SLAC-WP-125

A Hard X-Ray Study of a Manganese-Terpyridine Dimer Catalyst in a Chromium-Based Metal Organic Framework

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Office of Science, Science Undergraduate Laboratory Internship (SULI) Program

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ABSTRACT

Cleaner forms of energy are needed, and H_2 produced from water splitting is a possible source. However, a robust catalyst is necessary to carry out the water oxidation reaction. Plants utilize Photosystem II to catalyze water oxidation as a part of photosynthesis, and many synthetic water oxidation catalysts use Photosystem II as a model. In this study, the catalyst of interest was [(terpy)Mn(μ-O)2Mn(terpy)]3+ (MnTD), which was synthesized in a chromium-based Metal Organic Framework (MOF) to avoid degradation of MnTD molecules. Hard X-ray powder diffraction was the primary method of analysis. The diffraction data was used to detect the presence of MOF in samples at different catalytic stages, and lattice parameters were assigned to the samples containing MOF. Fourier maps were constructed to determine the contents of the MOF as preliminary studies suggested that MnTD may not be present. Results showed that MOF is present before catalysis occurs, but disappears in the initial stages of catalysis. Changes in the MOF's lattice parameters suggest attractive interactions between the MOF and catalyst; these interactions may lead to the observed MOF degradation. Fourier maps also reveal limited, if any, amounts of MnTD in the system. Molecular manganese oxide may be the source of the high rate of water oxidation catalysis in the studied system.
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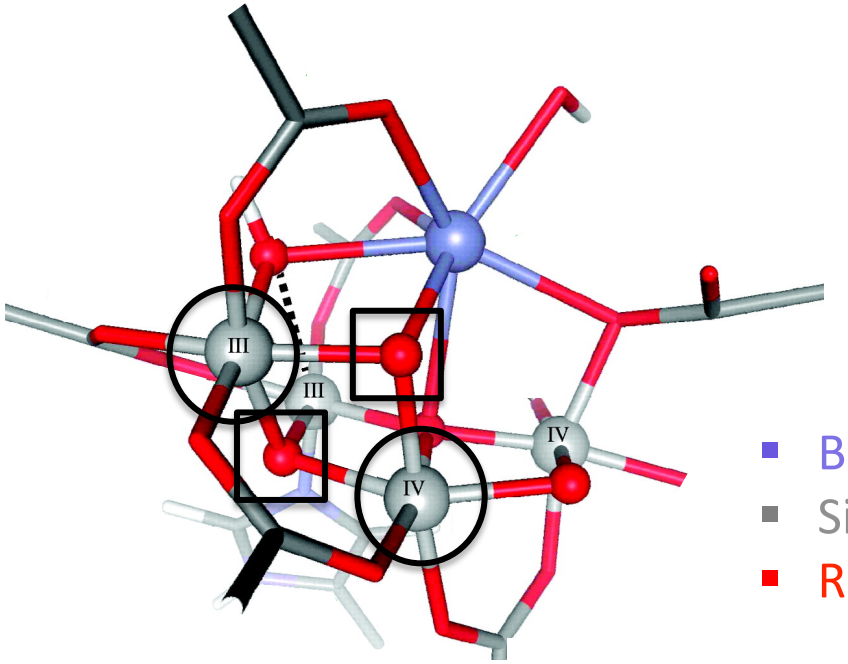
PRO


GMC

Water Splitting

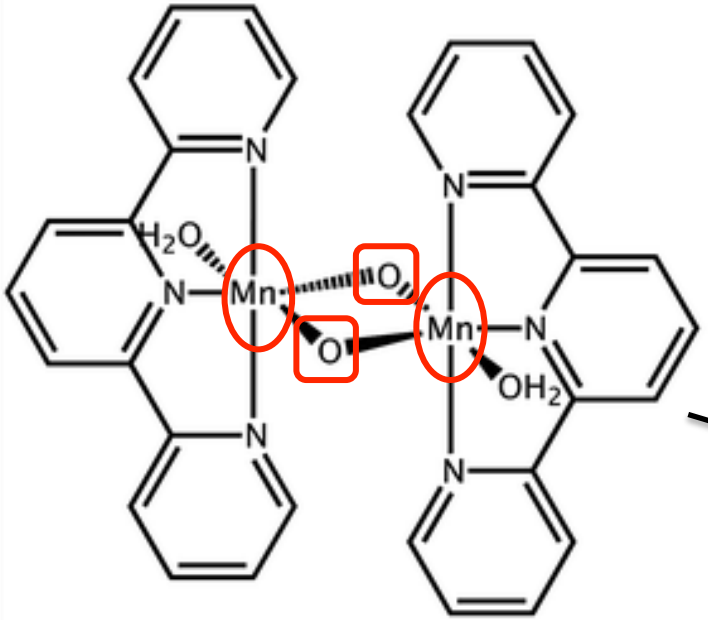
$2\,H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $\qquad$ $4H^+ + 4e^- \rightarrow 2\,H_2$



