A hard X-ray study of a manganese-terpyridine catalyst in a chromium-based Metal Organic Framework

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ABSTRACT

Hydrogen produced from water splitting is a promising source of clean energy. However, a robust catalyst is necessary to carry out the water oxidation step of water splitting. In this study, the catalyst studied was $[(\text{terpy})\text{Mn}(\mu\text{-O})_2\text{Mn}(\text{terpy})]^{3+}$ (MnTD) synthesized in the Metal Organic Framework (MOF) MIL-101(Cr), and the method used for analysis was hard X-ray powder diffraction. The diffraction data was used to detect the presence of MOF in different catalytic stages, and lattice parameters were assigned to the samples containing MOF. Fourier maps were constructed with GSAS II 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 by the time 45 minutes of catalysis has ensued. Changes in the MOF's lattice parameters and location of electron density in the Fourier maps suggest attractions between the MOF and catalyst that may lead to MOF degradation. Fourier maps also revealed limited, if any, amounts of MnTD, even before catalysis occurred. Molecular manganese oxide may be the source of the high rate of water oxidation catalysis in the studied system.

I. INTRODUCTION

A promising source of clean energy is H_2 , which can be produced from water, a clean and readily available source. Water splitting involves both a water oxidation step and a hydrogen ion reduction step. The first step, water oxidation, requires a very robust catalyst. Plants utilize the enzyme Photosystem II to catalyze the water oxidation reaction as a part of photosynthesis.¹ Because manganese is both cost effective and a primary component of Photosystem II, many synthetic water splitting catalysts are manganese-based.² However, some catalysts require specific conditions to be catalytically active; understanding these conditions is vital in determining the catalyst's potential for catalyzing water splitting on a practical level.

A recently developed synthetic catalyst $[(\text{terpy})\text{Mn}(\mu\text{-O})_2\text{Mn}(\text{terpy})]^{3+}$ (MnTD) mimics Photosystem II³ and has some of the highest rates of water splitting catalysis reported outside of plants.⁴ However when molecules of MnTD interact, they degrade, thus limiting the use of the catalyst.⁴ Metal Organic Frameworks (MOF) are porous materials that are excellent candidates for housing catalysts as their structural features allow individual chemical reactions to occur within the pores of the MOF.^{5,6} Thus to combat the degradation of MnTD, Hansen and Das⁴ synthesized individual molecules of the catalyst in the pores of a chromium based MOF known as MIL-101(Cr)⁵. However, this synthesis may not have been successful. In preliminary studies of MnTD in MIL-101(Cr), X-ray spectroscopy revealed that manganese oxide may be in the pores of the MOF instead of

MnTD. Manganese oxide is known to catalyze water oxidation but not at the high rates observed for what is thought to be MnTD in MIL-101(Cr).⁴ Using the known crystal structure of MIL-101(Cr), X-ray crystallography and Fourier difference maps can be used to identify which molecule is in the pores of MIL-101(Cr) and thus which molecule is responsible for water oxidation catalysis in the system.

X-ray crystallography is a useful tool because it is a non-destructive method for determining crystallographic changes of samples at the molecular level. Because the samples used in this study were powders, X-ray powder diffraction was the most convenient form of X-ray crystallography. By using powder diffraction patterns to examine changes in lattice parameters of the crystalline MOF under different catalytic conditions, it was possible to investigate interactions between the MOF and the catalyst that it contained. Powder diffraction data was also used to construct Fourier difference maps, which showed regions of electron density where atoms reside within the MOF structure. These maps were used to determine the location and possible identity of the molecules inside the MOF. This allowed us to examine sources of catalysis in the MnTD in MIL-101(Cr) system and yielded insight into factors affecting water oxidation catalysis.

II. MATERIALS AND METHODS

The samples of interest (Table 1) had been previously synthesized by Siddhartha Das^{3,4} and were stored at room temperature in 1 mm capillaries. All scans were carried out at the Stanford Synchrotron Radiation Lightsource (SSRL) at SLAC National Accelerator Laboratory.

Table 1: Description of samples analyzed.

