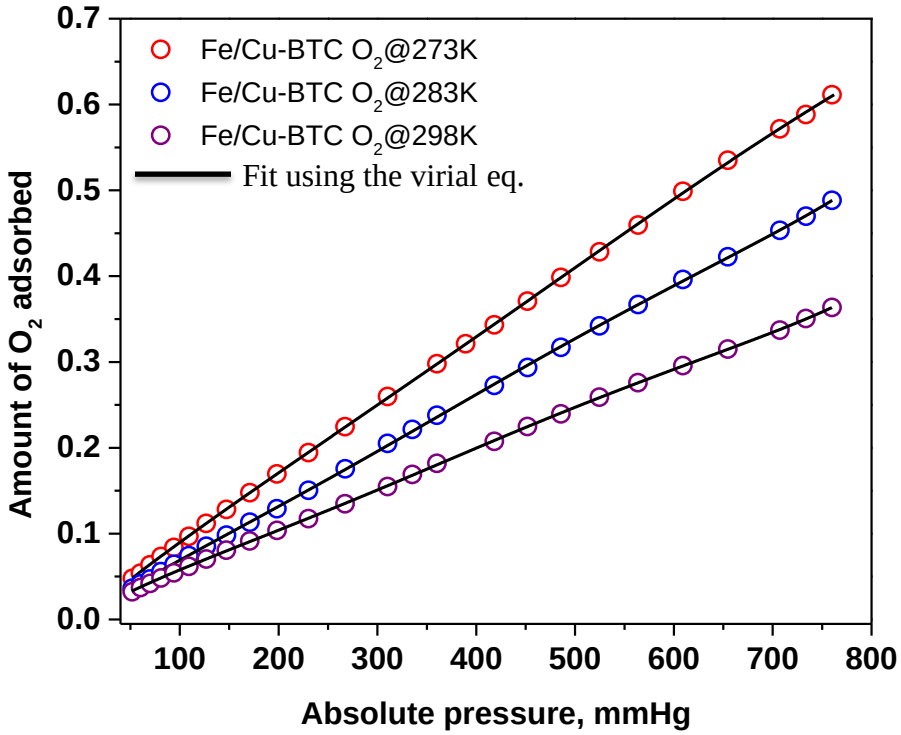
N_2@273 K in Fe/Cu-BTC : slightly higher N_2 uptake at lowest loading





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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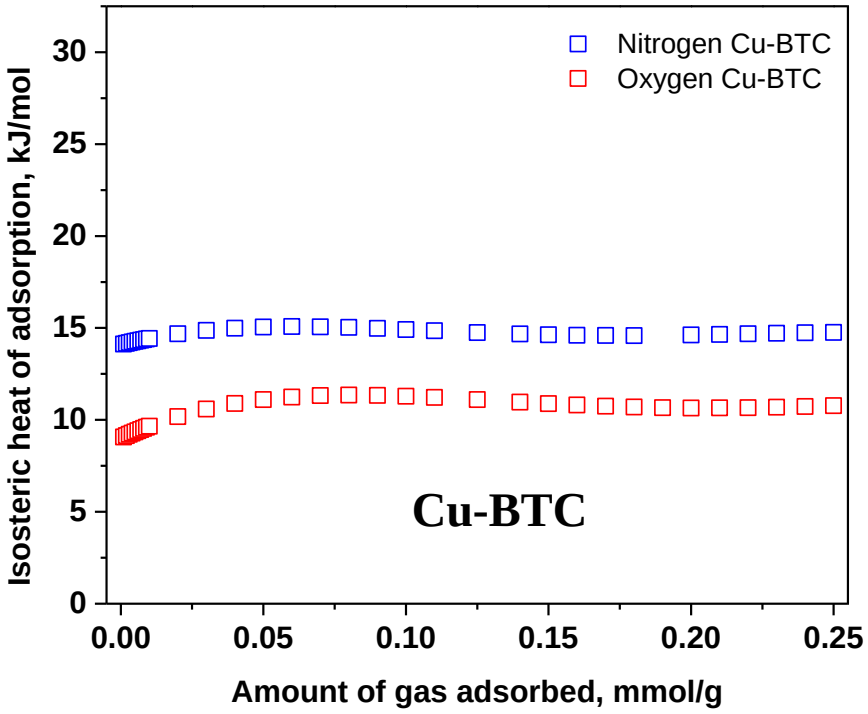
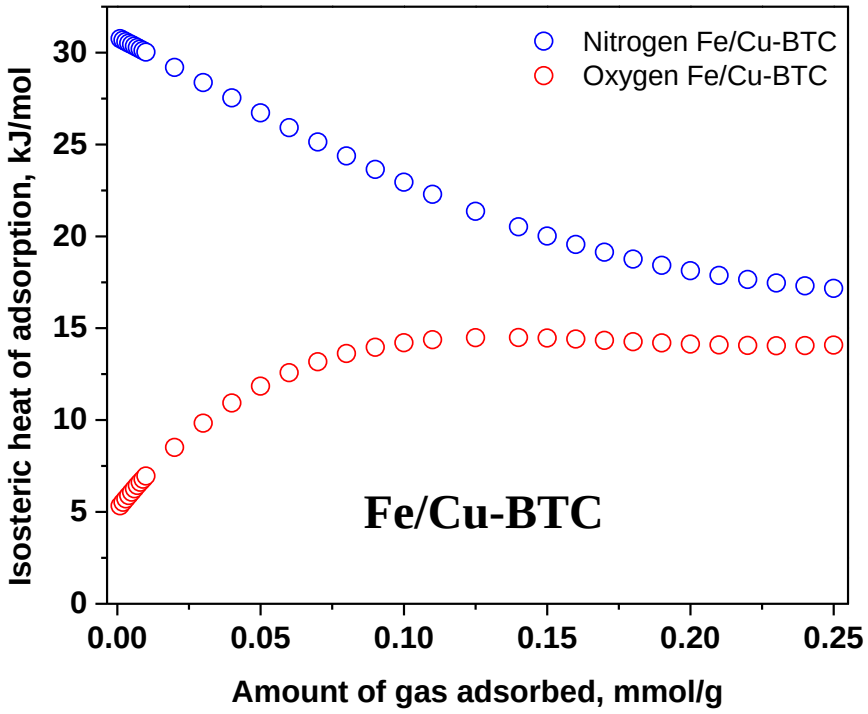
Isosteric heats of adsorption for O_2 (red) and N_2 (blue)