- Blue: Calcium
- Silver: Manganese
- Red: Oxygen

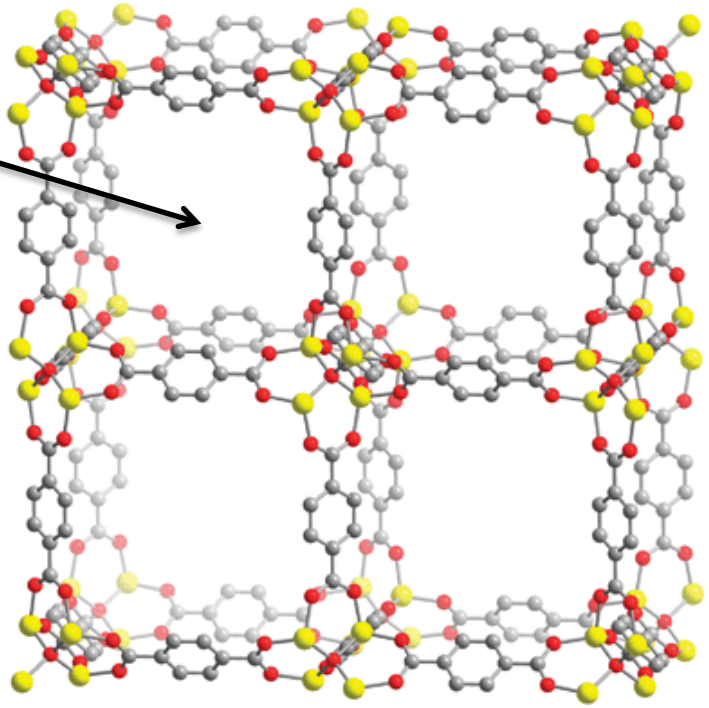
Dau, H., *et al.*, *The Royal Society* 363 (1494), 1237-1244 (2008).

The Manganese-Terpyridine (terpy) Dimer



Swierk, J. and Mallouk, T., *Chem. Soc. Rev.* 42, 2357-2387 (2013).

Metal Organic Framework (MOF)



Murray, L., Dinca, M., and Long, J., *Chem. Soc. Rev.* 38, 1294-1314 (2009).

