CO_2 Adsorption in Heterometallic Metal-Organic Frameworks

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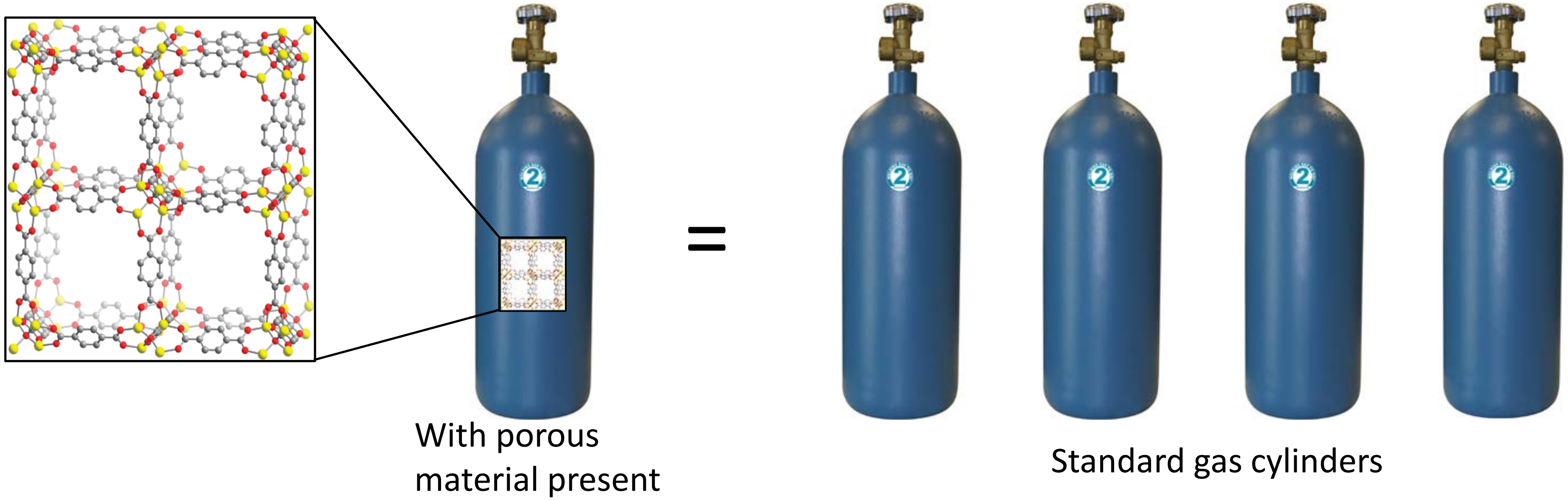
Background

Porous materials have the potential to play a large role in future energy technologies

H_2 and CH_4 storage and selective adsorption of CO_2 from industrial exhaust



Extremely high surface areas—~1,000 m^2/g for zeolites and ~10,000 m^2/g for metal-organic frameworks

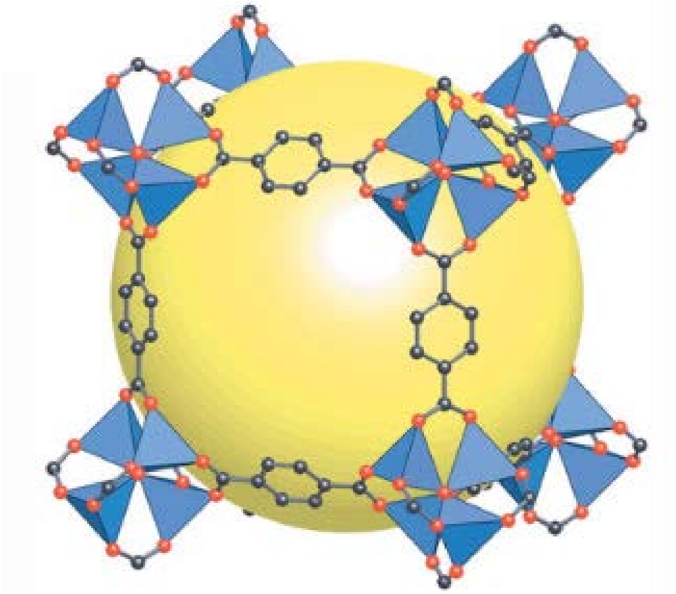
Metal-Organic Frameworks (MOFs)

Composed of organic ligands coordinated to a metal center

High surface-area to mass ratios, low densities and thermal expansion indices

Tunable—thousands of combinations of metals and ligands exist, with many more to be discovered

Heterometallic MOFs contain more than one metal

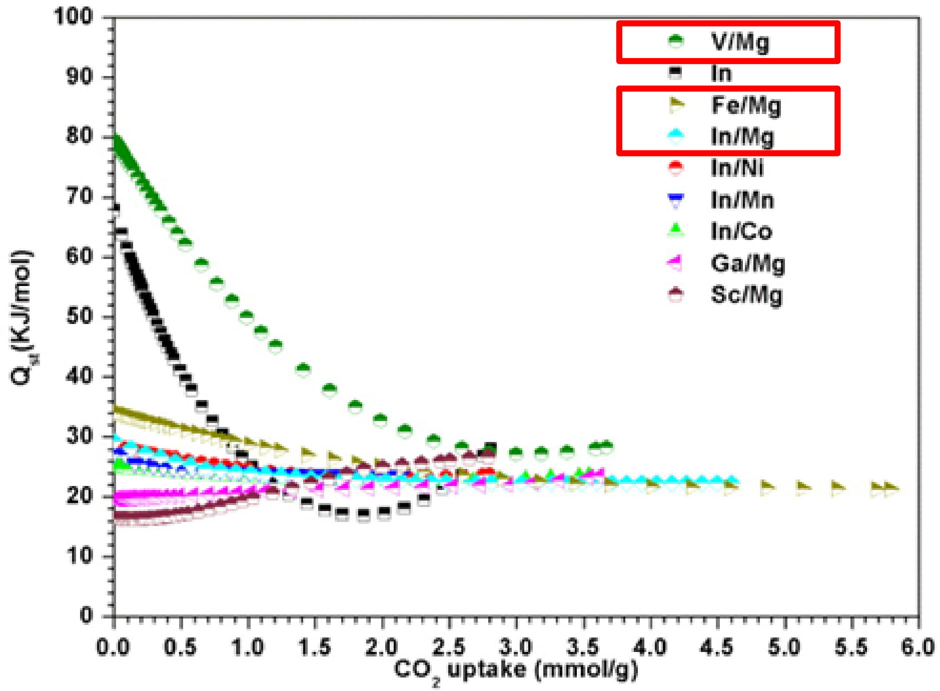


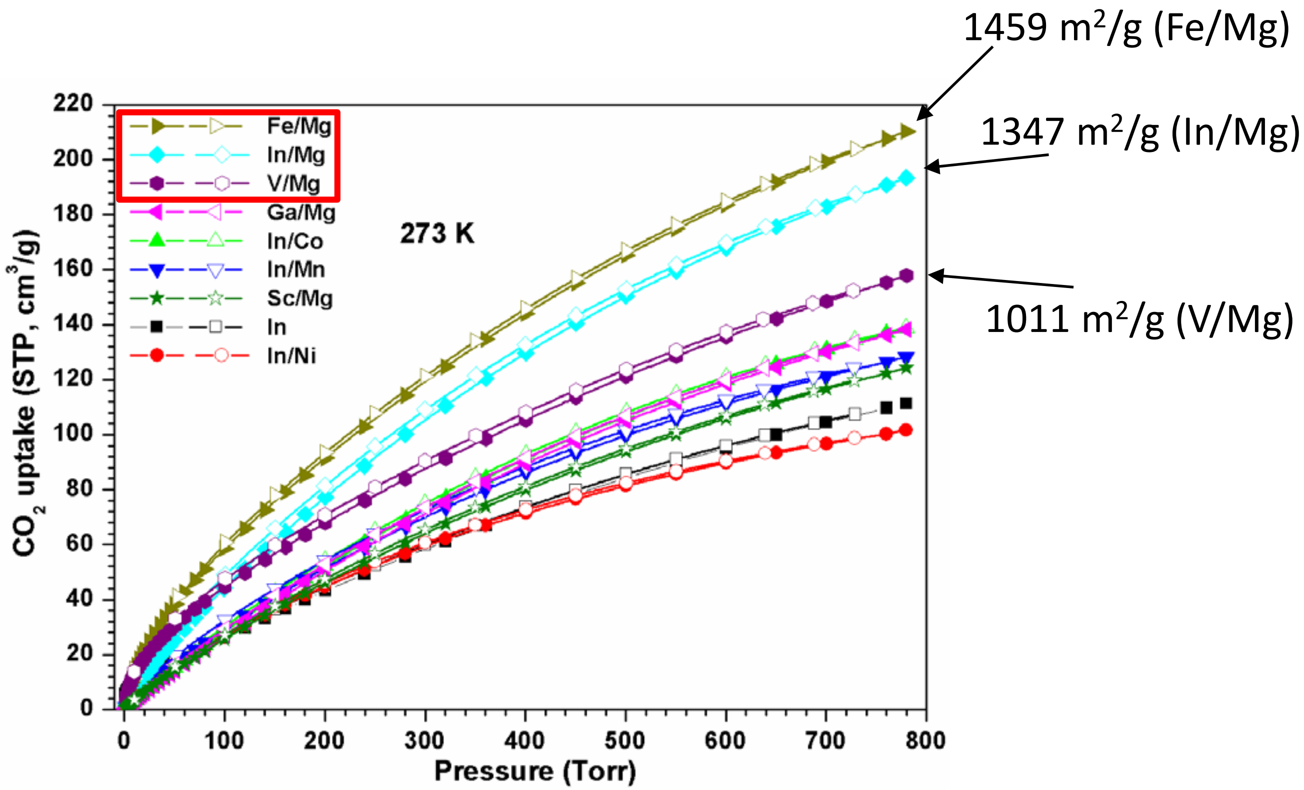
Eddaoudi, M. Science 2002, 295 (5554), 469–472.

Motivation

A recent paper published in JACS asserted that certain heterometallic MOFs had:

- Exceptionally high CO_2 uptakes, isosteric heats of adsorption (Q_{st}) and surface areas
- Q_{st} numbers for V/Mg are record breaking



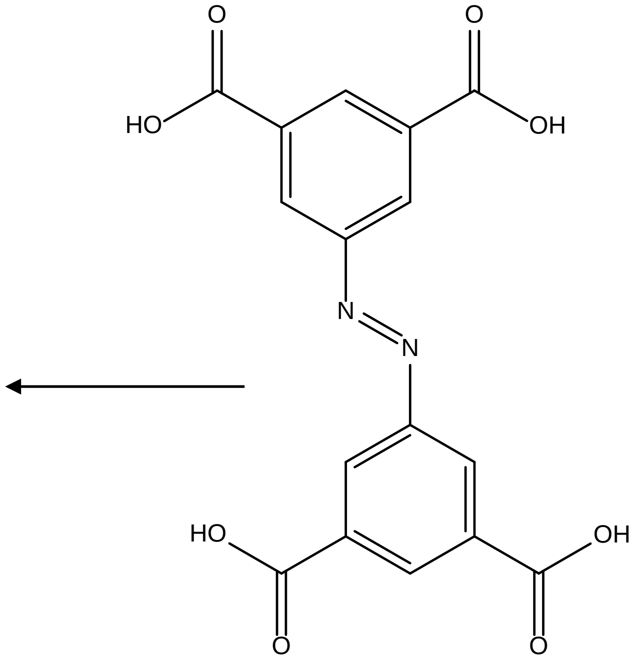


Zhai, Q.-G.; Bu, X.; Mao, C.; Zhao, X.; Feng, P. Journal of the American Chemical Society 2016, 138 (8), 2524–2527.

