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Synthesis of Molecular Organic Framework HKUST-1 and Catalysis of Benzyl Alcohol to Benzaldehyde.

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Supporting information is available.

ABSTRACT: The use of metal organic frameworks for the purposes of catalysis in organic synthesis were explored using the HKUST-1 framework and applying it as a catalyst in the conversion of benzyl alcohol to benzaldehyde. The HKUST-1 framework was synthesized, and its purity was confirmed via powder X-ray diffraction. The yield of HKUST-1 was 44%. The metal organic framework was then used to catalyze the oxidation reaction of benzyl alcohol to benzaldehyde. This reaction was analyzed by GCMS, where there was a negligible amount of benzaldehyde produced, but a significant quantity of benzoic acid detected. These results suggest that the catalytic process is likely more favorable towards benzoic acid rather then benzaldehyde. This is due to either the lack of selectivity in the HKUST-1 framework or the low stability of HKUST-1.

INTRODUCTION

Molecular organic frameworks (MOFs) are porous molecular structures comprised of metal nodes coordinated to organic ligands that function as links between nodes.[1] This combination of organic linkers and metal nodes creates either a two-dimensional or a three-dimensional structure that is referred to as a framework. The most valuable aspects of MOFs are the large pore size of the framework, as well as the tunability of both the organic and inorganic components of the compounds.[1] These aspects allow MOFs to potentially be used as absorbing materials for solvents and as storage for gasses.[2] Common research for MOFs is to explore hydrogen storage capabilities, due to the difficulty in transporting hydrogen gas.[2] Depending on the component of the MOF, molecules trapped inside the pores of a MOF can be released without the collapse of the MOF itself. This allows increased efficiency as the MOF can be reused. The containment attributes of MOFs also provide opportunities for drug carrying and delivery with higher degrees of accuracy than before.[1] MOFs can be designed so that the drug being carried will release under certain conditions, often relating to pH or ion concentration.[1]

Another important attribute of the porous nature of MOFs is the catalytic functionality of the compounds.[2] MOFs can function reasonably well as heterogeneous catalysts. The metal atoms located at the nodes of the MOF can behave as catalysts by behaving as Lewis acids and coordinating to and activating organic compounds. In all the catalytic methods, the specific components used in a MOF also allow catalysis to be size specific, due to the pore size of the framework.[3] The finally catalytic possibility for MOFs is the potential for the organic linker to be catalytically active. The linkers would need to have wide openings to allow reactants access to the metal nodes.

The MOF HKUST-1 is a framework that functions as a catalyst for the conversion of benzyl alcohol to benzaldehyde. The theoretical method of the conversion reaction is to first remove the water from the copper nodes of the HKUST-1 MOF.[4] The copper then behaves as a Lewis acid to catalyze the conversion of alcohol to aldehyde. The MOF theoretically makes this process more selective then simply having copper II in solution due to the framework around the copper nodes restricting possible reactants based on their ability to diffuse into the MOF.

EXPERIMENTAL

The synthesis of the HKUST-1 MOF involves the coordination of a copper compound with benzene-1,3,5-tricarboxylic acid. This was accomplished by combining 2.0720g of $Cu(NO_3)_2$*$5H_2O$ with 1.0452g of benzene-1,3,5-tricarboxylic acid in a 100mL glass bottle.

The mixture was dissolved in 50mL of a solvent mixture containing 1:1:1 DMF, ethanol, and deionized water. The solution was mixed for 15 minutes. After mixing, the solution was sealed and heated in an oil bath at 80ºC for 48 hours. After heating the solution had turned a vibrant blue color. The solution was then filtered and rinsed with roughly 30 mL of DMF and 15 mL of DCM. The powder after filtering was the same deep blue color and was transferred into an alumina thimble. The powder was rinsed to the bottom of the thimble with a small amount of DCM, then plugged with glass wool. The thimble and sample were then placed in a Soxhet extractor, which cycles DCM in a closed loop through the sample, for 15 hours. The thimble was then removed and placed in a vacuum oven for 48 hours at 100ºC.

