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

H₂ and CH₄ storage and selective adsorption of CO₂ from industrial exhaust

Extremely high surface areas—~1,000 m²/g for zeolites and ~10,000 m²/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

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

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
Synthesis and Activation

In/Mg MOF  Fe/Mg MOF  V/Mg MOF

$\text{MClo}_3 + 2\text{Mg(OAc)}_2 + 1.5\text{H_4ABTC} \rightarrow \text{Water + DMA} \rightarrow [\text{MMg}_2(\text{OH})(\text{ABTC})_{1.5}(\text{H}_2\text{O})_3]$  

Thermogravimetric Analysis (TGA)

- Solvent Removed (120 °C)
- Water Removed (250 °C)
- Structure Decomp (350 °C)
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

BET Surface Area: 1459 m$^2$/g
Pore Volume: 0.72 cc/g

Experimental Isotherm

BET Surface Area: 1246 m$^2$/g
Pore Volume: 0.55 cc/g

N$_2$ Adsorption Isotherms for V/Mg MOF

**Published Isotherm**

- BET Surface Area: 1011 m$^2$/g
- Pore Volume: 0.50 cc/g

**Experimental Isotherm**

- BET Surface Area: 1019 m$^2$/g
- Pore Volume: 0.429 cc/g

Comparison to the Full Data

CO$_2$ Adsorption Isotherms for Fe/Mg

Published Isotherm

Experimental Isotherm

Fe/Mg MOF CO$_2$ Adsorption

CO₂ Adsorption Isotherms for V/Mg

Published Isotherm

Experimental Isotherm

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 CO₂ during diffraction experiment
Powder sample in vanadium can
Sample in aluminum can—ready for the beam

CCR attached to CO₂ 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$_2$

- 50/50 Occupancy of Fe/Mg
- 1/3 Occupancy of CO$_2$
- Multiple Orientations of Water

Intensity (Counts)

2θ (°)

2.1 Å
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
CO₂ 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
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