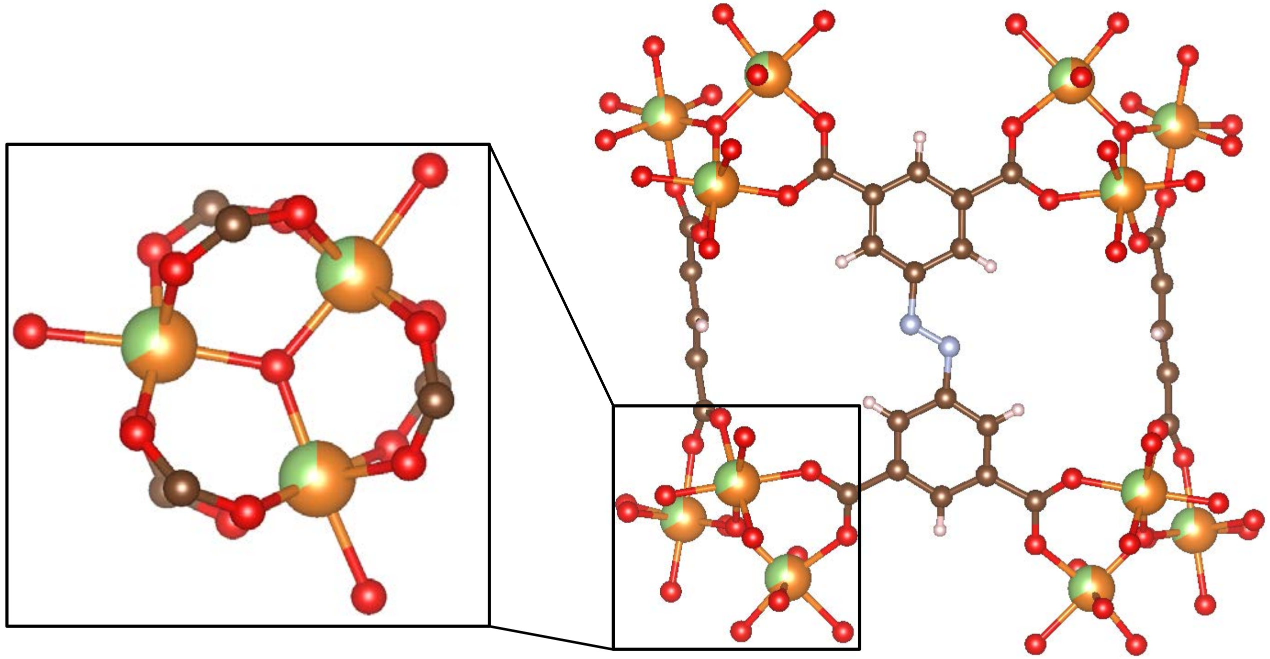
The MOFs Investigated

Synthesized in collaboration with Prof. Eric Bloch's lab at the University of Delaware

Activated and prepared for characterization at the NCNR



Ligand (H_4ABTC)



MOF Metal Cluster

MOF Unit Cell

Synthesis and Activation

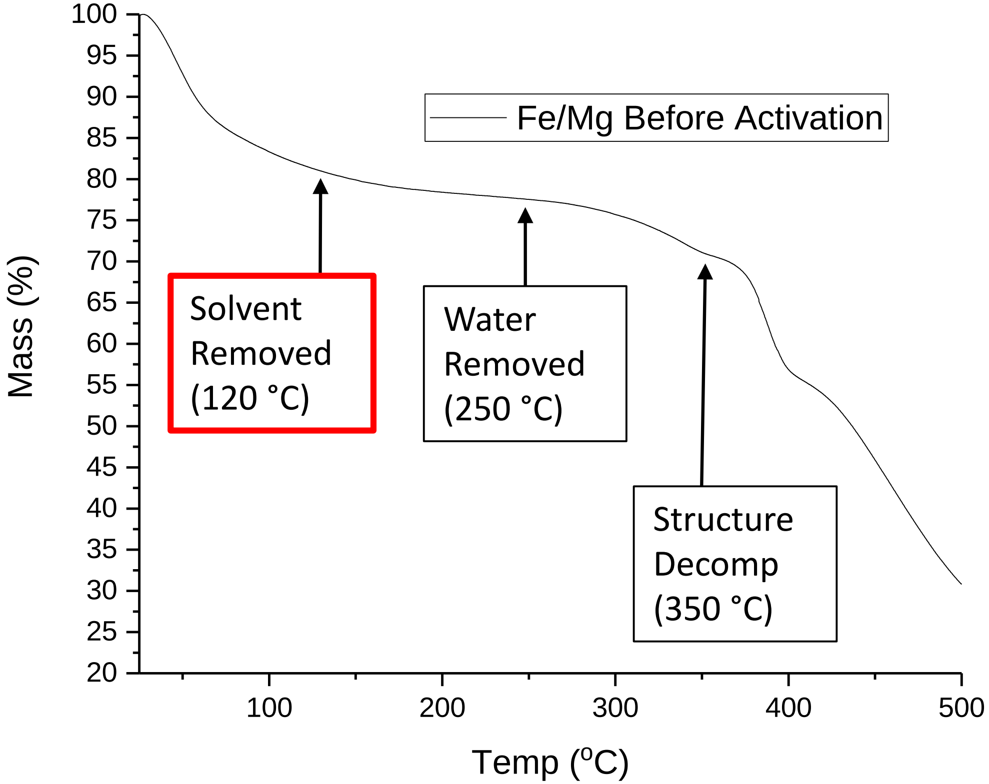
$$MCl_3 + 2Mg(OAc)_2 + 1.5H_4ABTC \xrightarrow[90\,^{o}C\ \ 2\text{-}5\ \text{Days}]{\text{Water + DMA}} [MMg_2(OH)(ABTC)_{1.5}(H_2O)_3]$$

In/Mg MOF

Fe/Mg MOF

V/Mg MOF

Thermogravimetric Analysis (TGA)



Gas Adsorption

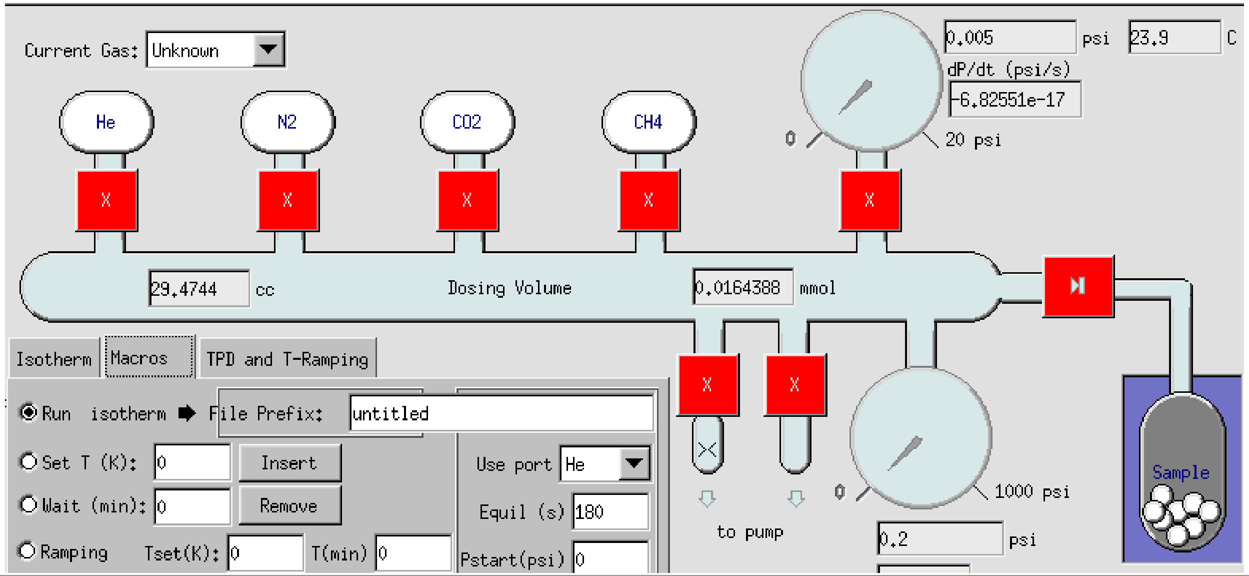
Conducted on a system built in house

Surface area, pore volumes, and Q_{st} can be determined from adsorption data

Brunauer-Emmett-Teller (BET) theory describes multilayer adsorption

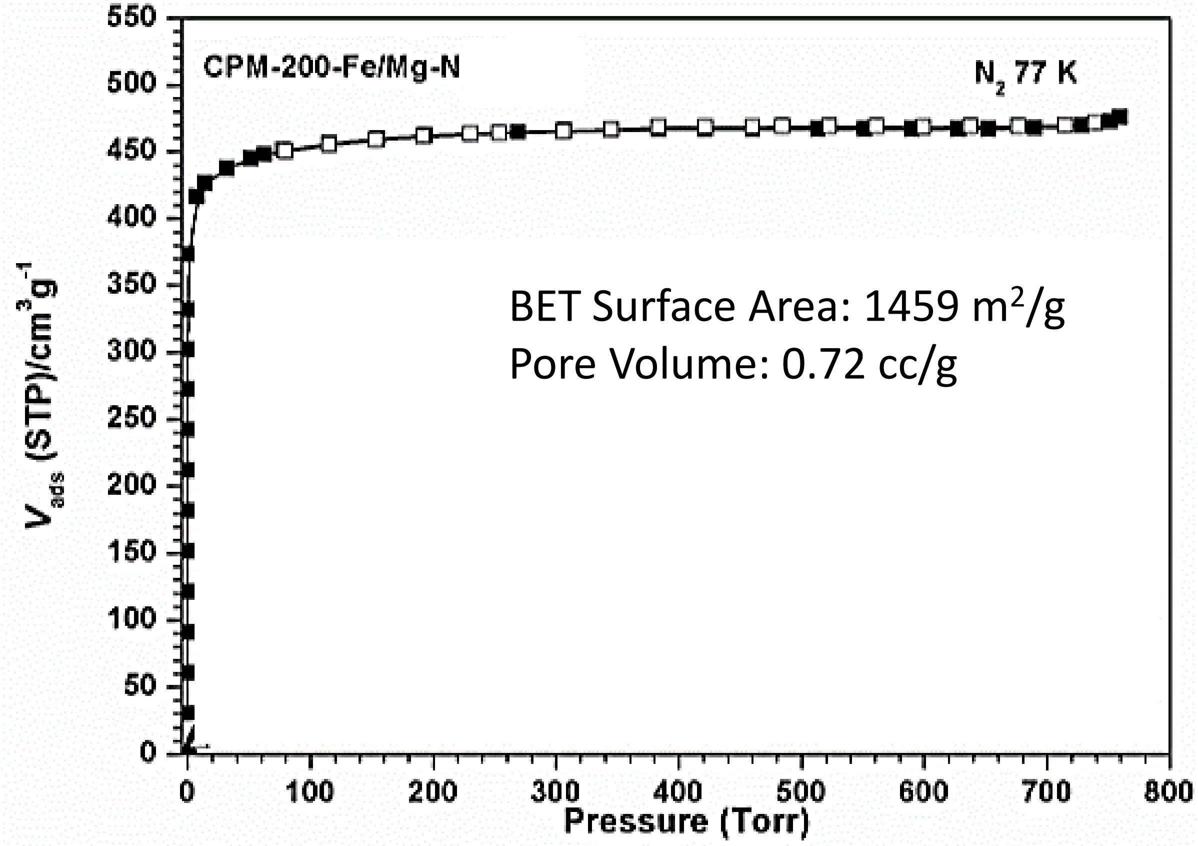
CO_2 isotherms at two temperatures can be used to determine Q_{st} through the Virial Equation