After drying in a desiccator for 24 hours, the sample inside the thimble was assumed to be the HKUST-1 MOF. There was 2.164 g of product synthesized, which is equivalent to 44% yield. To confirm that the MOF was successfully synthesized a portion of the product was ground with a mortar and packed and run through powder X-ray diffraction (PXRD). Figure.1 below shows the PXRD spectra collected.
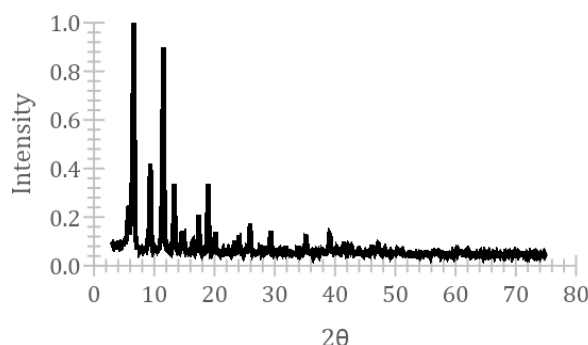

Figure 1: This is the experimental PXRD spectra for the HKUST-1 MOF that was synthesized. The data was normalized to a value of 1.

After the synthesis if HKUST-1 was confirmed, the MOF was used to catalyze a conversion reaction of benzyl alcohol to benzaldehyde. This reaction used 105mg of benzyl alcohol, 150 mg of the HKUST-1 MOF, and 26.9 mg of TEMPO. All of this was dissolved in 6 mL of acetonitrile. The solution was sealed with an oxygen balloon and stirred and heated at 70ºC for 48 hours. The conversion between benzyl alcohol and benzaldehyde was determined by GCMS. The sample was prepared for GCMS by running through a pipette sized silica column with DCM as the mobile phase. The eluent of the column was put into a GCMS autosampler vial and run through a GCMS instrument using a polar column. From the compounds that eluted from the GC, there should have been two peaks that corresponded to benzyl alcohol and benzaldehyde, and one peak that most likely corresponds to benzoic acid. Figure.2 shows the region for these peaks.
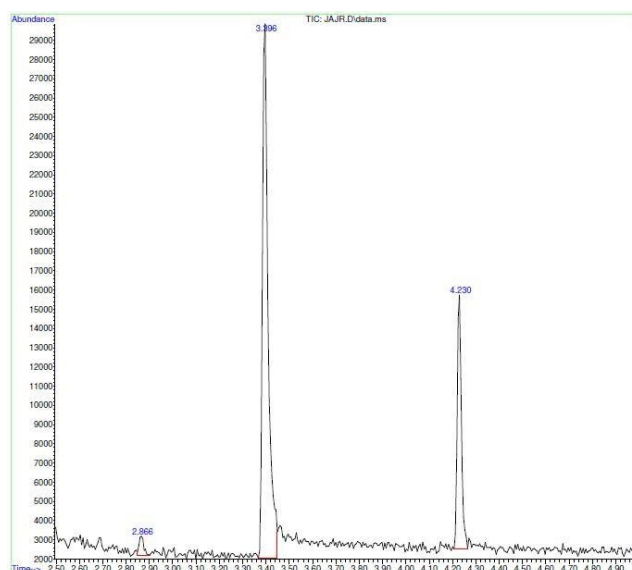

Figure 2:The GC spectra produced by the GCMS. There are 3 identified peaks. The peak at 2.866 min is for benzaldehyde. The peak at 3.396 min is benzyl-alcohol. The peak at 4.230 min is for benzoic acid.

The first peak should be located around 2.8 minutes, and should correspond to the product, benzaldehyde. The second peak was located at 3.396 and corresponds to the starting material, benzyl alcohol. The third peak appears at 4.230 minutes and corresponds to benzoic acid. A Total Ion Chromatogram (TIC) of the two areas of the GC output that correspond to the starting material and the desired product were taken. The TICs are shown in Figure.3.
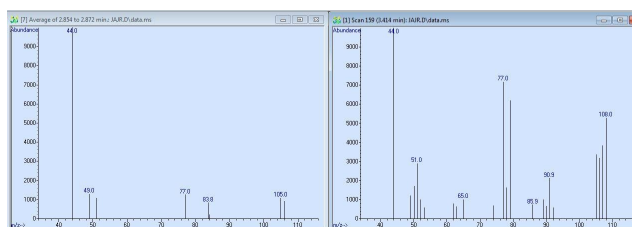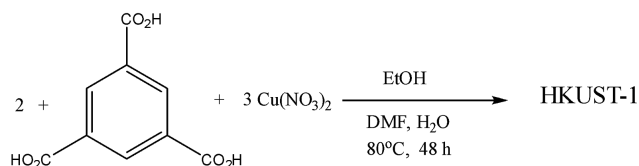

Figure 3: The TIC for the 2.866 min peak on the left, and the 3.396 min peak on the right.