http://www.mare2.com/popup_image.php/pID/655/imgID/0

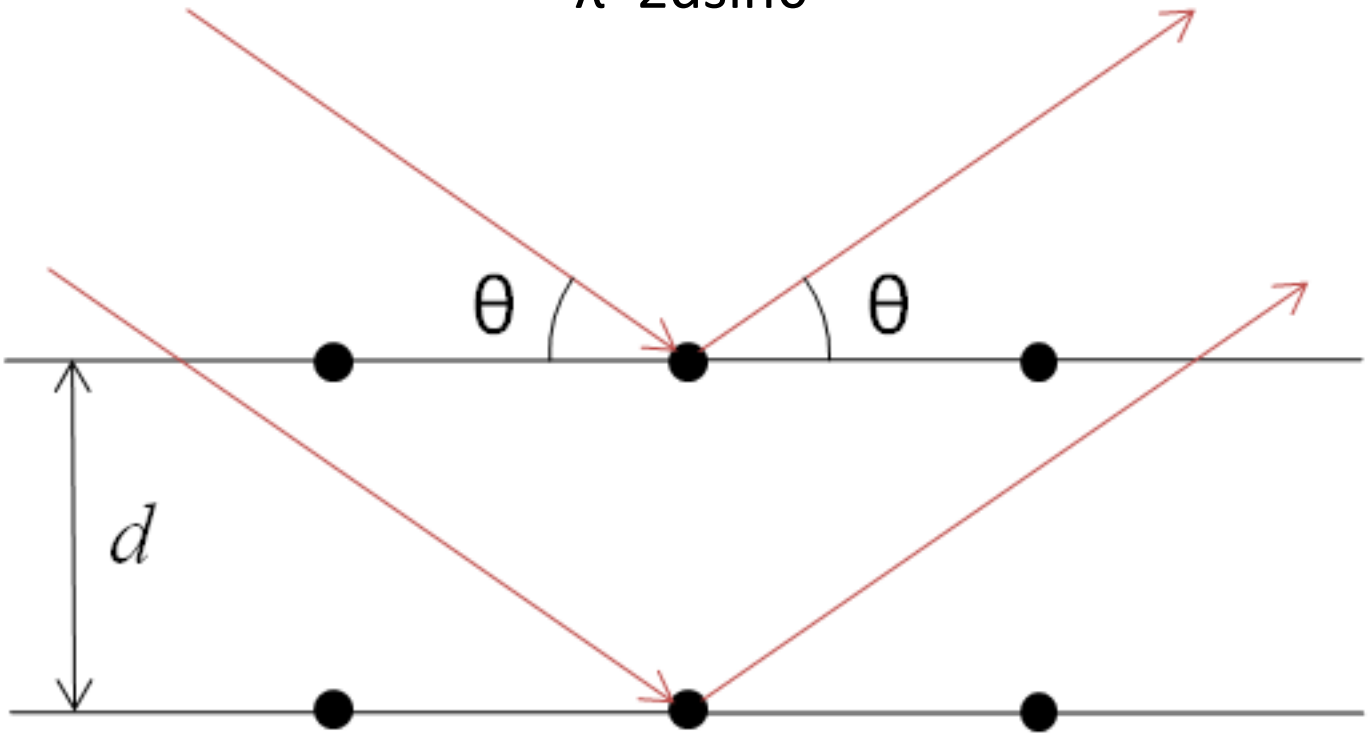
Questions

- Is the manganese-terpy dimer the catalytically active molecule?
- Has the manganese-terpy dimer been synthesized inside of the MOF?
    - MOF
    - MOF in acetate buffer
    - MOF with catalyst but before catalysis occurs
    - MOF with activated catalyst after 45 minutes of catalysis
    - MOF with activated catalyst after 2 hours of catalysis