- $\ln(P) = \ln(n) + \frac{1}{T}\sum a_i n^i + \sum b_i n^i$
- $Q_{st} = -RT^2\left(\frac{\delta \ln(P)}{\delta T}\right) = -R\sum a_i n^i$

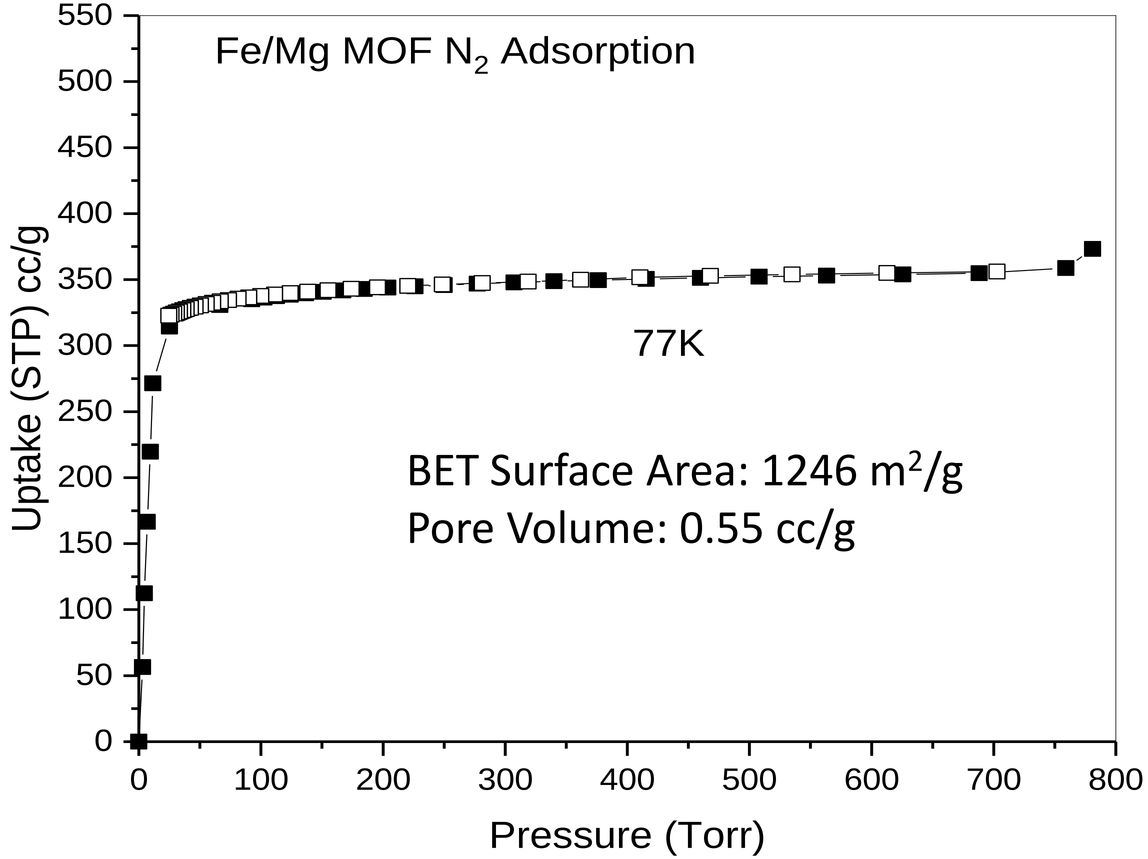


N_2 Adsorption Isotherms for Fe/Mg MOF

Published Isotherm



Experimental Isotherm



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N_2 Adsorption Isotherms for V/Mg MOF

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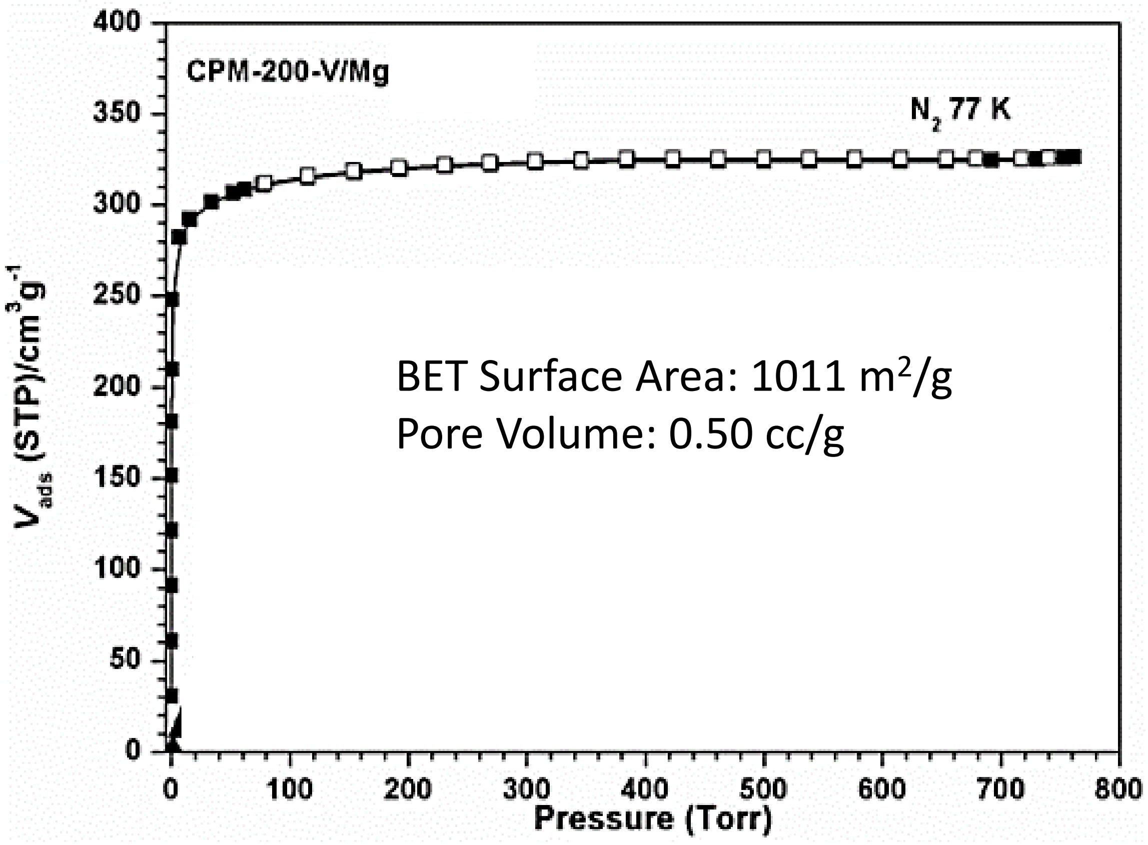

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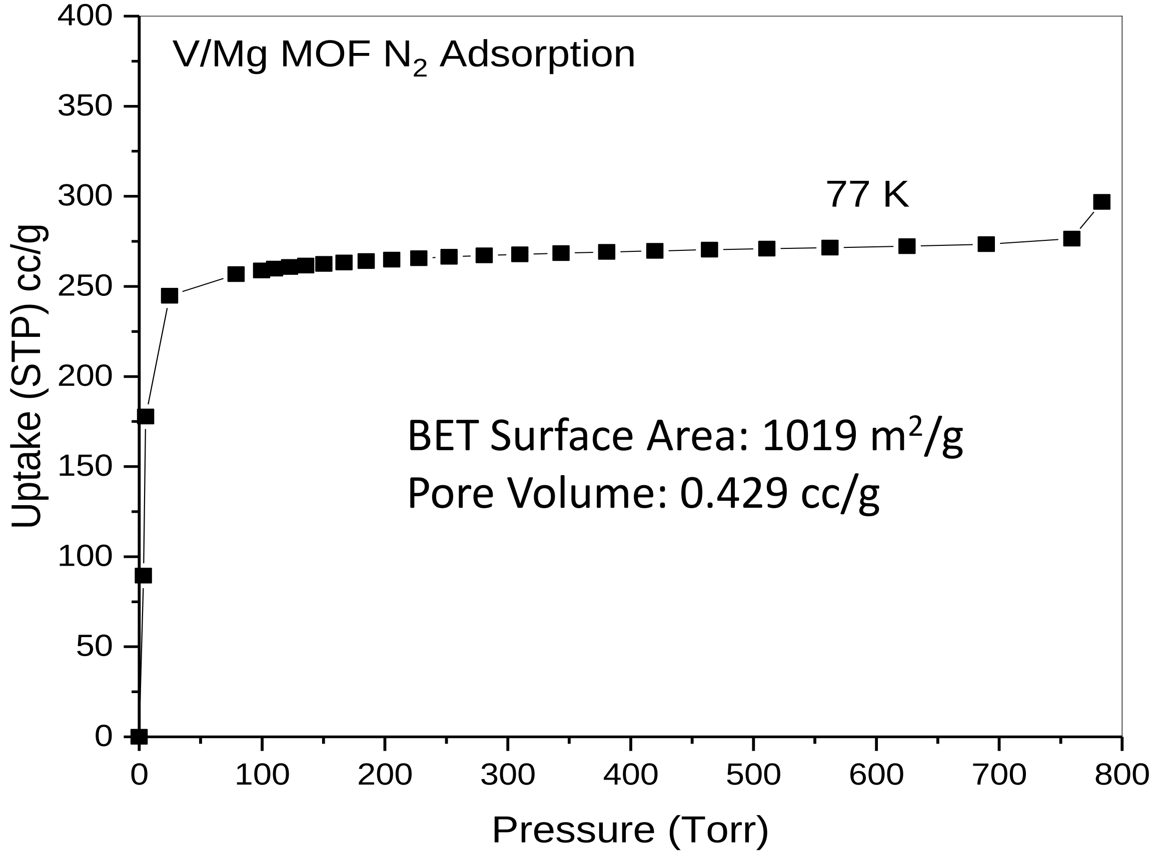