RESULTS & DISCUSSION

The HKUST-1 MOF was successfully synthesized in a solvothermal reaction using copper nitrate and benzene-1,3,5-tricarboxylic acid, according to Scheme.1.

Scheme.1: This is the scheme used to generate the HKUST-1 catalyst.

The MOF structure was confirmed with PXRD by comparing it to a predicted HKUST-1 PXRD spectra that was generated from single crystal X-ray diffraction data using Mercury software from Cambridge Crystallography Data Center. This spectrum is shown in Figure.4. A comparison between the experimental spectra and the predicted single crystal spectra show peaks of comparable intensity at the same $2\theta^{o}$ angles. This confirms that the crystal structure of the product compound is the same as the HKUST-1 MOF. The overall crystallinity of the MOF can be determined based on how sharp the peaks in the experimental spectra are when compared to the single crystal spectra. In the single crystal, each peak is very sharp, with no visible shoulder at the base of the peaks. The experimental spectra's peaks have some visible shoulders and wider bases that the single crystal. This indicates that there are some defects in the crystal structure of the synthesized MOF. The residual difference between the single crystal prediction and the experimental data gives insight into how crystalline the MOF is. A plot of the residuals according to $2\theta^{o}$ angle is shown in Figure.5. The relative intensity for the residual data is all less than 10%, with a majority of the data being less than 5%. These low differences between the single crystal and the powdered MOF sample imply a very crystalline framework.[5]
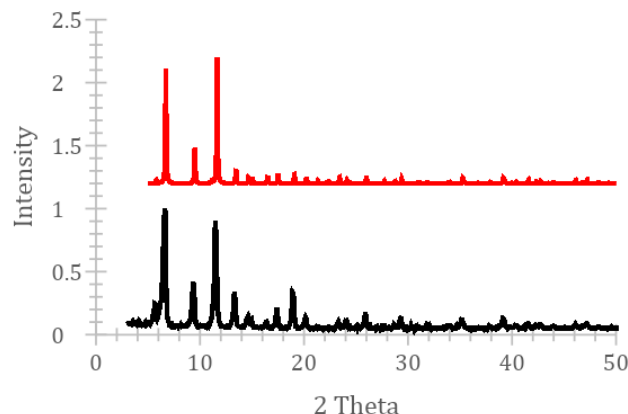

Figure 4: The stacked PXRD spectra related to the HKUST-1 MOF sample. The upper spectra in red is the single crystal prediction, and the lower spectra in black is the experimental spectra. The data was normalized to a value of 1, and the single crystal prediction was shifted upwards to allow comparison.
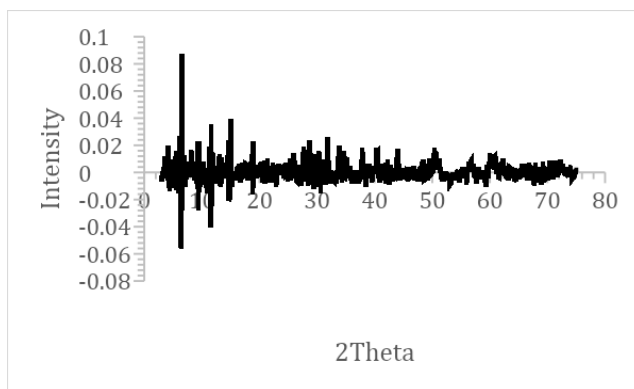

Figure 5: This figure is the plotted residual data between the single crystal PXRD spectra prediction and the experimental PXRD spectra. The data was normalized in the same manner as in Figure.4

The HKUST-1 MOF was intended to be used to catalyze the oxidation of benzyl alcohol to benzaldehyde, along with a co-catalyst called TEMPO, all according to Scheme.2. The outcome of this reaction was measured by means of placing the reaction solution in a GCMS sample and determining the amount of reactant and product in the sample solution with the eluent peak size. The identity of the peaks was determined by the order they eluted, as well as with the use of the TICs.
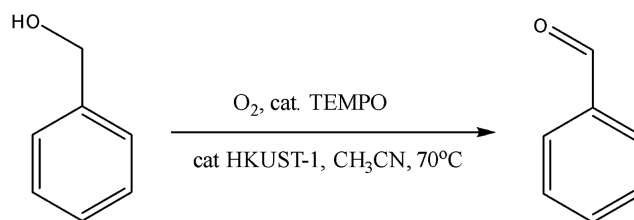
Scheme.2: This is the scheme used to attempt the conversion of benzyl alcohol to benzaldehyde.