SSRL

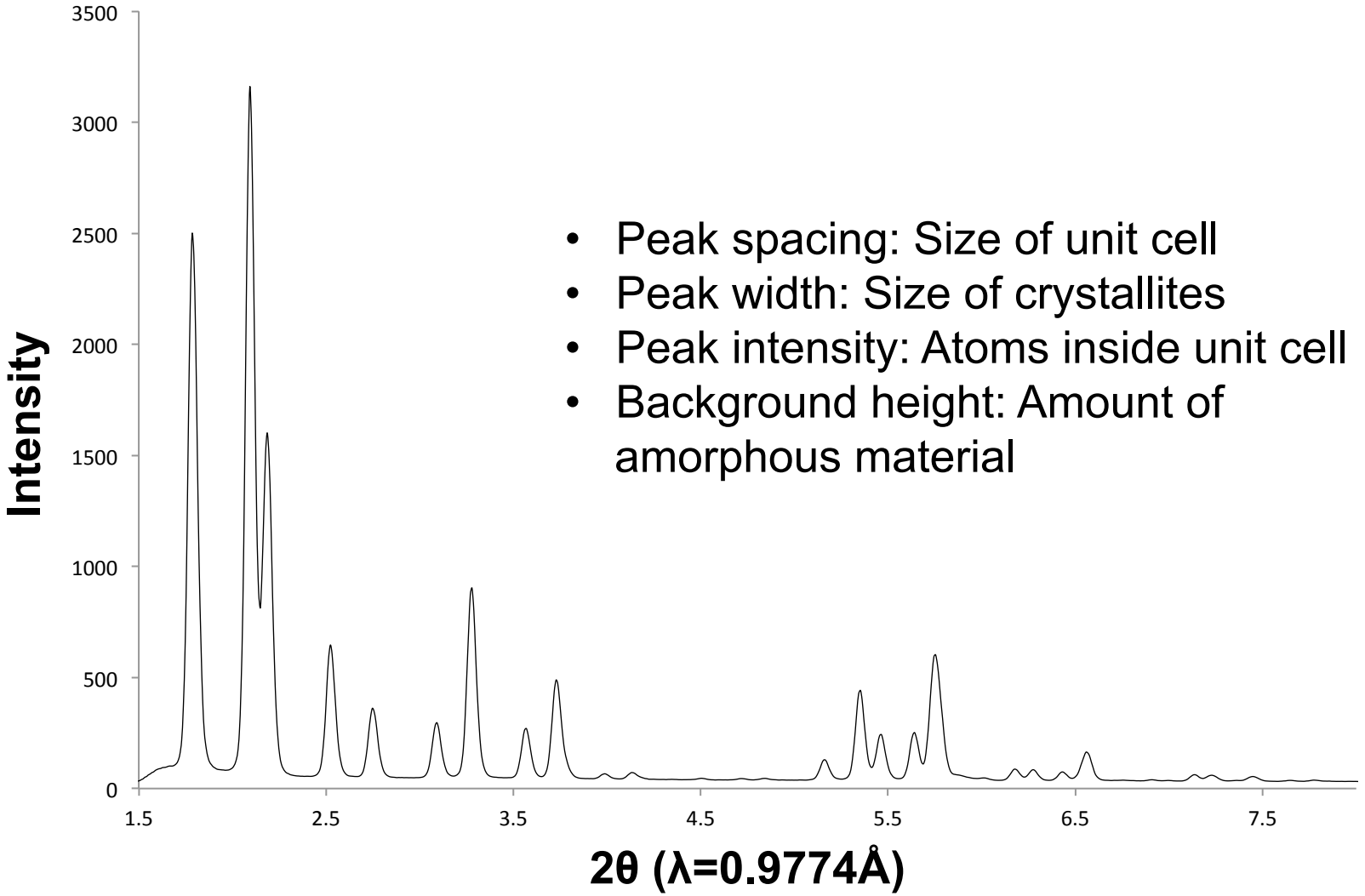
X-Ray Diffraction

Bragg's Law:
$\lambda = 2d\sin\theta$



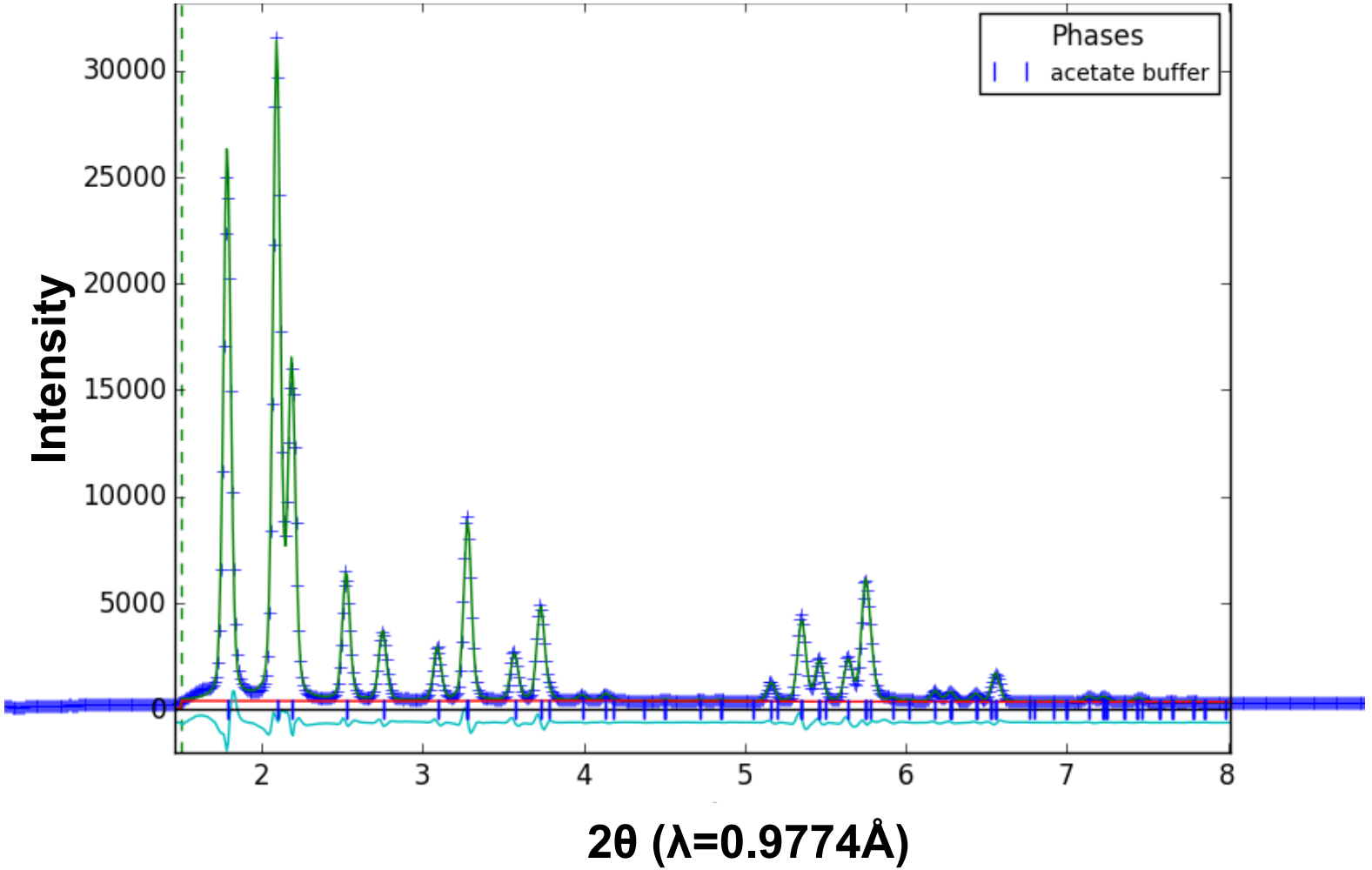
http://chemwiki.ucdavis.edu/Analytical_Chemistry/Instrumental_Analysis/Diffraction/Powder_X-ray_Diffraction