Sample name	Sample description
Activated	Empty MOF
Acetate Buffer	MOF filled with acetate buffer solution prior to being transformed into a powder
No Catalysis	MOF with catalyst isolated inside but before any catalysis occurs
45 Minutes Catalysis	Sample after 45 minutes of water splitting
2 Hours Catalysis	Sample after 2 hours of water splitting
7 Days Catalysis	Sample after 7 days of water splitting

A. Preliminary studies on Beamline 2-1

Preliminary scans of the activated, acetate buffer, and no catalysis samples were performed on Beamline 2-1 at a wavelength of 1.0332 Å. A silicon 111 analyzer crystal and PMT detector were also used, and the wavelength and 2-theta offset were calibrated with LaB₆. The samples were analyzed in the same 1 mm capillaries that they were stored in, and these preliminary scans were taken shortly after synthesis of the samples.

B. Scans on Beamline 11-3

Secondary scans (approximately six months after the preliminary scans) were carried out for all samples on Beamline 11-3 at a wavelength of 0.9744 Å and with a Mar 3450 image plate detector. GSAS II⁷ was used to integrate the diffraction images and the calibrant was, once again, LaB₆. The samples were analyzed in the same 1 mm capillaries that they were stored in.

C. Temperature-dependent scans

The temperature-dependent studies were also carried out on Beamline 11-3 with the same parameters as mentioned previously, but the capillaries were opened and the contents transferred to a silicon zero-background plate in a helium chamber for analysis. The temperature ranged from 35 to 205°C, and only the 45 minutes and 2 hours catalysis samples were analyzed.

D. In situ experiments

In situ studies were carried out on Beamline 7-2 with a wavelength of 0.8265 Å and a Piatas 100k detector. The *in situ* studies involved adding a solution of Cerium (IV) Ammonium Nitrate (CAN) to the powdered samples. CAN is a necessary component of the catalysis as it activates MnTD by oxidizing it.⁴ Following the procedure outlined by Das,⁴ a CAN solution was diluted to 1.6 mM with a previously prepared solution of 1% nitric acid. The powdered samples were transferred to an open capillary tube that was suspended in the beam by a tube of coiled metal wire (Figure 1). A micropipette was used to inject approximately 50 µL of the CAN/nitric acid solution into the powdered sample, and then a series of scans was collected.

Figure 1: Experimental set-up of *in situ* experiments. The tip of the capillary, which contains the sample, is suspended in the path of the X-ray beam by a self-engineered coil of metal wire.

E. Fourier maps

Fourier maps for the activated, acetate buffer, and no catalysis samples were created using GSAS II and visualized and subtracted using VESTA⁸. Three maps were created: one in which the activated sample was subtracted from the acetate buffer sample; one in which the activated sample was subtracted from the no catalysis sample; and one in which the acetate buffer sample was subtracted from the no catalysis sample. The first two maps were used only as references to verify the accuracy of the last map. The last map, the difference between the no catalysis and acetate buffer samples, was the focus and is the only one discussed in the remainder of the paper.

III. RESULTS AND DISCUSSION

X-ray powder diffraction patterns on Beamline 2-1 were obtained for the activated, acetate buffer, and no catalysis samples (Figure 2). The location of peaks showed that all three samples contained the MOF, but that the no catalysis sample also contained amorphous material, as shown by the increased background level. The unit cell lengths for the MOF in each sample were determined and are shown in Table 2. The increase in unit cell length upon addition of acetate buffer solution to the MOF was expected as the MOF likely absorbs the solution and swells. However, the decrease in unit cell length upon addition of the catalyst was not expected and suggests an attractive interaction between the MOF and the catalyst. This attraction was also evident in the Fourier maps as much of the electron density resided near the framework.

Figure 2: X-ray powder diffraction patterns for MIL-101(Cr) (top left), MIL-101(Cr) soaked in an acetate buffer solution (top right), and MIL-101(Cr) with water oxidation catalyst inside but before any catalysis has occurred (bottom).

Table 2: Unit cell length of the MOF for the samples that contained MOF. The first two samples were analyzed at two different Beamlines while the last two samples were only analyzed at one Beamline.

Sample	Beamline 2-1 unit cell length (Å)	Beamline 11-3 unit cell length (Å)
Activated	88.0720 ± 0.0015	88.042 ± 0.008
Acetate Buffer	88.5120 ± 0.0016	88.594 ± 0.007
No Catalysis	87.19 ± 0.04	N/A
7 Days Catalysis	N/A	88.4 ± 0.3

Additional X-ray diffraction patterns on Beamline 11-3 were obtained for all samples. The patterns for the activated and acetate buffer samples were consistent with those from Beamline 2-1 (unit cell lengths are reported in Table 2) while the no catalysis pattern revealed a lot of amorphous character that was not present in the 2-1 pattern. It appeared that the no catalysis sample degraded over time, and no unit cell length could be

obtained. Both the 45 minutes and 2 hours catalysis samples (Figure 3) revealed no presence of MOF as their diffraction patterns revealed few, if any, peaks that were consistent with those in the MOF diffraction pattern. Thus it was determined that the MOF must fall apart over the course of catalysis and that the attractive interaction between the catalyst and framework could be the source of MOF degradation.