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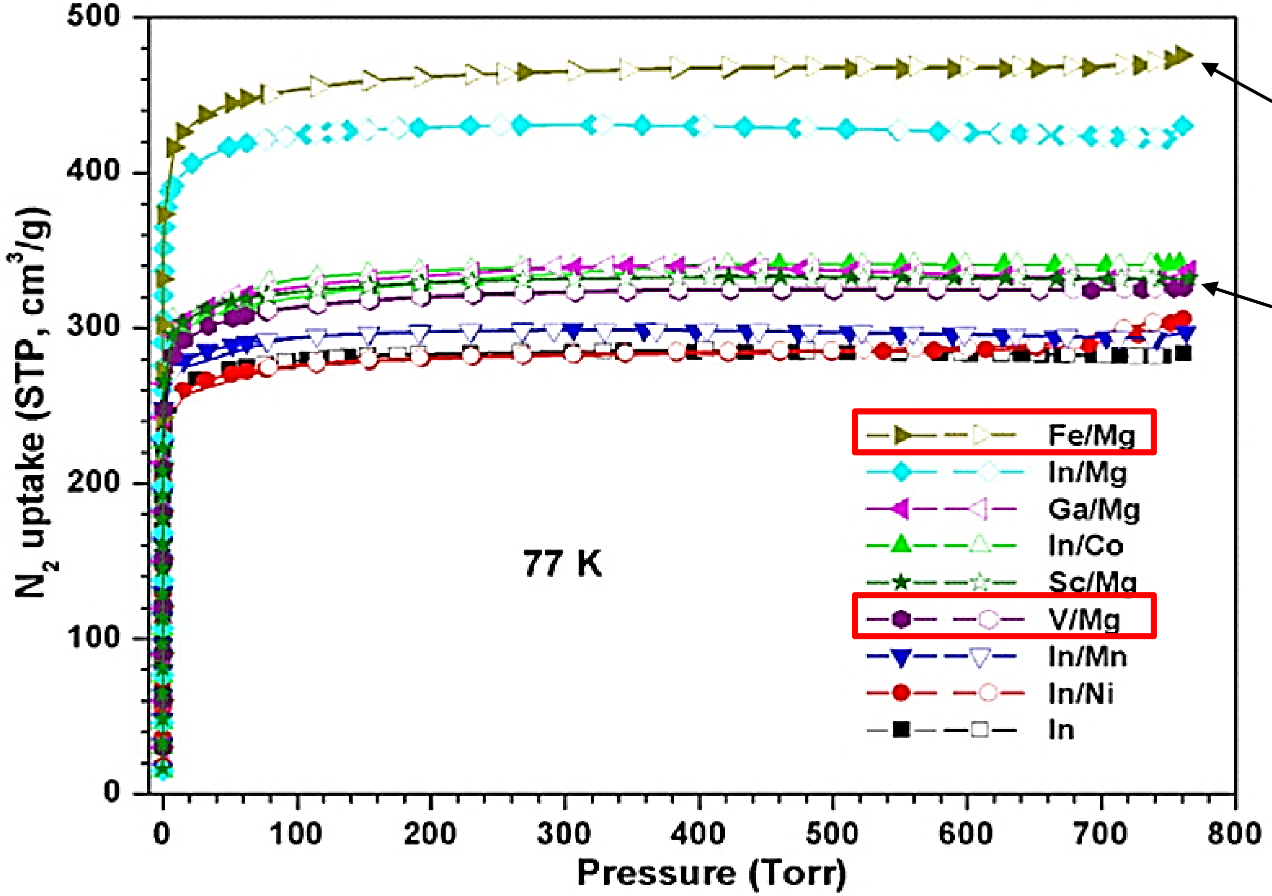
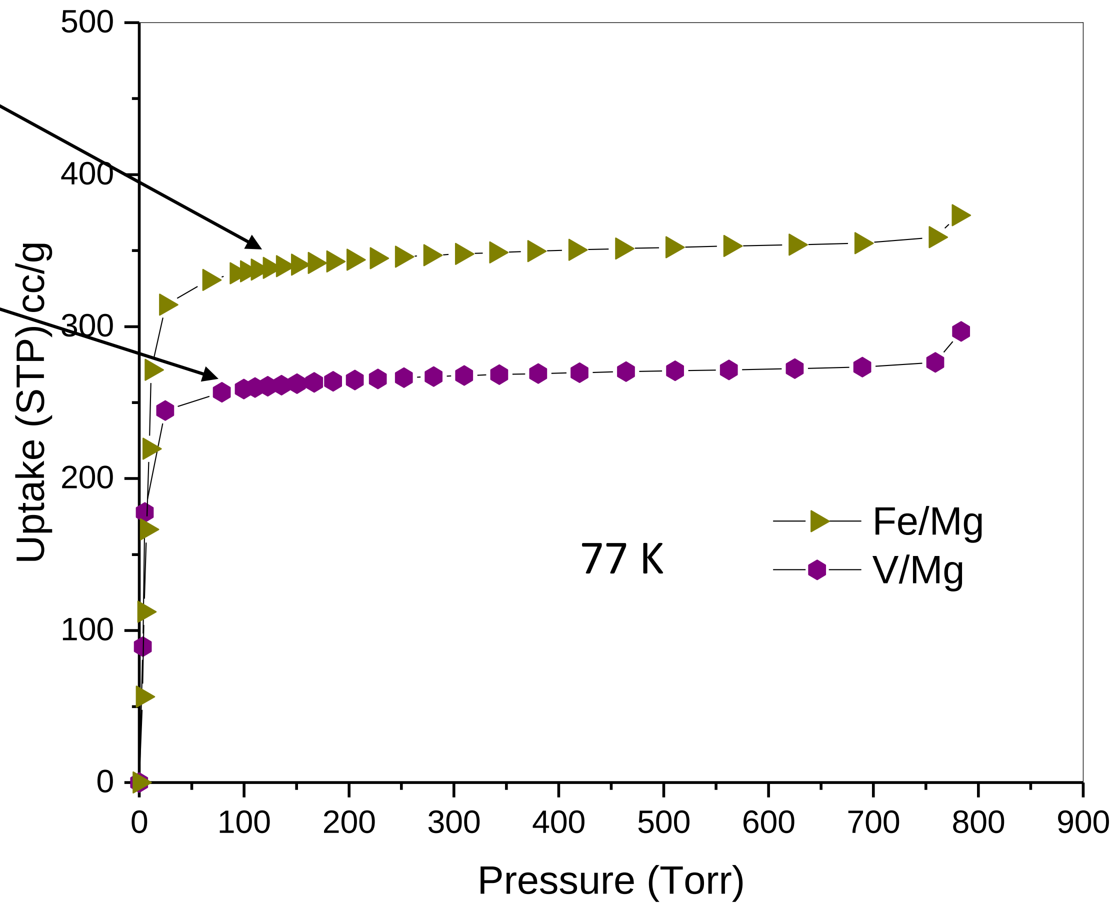
Comparison to the Full Data





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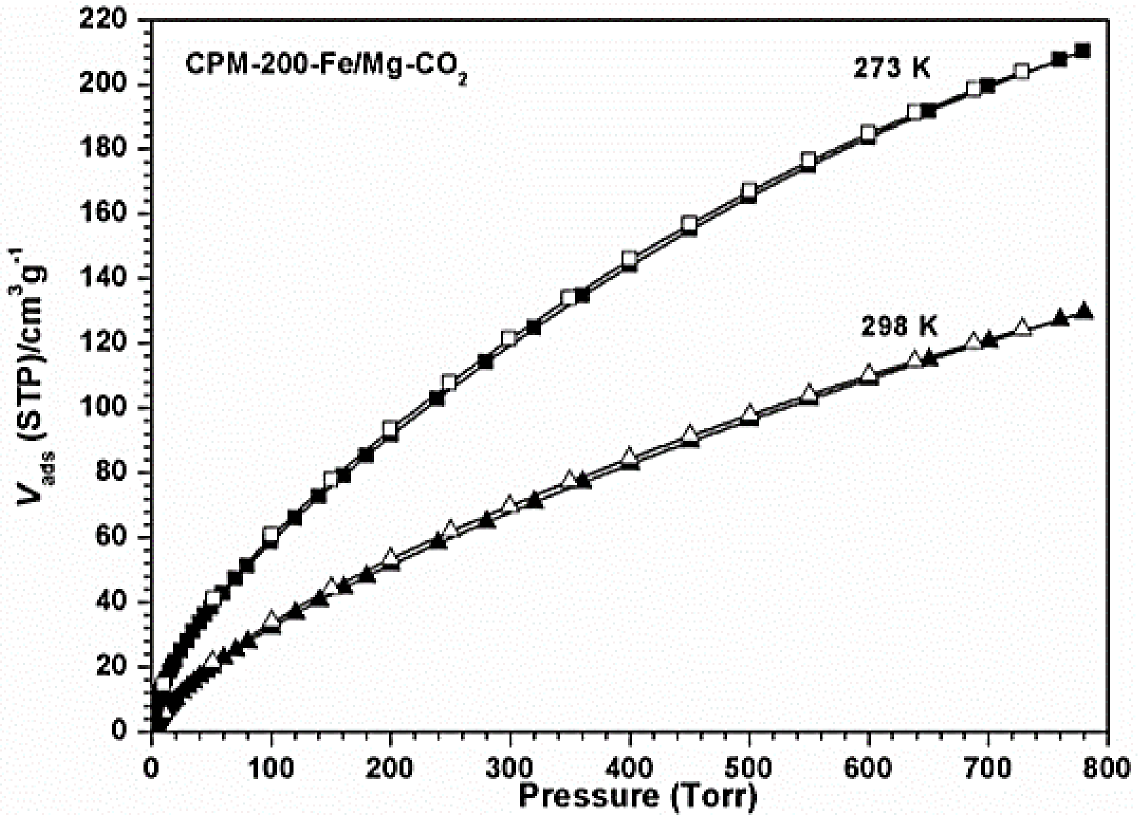

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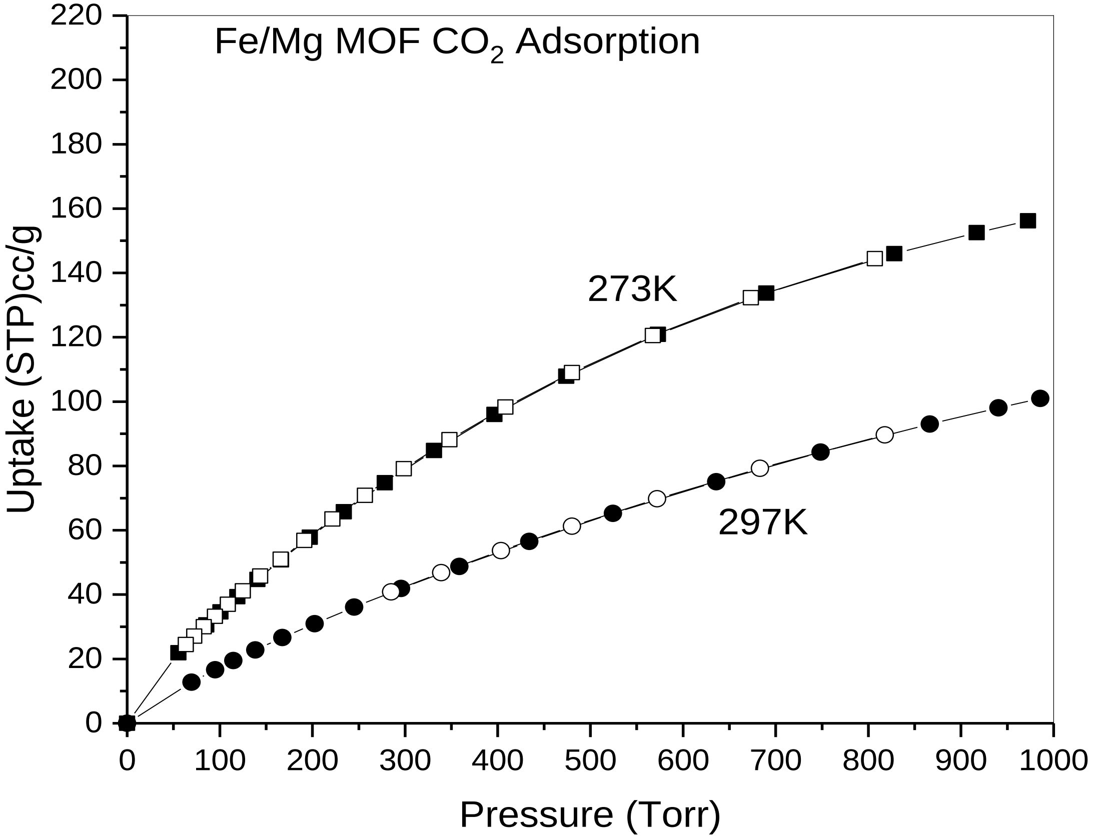