X-Ray Diffraction Pattern



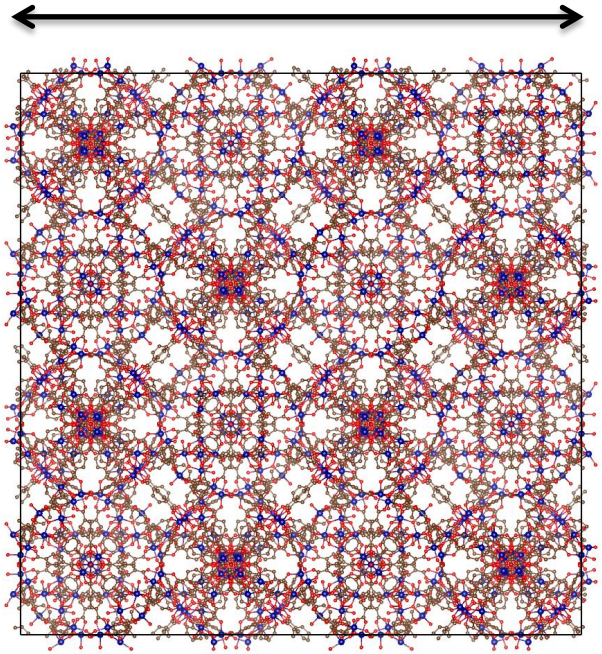
- Peak spacing: Size of unit cell
- Peak width: Size of crystallites
- Peak intensity: Atoms inside unit cell
- Background height: Amount of amorphous material