Figure 3: X-ray powder diffraction patterns for MIL-101(Cr) with water oxidation catalyst after 45 minutes of catalysis (top left), after two hours of catalysis (top right), and after seven days of catalysis (bottom).

Additional analysis of the diffraction patterns for the 45 minutes and 2 hours catalysis samples suggested that these samples were multi-phase. In addition, the large background indicates formation of amorphous material. It should be noted that a previous study showed retention of the MOF after three days of catalysis.⁴ This discrepancy could be due to difference in storage parameters as the samples in the previous study were frozen in liquid nitrogen before storing while our samples were stored at room temperature. As a result, our samples may have been less stable and more sensitive to air, heat, and/or time. This could also explain why the no catalysis sample appears to have degraded over time.

The 7 days catalysis diffraction pattern also revealed a lot of amorphous character. However, the presence of MOF was still evident (Figure 3), and a unit cell length was calculated (Table 2). This is inconsistent with the previously discussed results as it suggests reformation of the MOF after it has fallen apart, which is highly unlikely. There

was some confusion in sample preparation, and it is unclear whether or not the 7 days catalysis sample came from the same starting batch as the no catalysis, 45 minutes catalysis, and 2 hours catalysis samples. Therefore, the 7 days catalysis sample was determined to be unreliable and will not be discussed henceforth.

Temperature-dependent scans were carried out in an attempt to separate phases of the 45 minutes and 2 hours catalysis samples. These two samples were still effective at catalyzing water oxidation, and we wanted to know why. The goal was to separate the phases by melting or damaging one set of peaks. Unfortunately, all of the scans obtained (including the first scan) were noticeably different than the initial scans obtained on Beamline 11-3, containing few, if any, of the same peaks. Thus it was concluded that the samples had degraded by the time the first temperature-dependent scan was obtained. The reason for sample degradation is likely air exposure as the samples were removed from the capillaries. The degradation could also be a product of heat damage as the first scan for each sample was taken at 35°C and not 25°C. It should be noted that the samples were exposed to air when initially prepared, and thus it is possible that the samples had already degraded from the time they were prepared to the time when they were analyzed, a difference of about six months. This appears to be the case for the no catalysis sample, based on the increase in amorphous character from the preliminary to the secondary scans. Thus it may also be the case for the 45 minutes and 2 hours catalysis samples, especially considering that they also contained the catalyst, which was hypothesized to be the cause of degradation.

We carried out *in situ* experiments in another attempt to discern the contents of the 45 minutes and 2 hours catalysis samples. The goal was to watch the MOF degrade over the course of catalysis and observe the species that resulted. We reasoned that these species should be the same as those in the samples that had undergone catalysis. While we suspected that the catalyst was the cause of degradation, we also tested the possibility that the CAN was the cause of degradation by performing *in situ* experiments on the acetate buffer sample. Our initial hypothesis was confirmed when the acetate buffer sample remained intact upon both exposure to air and to the CAN solution (Figure 4, a-c, on the next page).

While the catalyst was shown to be crucial to degradation of the MOF, there was some question as to whether the catalyst needed to be activated to cause degradation. The diffraction pattern of the no catalysis sample did reveal the MOF, suggesting that it is activation of the catalyst that leads to full degradation. Still, the no catalysis sample was more amorphous than the activated and acetate buffer samples and did appear to degrade over time, so it is possible that activation of the catalyst through addition of the CAN solution enhances the adverse effects of the catalyst, causing the degradation to occur more rapidly.

We also carried out an *in situ* experiment on the no catalysis sample. In agreement with the scan from Beamline 11-3, the no catalysis sample appeared to have degraded before the *in situ* experiments proceeded. In comparison to the acetate buffer sample, the no catalysis sample revealed very few of the diffraction rings characteristic of the MOF

(Figure 4, d). However, exposure to air degraded the sample further, to the point of complete disappearance of the diffraction rings associated with the MOF (Figure 4, e). Again, this shows the sensitivity of the samples containing the catalyst.