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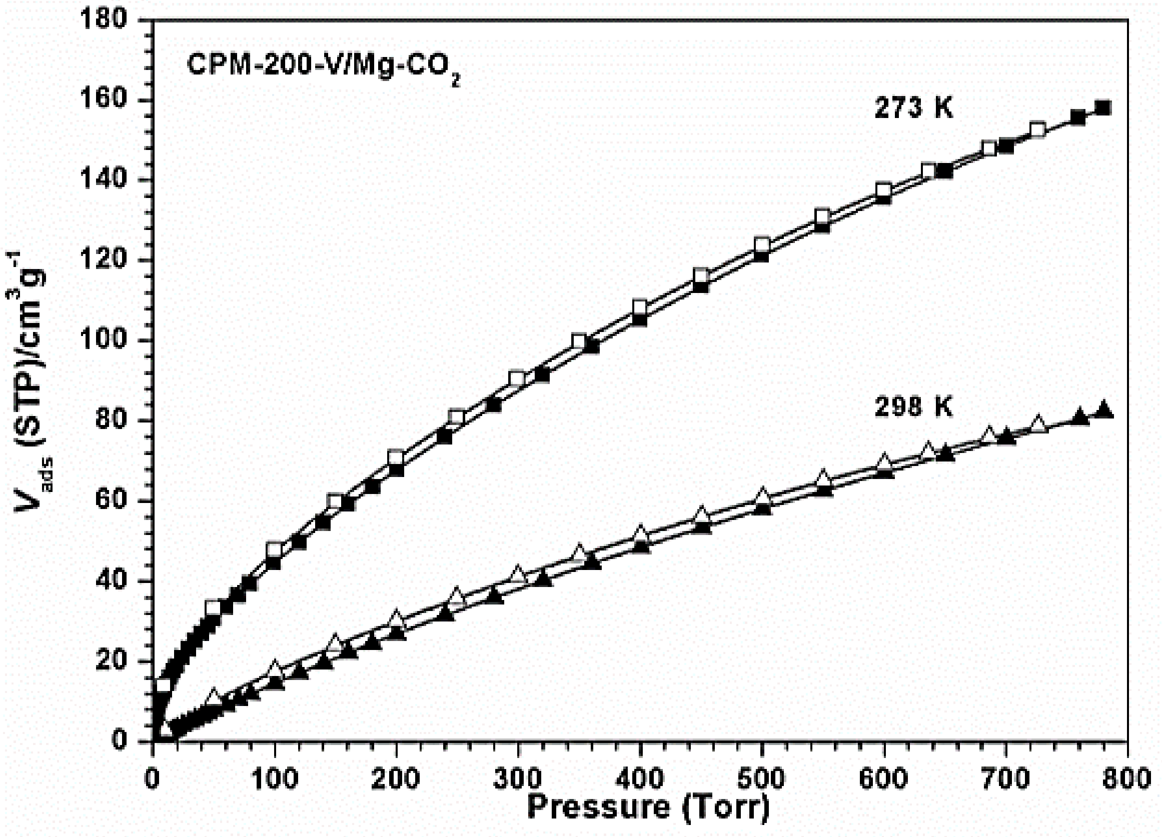

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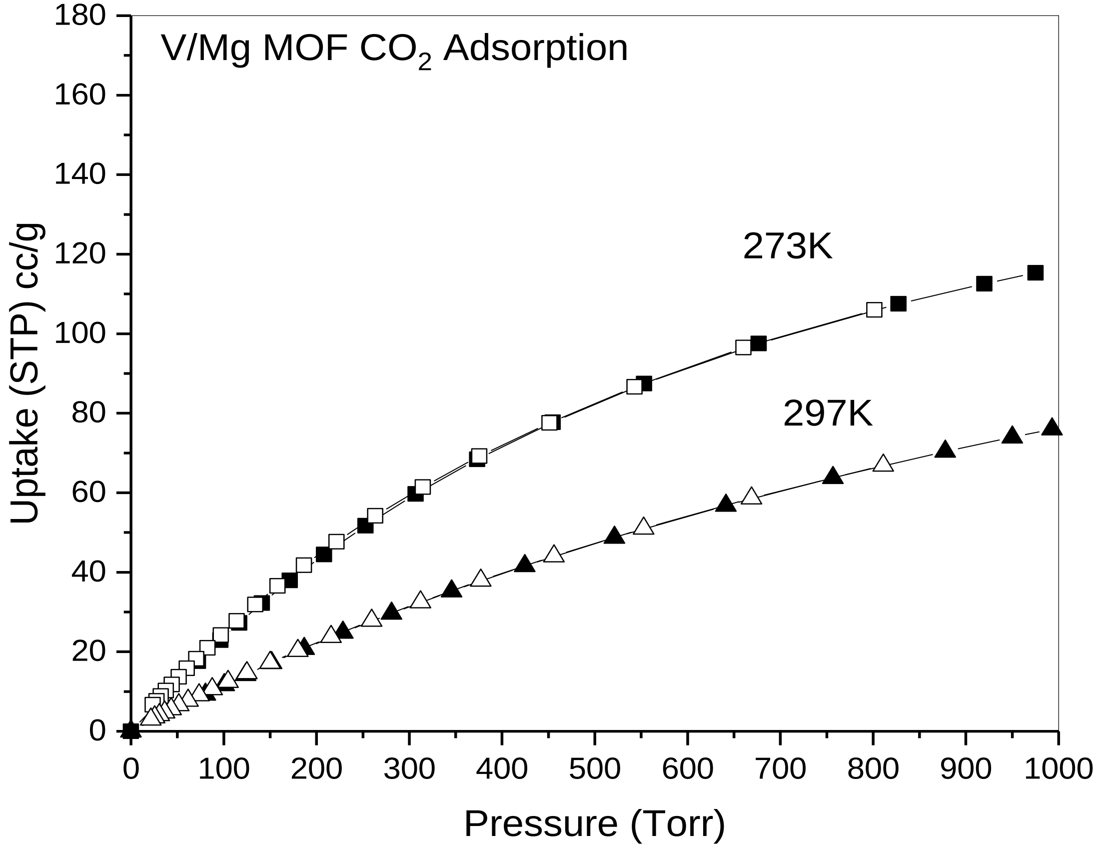

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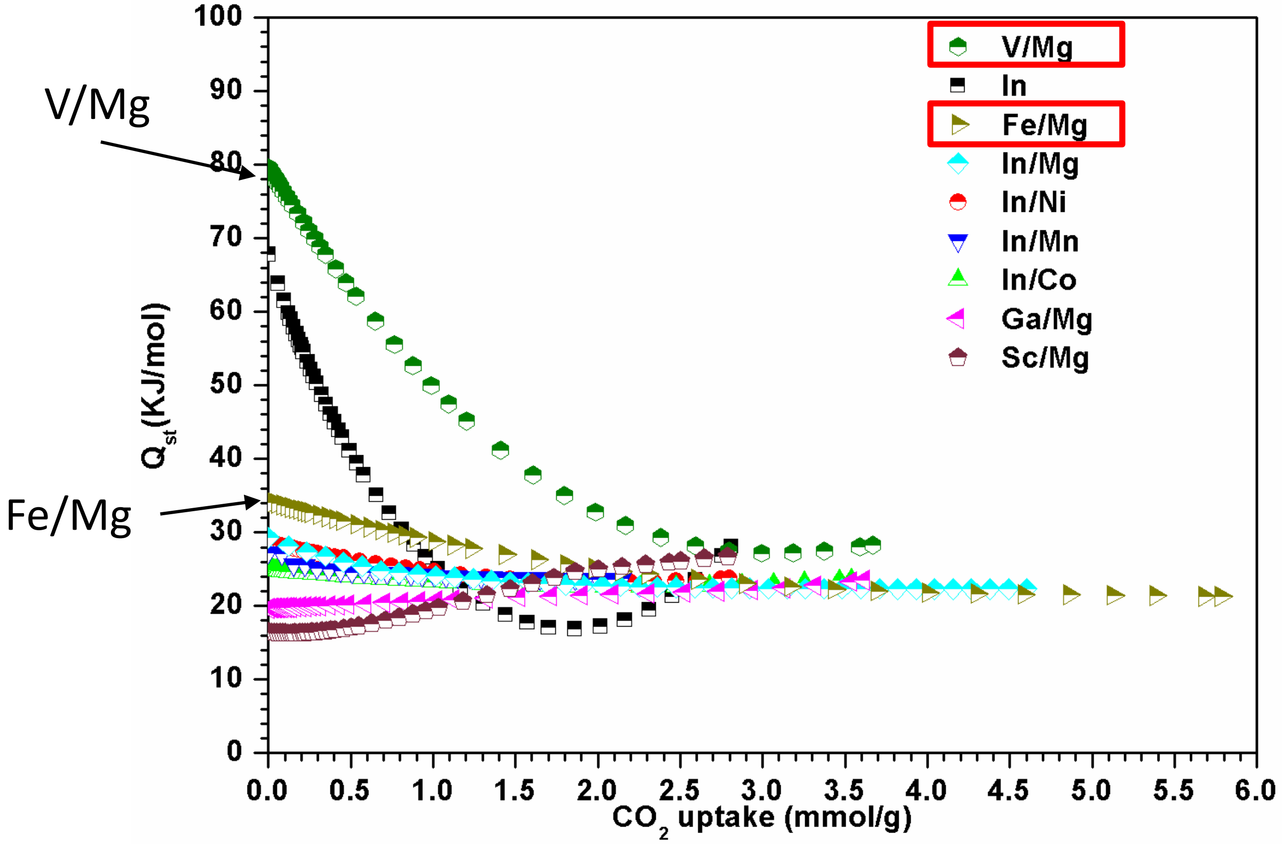
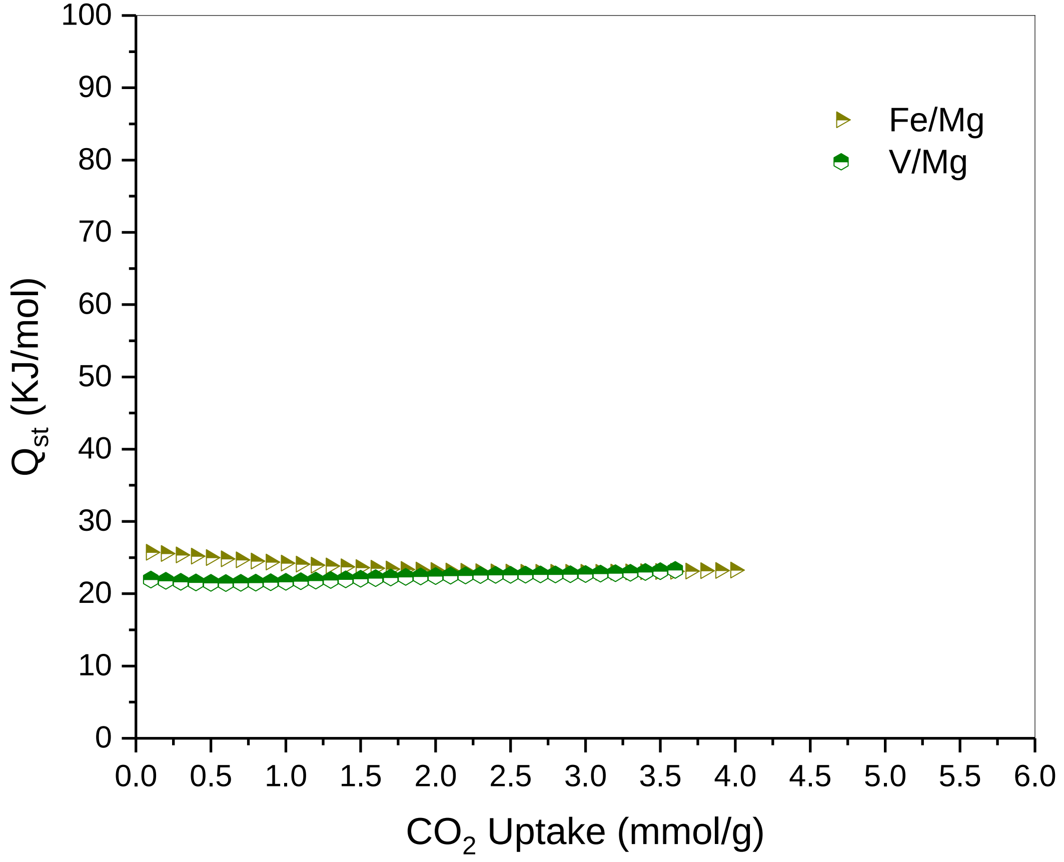
Heats of Adsorption