MOF in Acetate Buffer Diffraction Pattern



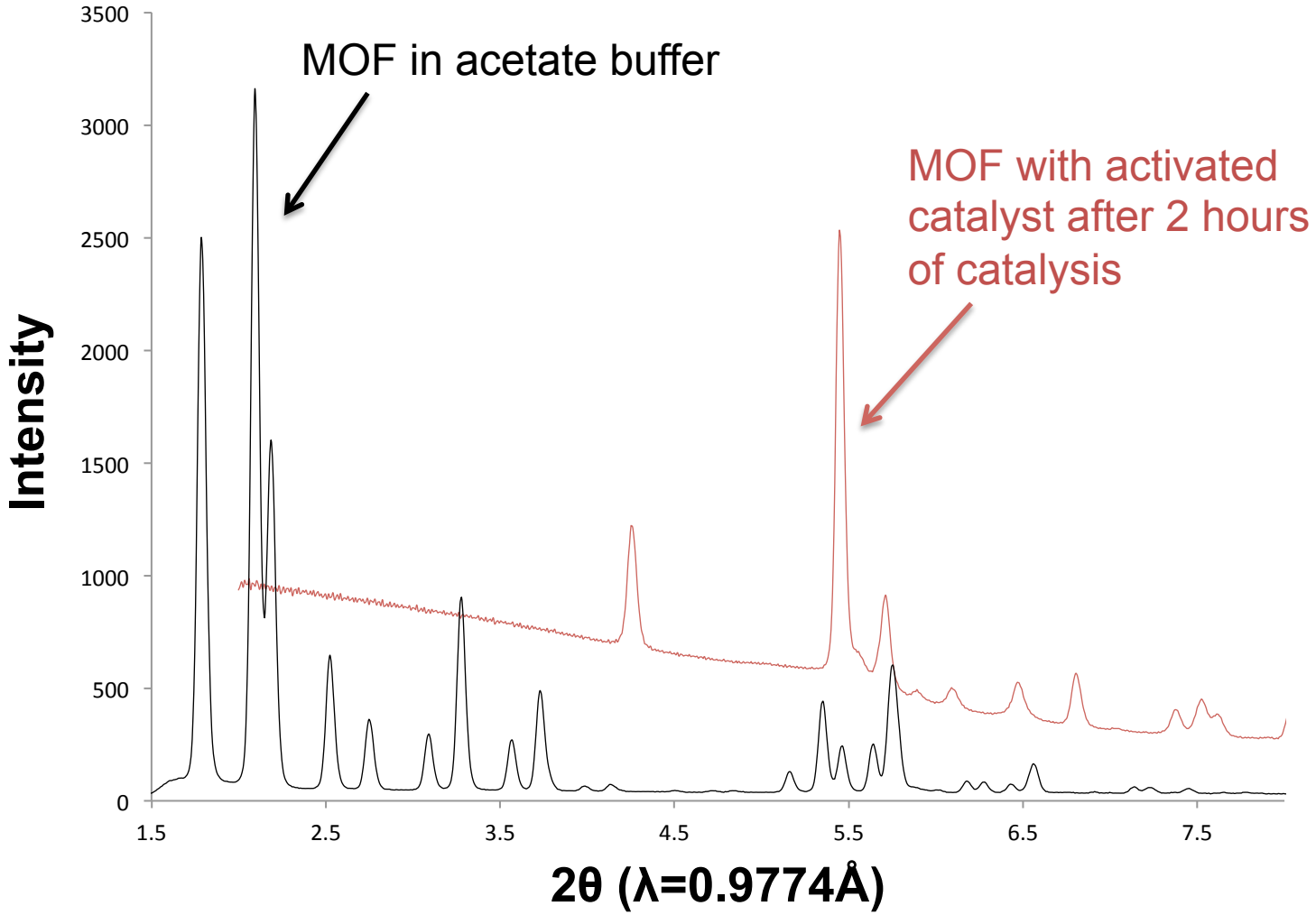
Unit Cell Length of MOF for Different Samples

Sample	Unit cell length
Only MOF	88.0720 ± 0.0015 Å
MOF in Acetate Buffer	88.5120 ± 0.0016 Å
MOF with catalyst but before catalysis	87.19 ± 0.04 Å
Literature Unit Cell Length for MOF: 88.9 Å*	