Figure 4: X-ray powder diffraction scans of the acetate buffer sample (MIL-101(Cr) soaked in an acetate buffer solution) in capillary (a); exposed to air (b); and with a solution of cerium(IV) ammonium nitrate (CAN) added (c). Also shown are X-ray powder diffraction scans of the no catalysis sample (MIL-101(Cr) with water oxidation catalyst inside but before any catalysis has occurred) in capillary (d); and exposed to air (e).

While the temperature dependent scans and *in situ* experiments yielded useful information, they did not lend insight into the causes of catalysis in the 45 minutes and 2 hours samples. Thus we turned our focus towards identifying the catalyst present in the no catalysis sample. It would be expected that the densest electron density regions in the Fourier map of the no catalysis sample would be MnTD, assuming that MnTD was successfully synthesized in the MOF. However, the densest regions were much too small to represent a MnTD molecule. In addition their locations in the MOF (Figure 5) were not physically large enough to accommodate the size of an MnTD molecule. Thus it was concluded that there was little or no MnTD in the no catalysis sample; MnTD is not the origin of catalysis in this system as previously speculated by Das.⁴

Figure 5: Most dense positive electron density regions in the Fourier map of the no catalysis sample (which consisted of MIL-101(Cr) with the water oxidation catalyst inside but before any catalysis had occurred).

It is possible that the densest electron density regions represent manganese oxide. This is consistent with preliminary X-ray spectroscopy scans, which also show the presence of manganese oxide, specifically α - MnO_2 . The small size of the electron density patches suggests molecular versus crystalline manganese oxide. The increased surface area of molecular manganese oxide may be the reason for increased catalytic activity relative to what is known for the crystalline form, which catalyzes water oxidation at extremely low rates.⁹ Several studies have shown that nano-particle manganese oxide has much higher catalysis rates than crystalline manganese oxide.^{10,11} However, our system displays even greater rates of catalysis as it was reported to have a catalytic turnover frequency of $40 \text{ (hr}^{-1}\text{)(molO}_2\text{•catalyst}^{-1}\text{)}$ ⁴ while other studies have reported values of 14.4^{10} and $0.317^9 \text{ (hr}^{-1}\text{)(molO}_2\text{•catalyst}^{-1}\text{)}$ for nano-particle $\text{CaMn}_2\text{O}_4\text{•H}_2\text{O}$ and water-soluble nano-scale colloidal MnO_2 , respectively.

The difference between our system and those containing nano-particle manganese oxide could be attributed to the even greater surface area of molecular manganese oxide as compared to nano-particle clusters. Although the MOF appears to fall apart once catalysis commences, the pieces of the MOF resulting from degradation may provide an environment that prevents individual manganese oxide molecules from interacting to form clusters. Currently, however, the presence of manganese oxide molecules is only speculation.

IV. FUTURE WORK

While *in situ* experiments were attempted in this study, they could be improved. First, they should be executed directly after synthesis of the samples, and second, they should be carried out in an inert atmosphere. In an improved experimental setup, the *in situ* experiments could reveal at what stage during catalysis the MOF begins to degrade, which could lend insight into the source of degradation.

Future studies are also needed to verify the identity of the water oxidation catalyst in this system. We would like to synthesize molecular manganese oxide, determine its rate of water oxidation catalysis, and then compare this rate to the rate of catalysis for manganese oxide molecules infused in MIL-101(Cr). These experiments should either identify or rule out molecular manganese oxide as the source of catalysis. In addition, they may reveal the role of the degraded MOF in the water oxidation catalysis process.

It should be noted that when creating the Fourier maps, full refinement of MOF structures from the samples was not achieved; thus it is possible that the regions of electron density observed in the Fourier maps are not entirely accurate. Still, the proposed hypothesis is most consistent with the data obtained. To further verify the results, full refinement of the MOF structures should be undertaken.

V. CONCLUSION

The high water oxidation rates for what was thought to be MnTD in MIL-101(Cr) were found to originate from a different catalyst. The water oxidation catalyst may instead be molecular manganese oxide, although further studies are needed to verify this. In addition, the structure of the MOF does not stay intact during catalysis, most likely due to attractive interactions between the MOF and the activated catalyst. However, even samples containing the degraded MOF have proven to be effective water oxidation catalysts. While attempts were made to better understand the reasons for this surprising result, no conclusive results were obtained. Hopefully future studies can build upon these findings so that systems can be developed that achieve maximum water oxidation catalysis as a way to produce cleaner energy.

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