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

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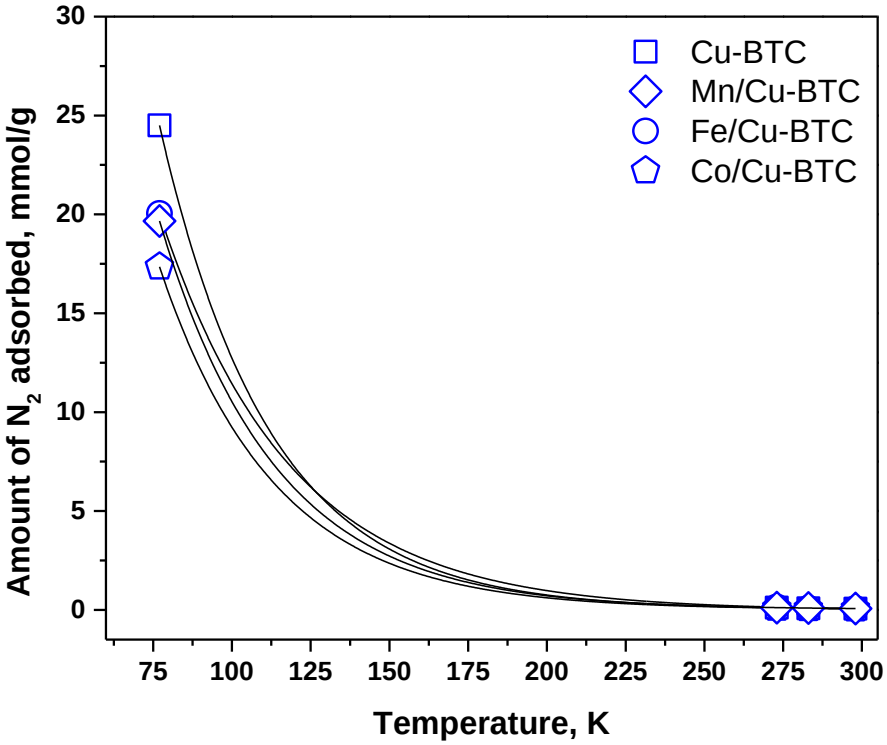
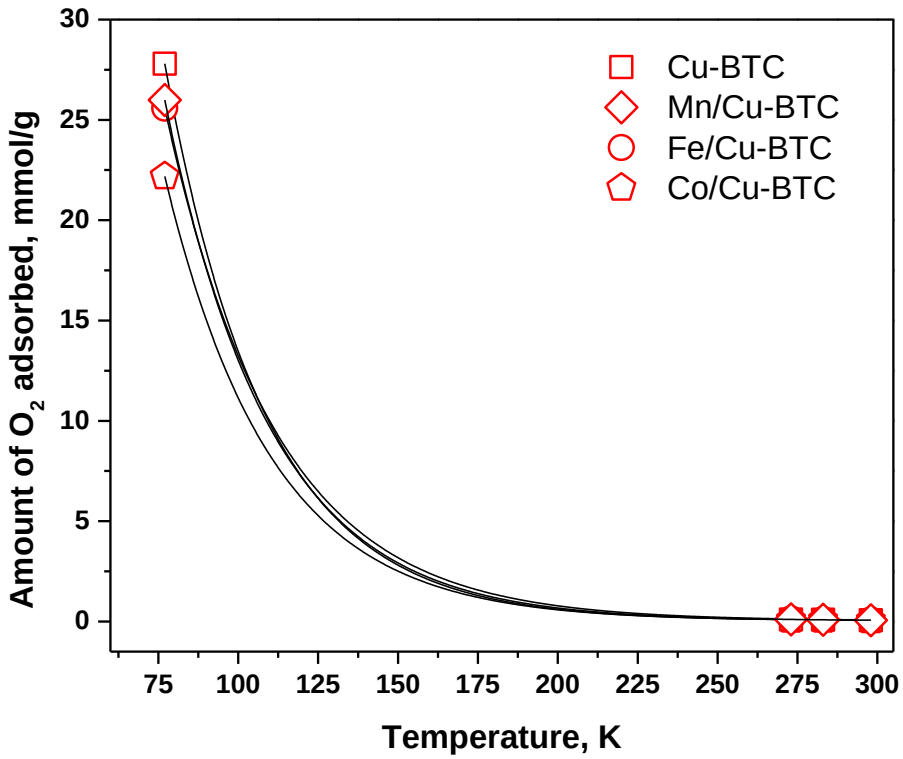
At 77K the metal sites play an important role, while at 273-298 K have a less pronounced effect

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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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
- O_2 preferentially adsorbs over N_2 at 77K
- The trend is reversed at 298K, where N_2 preferentially adsorbs over O_2
- The Fe/Cu-BTC sample is an unique case in the room temperature range, with very significantly higher N_2 binding energy over O_2 at lowest loadings
- Future studies will focus on the synthesis of the most promising candidates identified by the DFT calculations

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