The mass spectrometer of the GCMS produces TICs for each peak or range of peaks eluted from the GC. The peaks of interest in this data set are the region around 2.8 minutes and the peak at 3.396 minutes. The TIC for each of these regions provides the mass spectrum for the compound detected there. Figure.3 has the TICs for both of these regions. These chromatograms have parent peaks that correspond to benzyl alcohol and benzaldehyde, at 108 m/z and 105.9 m/z respectively. There are also fragmentation peaks that correspond with benzene rings at 77m/z in each TIC. This indicates that these two compounds contain benzene rings, which supports the claim that the parent peak mass correspond to benzyl alcohol and benzaldehyde respectively.

The noise of the GC data is rather large, and the standard deviation of the noise is necessary to determine the limit of detection. The GCMS software does not provide the standard deviation of the noise, and so an

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estimate was made for the standard deviation to be roughly 600 units in abundance. This would require a peak to have a minimum of 1800 units in abundance to be considered detected. The first peak at 2.866 minutes is very small; the instrument reports the peak to have a height of 976 units in absorption. This falls short of the limit of detection, and so the peak corresponding to the product is too small to be detected by the instrument.[6] However, there is enough trace benzaldehyde to provide a TIC for the mass spectrometer to detect, allowing the confirmation that 2.866 minutes is the retention time of benzaldehyde on the column used. The large peak located at 3.396 minutes corresponds to benzyl alcohol, which is confirmed by the TIC. The last peak at 4.230 minutes is likely benzoic acid. It is very possible that the oxidation of benzyl alcohol can proceed in a manner to produce a carboxylic acid instead of an aldehyde.

These materials have eluted in an order corresponding to the affinity of the material with the polar GC column. The product, benzaldehyde, elutes first due to it having less bonding with the coating of the column then the other compounds. Benzyl alcohol has the potential to hydrogen bond with the coating of the column, increasing its retention time. Benzoic acid is a very polar compound with large potential to bond with any polarized coating on the inside of the column, thus explaining it being the last to elute from the column.

CONCLUSION

The evidence indicating that only negligible amounts of benzaldehyde was generated from the catalyzed conversion reaction implies that the reaction was not catalyzed in the manner expected. The catalyzation from alcohol to aldehyde was expected from this reaction, but it was also possible that the conversion from aldehyde to carboxylic acid, or from alcohol to carboxylic acid, was possible. It appears that the TEMPO catalyst performed as it should, but it appears that the catalysis is much more favorable towards the benzoic acid rather than benzaldehyde. This implies that the generation of benzaldehyde is dependent on the selectivity of the HKUST-1 MOF. Unfortunately, it appears that the MOF was not as selective as expected in the species it catalyzed or its catalysis mechanism. The smallest pore size of the HKUST-1 MOF is 8.0Å, and benzene rings have a diameter of 1.4Å. This information supports the claim that there is little issues with the diffusion of benzene species into the MOF, but there also is likely little exclusion of specific benzene species. The other explanation for why the catalysis did not go as expected is that the MOF

decomposed in solution into copper ions and organic linkers. this would explain why there was so little benzaldehyde detected in the GC, especially if the TEMPO catalysis is more favorable towards benzoic acid.

Future work in this field involve repeating this study to confirm the functionality of HKUST-1 as a catalyst for the conversion of benzyl alcohol to benzaldehyde, as well as trying the catalysis with just copper ions in solution. This might confirm the favorability of the catalysis towards benzoic acid. The study can then be repeated with other MOFs that are more stable than HKUST-1.[3] Beyond this, the manipulation of the metal nodes and organic linkers to change the selectivity and catalytic properties of MOFs would be a large advancement in MOF chemistry.[5] The selective catalysis of alcohols and other functional groups could be exceedingly applicable in synthetic chemistry, leading to more advancements in that field as well.

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