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Diffraction

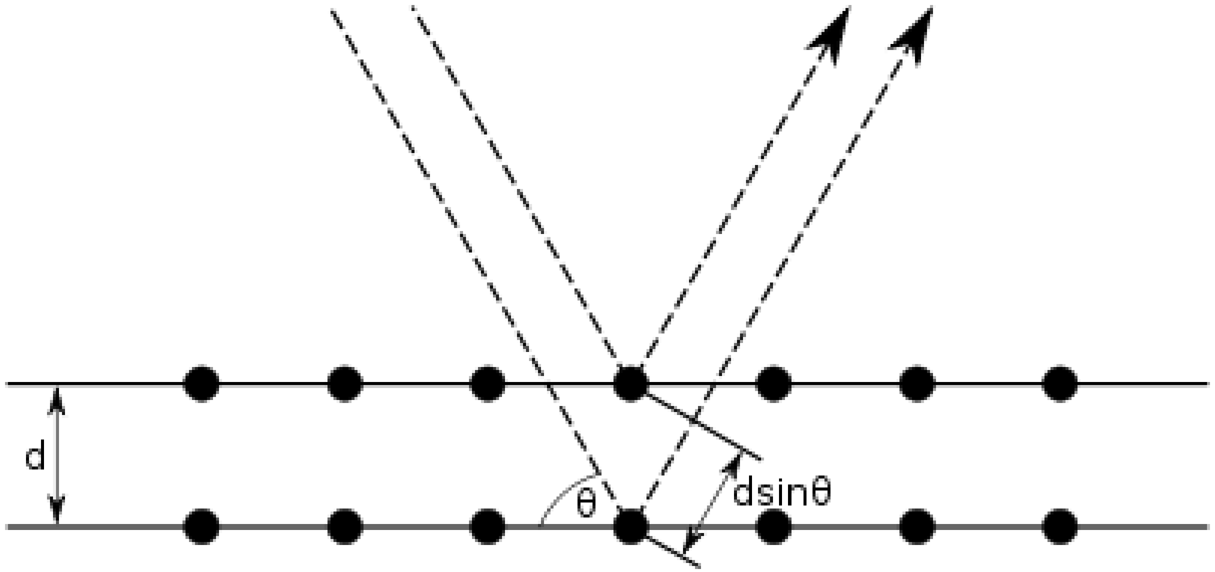
Waves of angstrom scale diffract off of a crystal lattice and produce a distinct pattern

This diffraction is described in Bragg's Law:

- $2d \sin \theta = n\lambda$

X-rays and thermal neutrons have the correct wavelength ranges

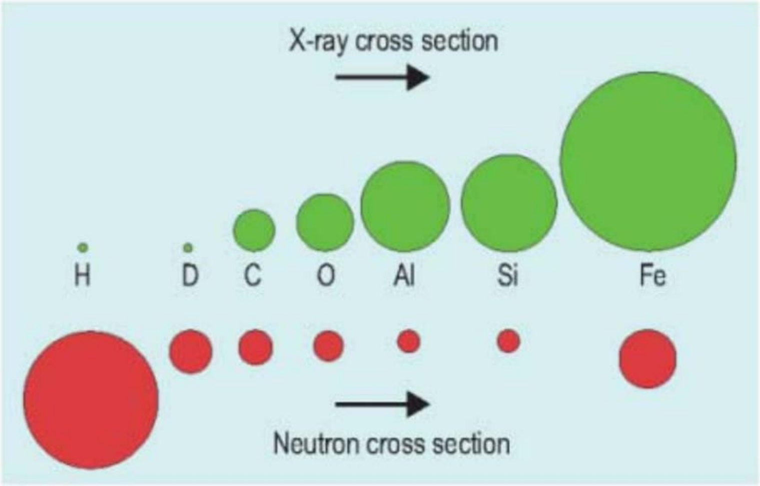
- X-rays: 1 Å - 2 Å
- Neutrons: 1.2 Å - 2.08 Å



Neutron Diffraction

Why neutrons?

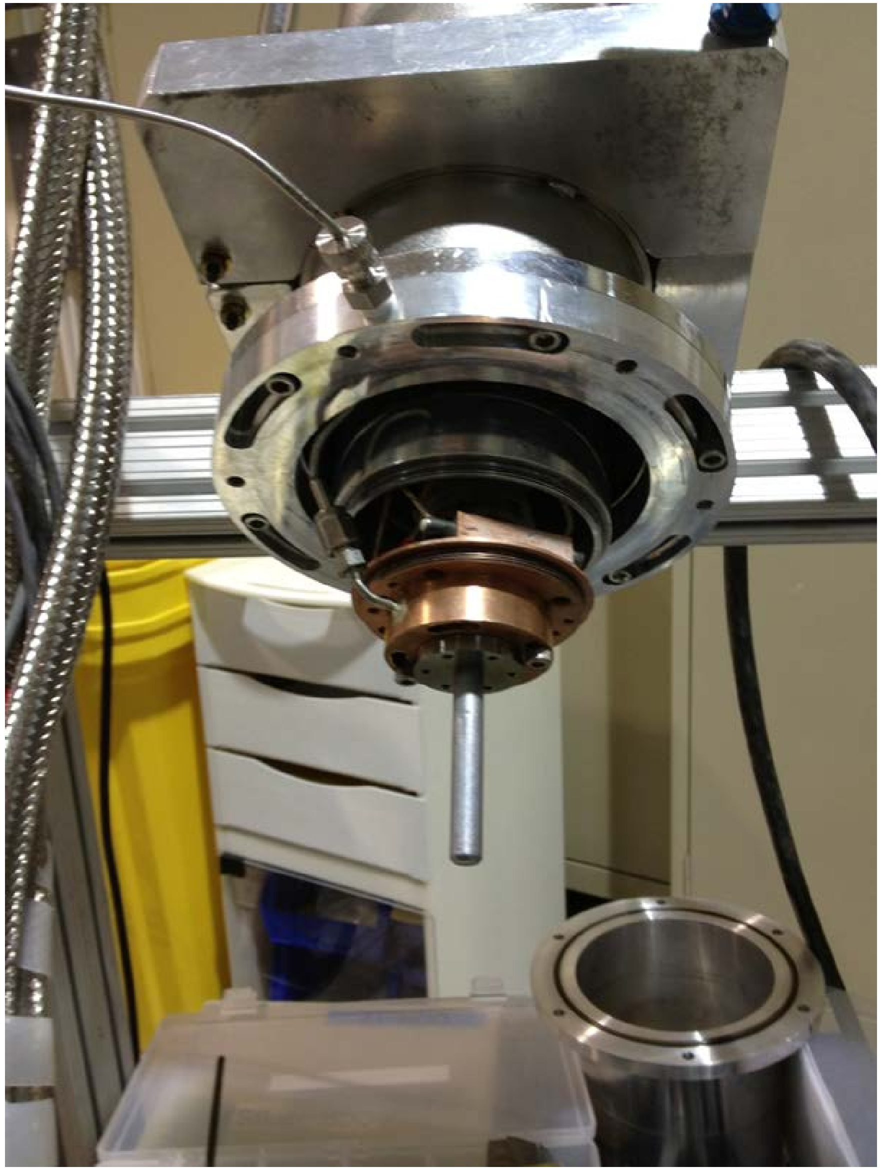
- With X-Ray diffraction there is difficulty seeing lighter elements when contrasted by metals
- Neutrons can detect these lighter elements in conjunction with the metals



High-Resolution Powder Diffractometer (BT-1) was used to confirm structure of synthesized MOFs

MOFs were dosed with stoichiometric amounts of CO_2 during diffraction experiment