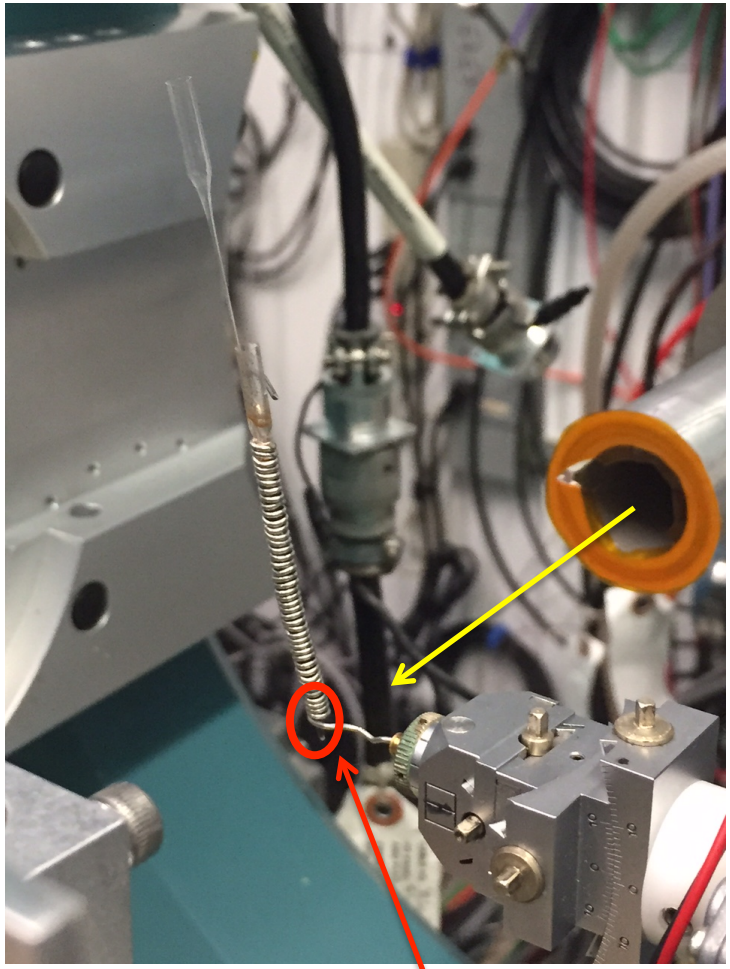


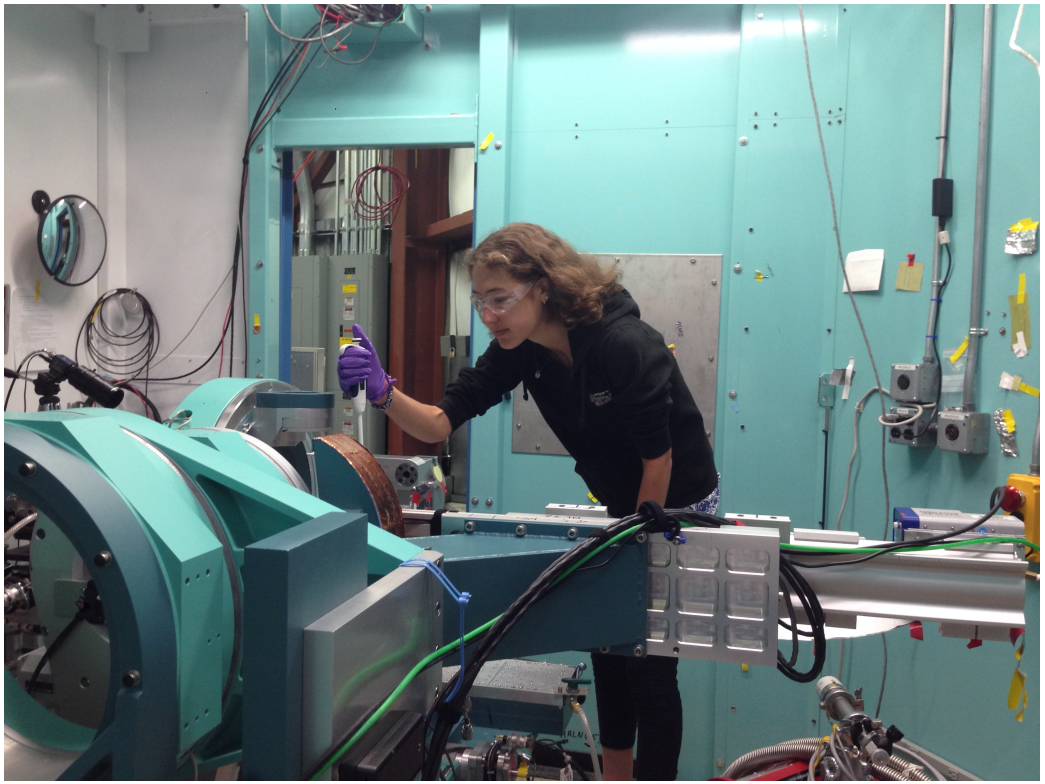
*Férey, G. *et al. Science* 309 (5743), 2040-2042 (2005).