BT-1

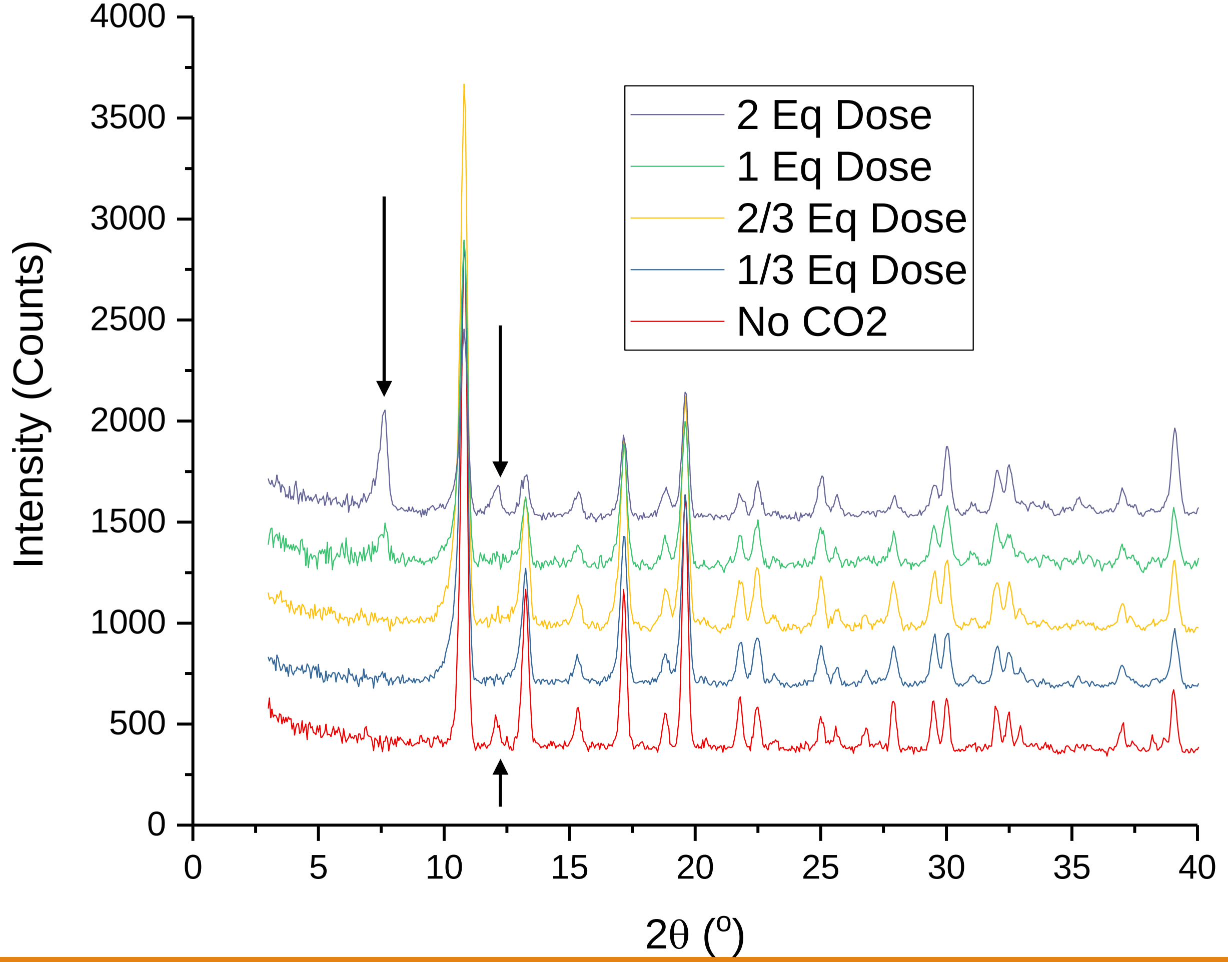


Powder sample in vanadium can

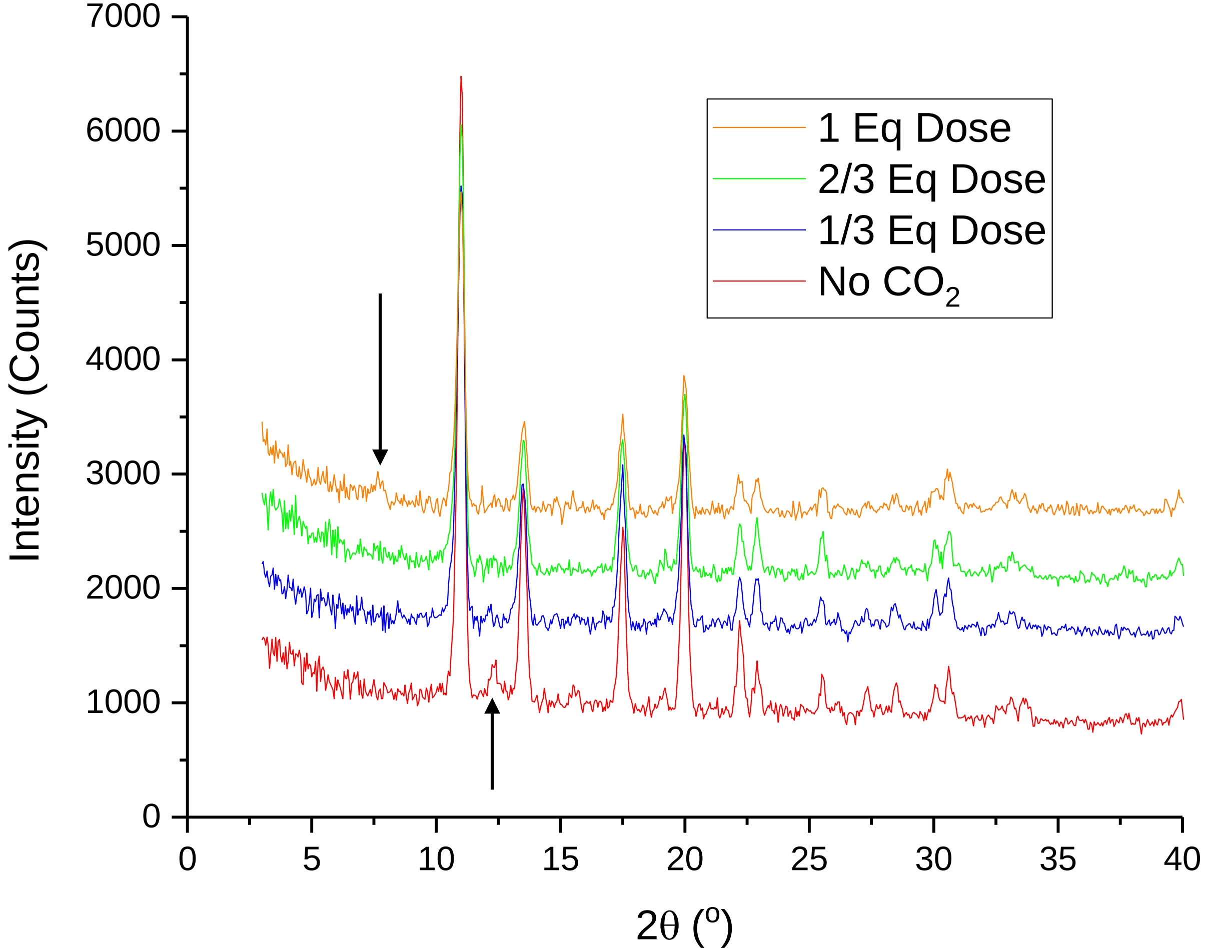
Sample in aluminum can—ready for the beam