2 Hour Catalysis Sample Overlaid with MOF in Acetate Buffer Sample



Temperature Dependent Scans and In Situ Experiments





Goals

Temperature dependent scans:

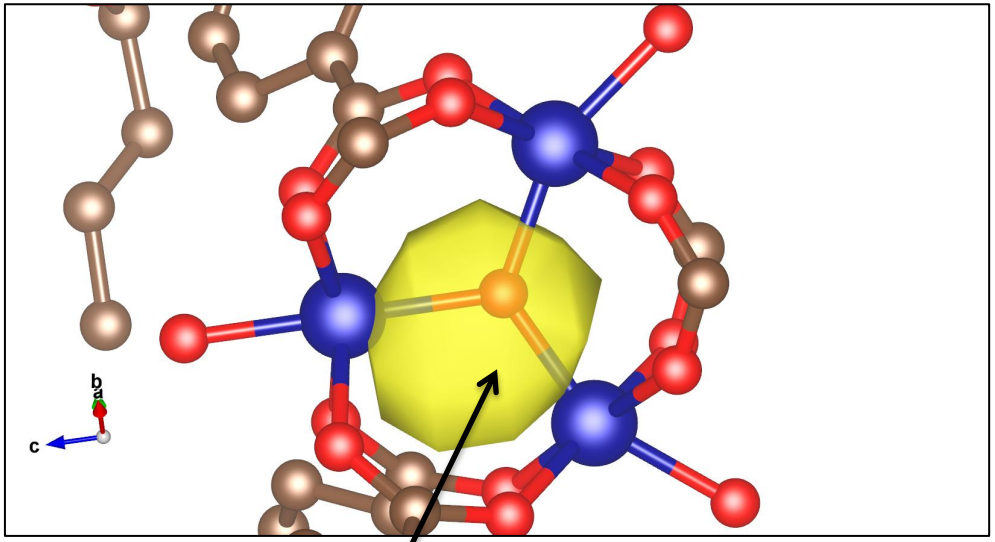
- 45 minute and 2 hour catalysis samples are still good catalysts, so why?
- Split up phases by separating peaks based on heat damage (i.e. one phase might melt)

In situ experiments:

- Better understand cause of MOF degradation
- Watch MOF fall apart over course of catalysis

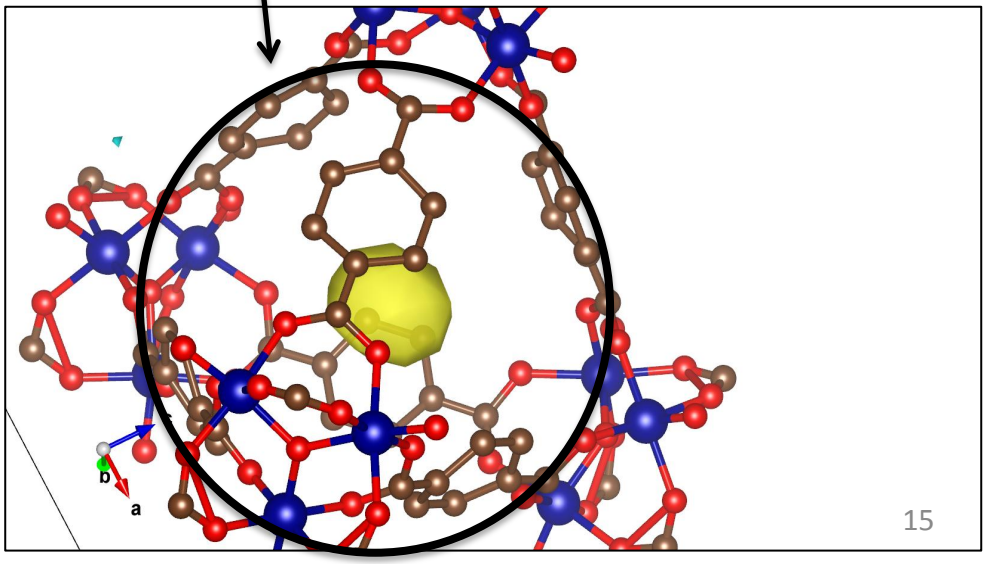
Results: Samples are sensitive to heat, air, and/or time

Densest Electron Density Regions in Fourier Maps



Too small to be the manganese-terpy dimer

Not large enough to house the manganese-terpy dimer



- Brown: Carbon
- Blue: Chromium
- Red: Oxygen

Conclusions

- There is an attractive interaction between the catalyst and MOF, which may destroy the MOF
- The manganese-terpy dimer catalyst is not the source of water oxidation catalysis in this system
- The actual catalyst might be molecular manganese oxide

Acknowledgements

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Temperature Dependent Scan for 2 Hour Catalysis Sample