CCR attached to CO_2 line for gas dosing

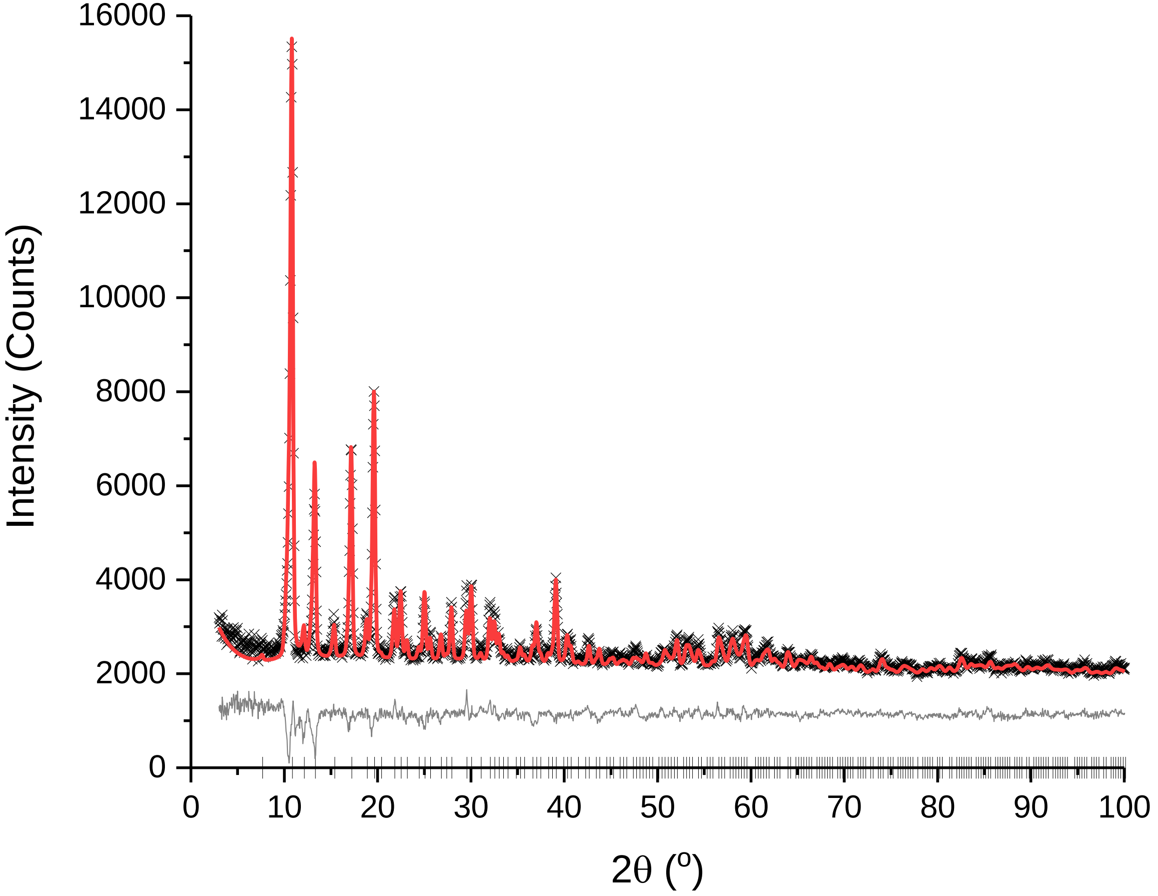
Diffraction Patterns of Fe/Mg MOF

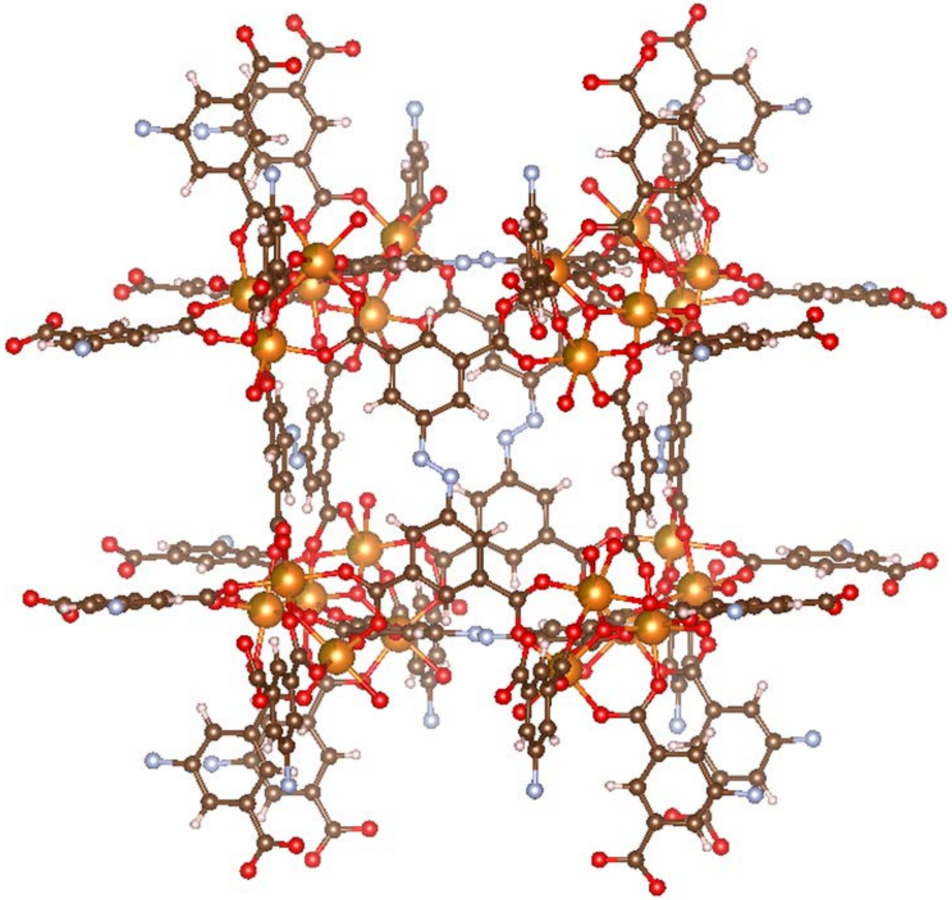


Diffraction Patterns of In/Mg MOF

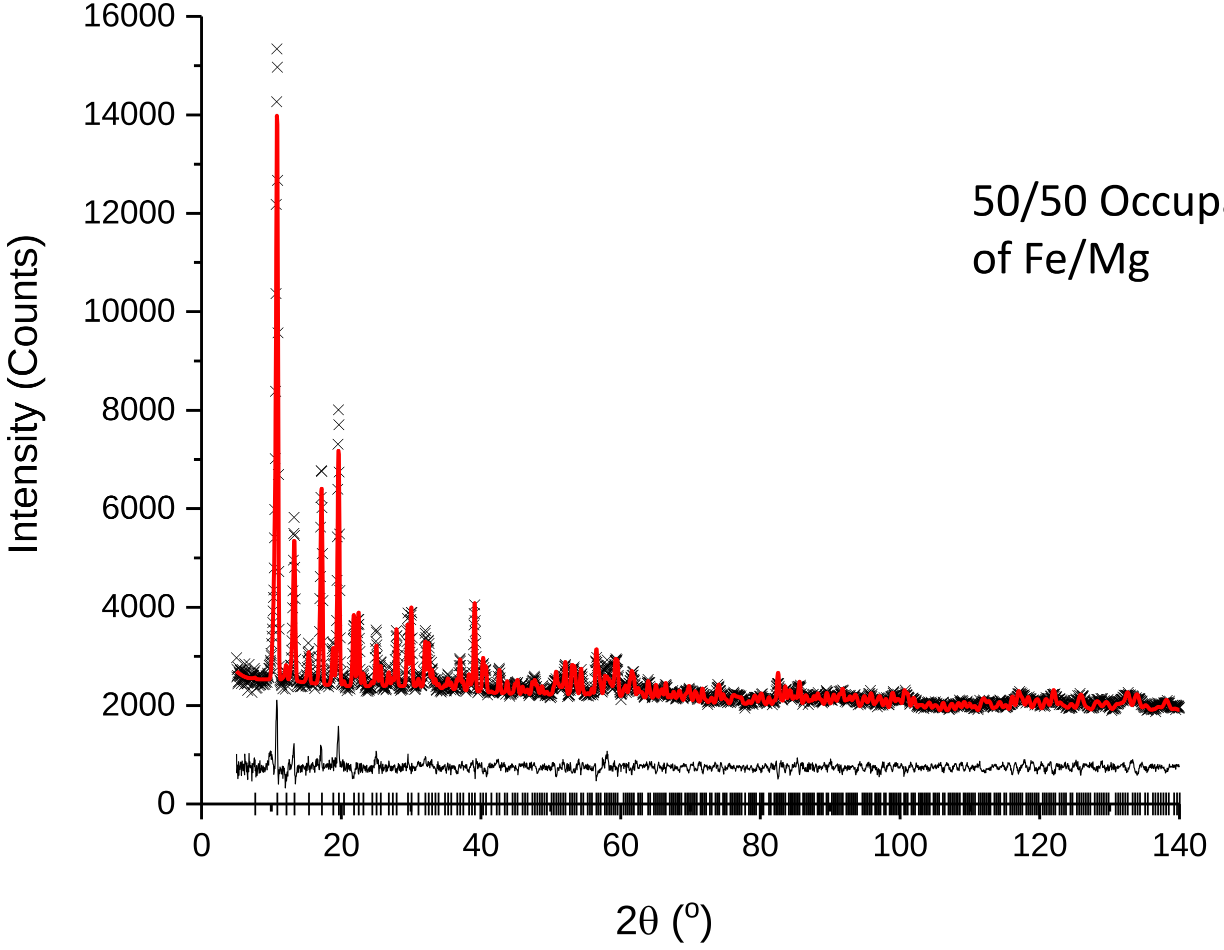


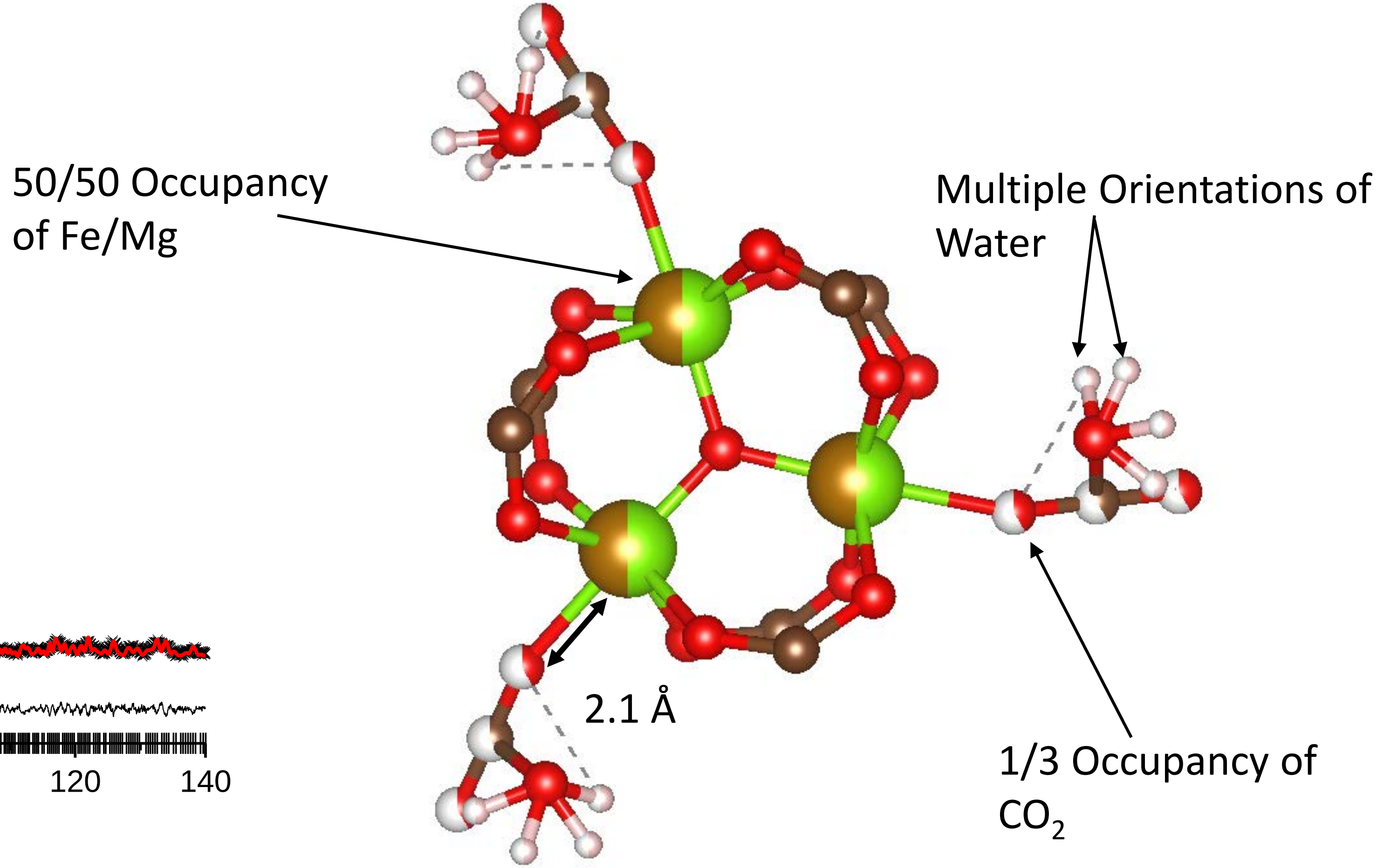
Bare Structure Fit of Fe/Mg MOF

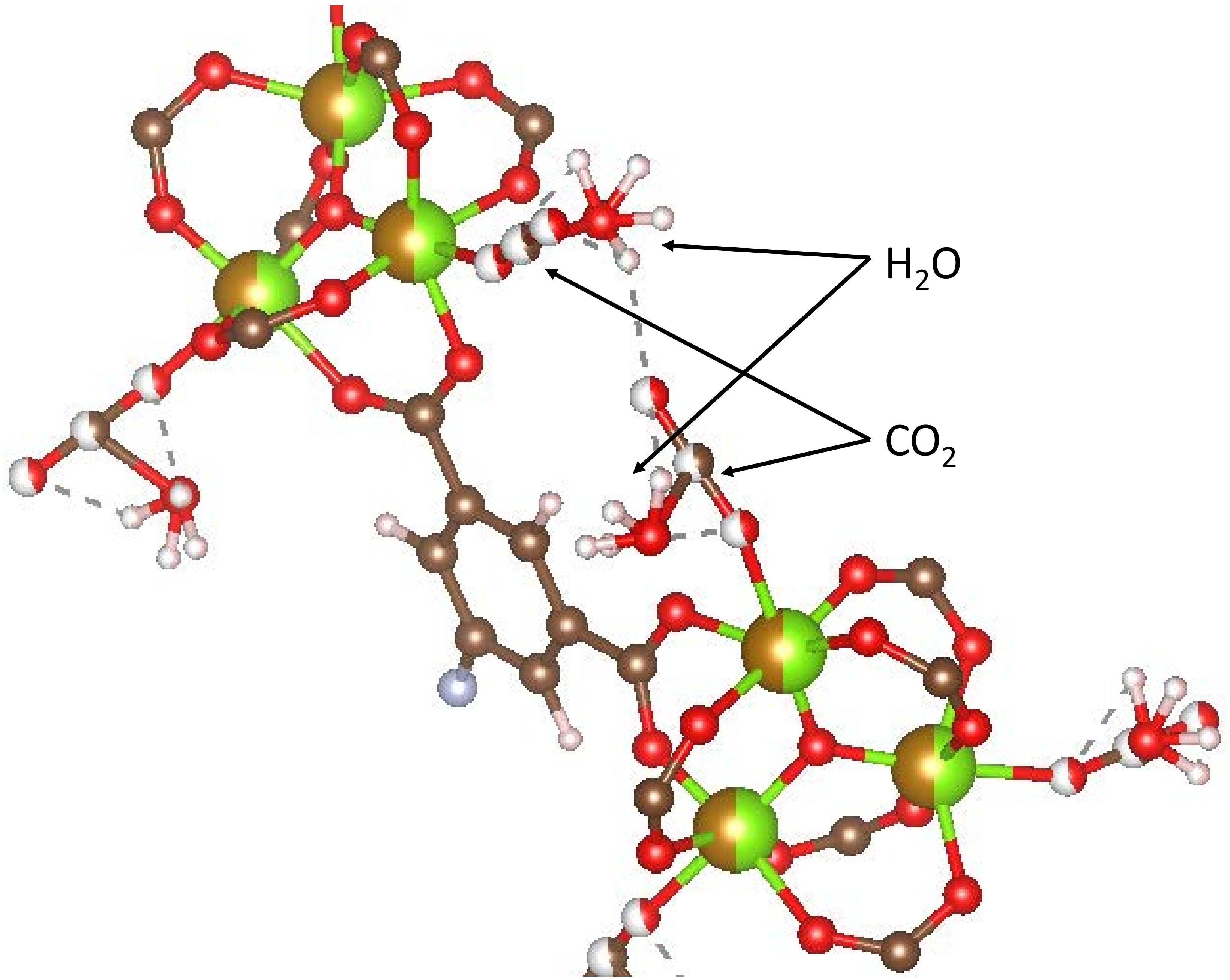




Preliminary Refined Structure with CO_2







H_2O
CO_2

Conclusions and Future Work

Data derived from adsorption isotherms fall in the expected range for open metal site MOFs

Structure is correct—Right materials are produced

CO_2 binds to open metal site, displacing water molecule

Further studies into the effects of water on adsorption

Inductively Coupled Plasma-Optical Emission Spectroscopy to determine metallic ratios

More structural and isotherm data

Acknowledgements

Mentors: Ben Trump & Craig Brown

Prof. Eric Bloch, Eric Gosselin

Dr. Taner Yildirim

Drs. Joseph Dura, Julie Borchers, and Brandi Toliver

Center for High Resolution Neutron Scattering

All the NCNR SURFers