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جامعة الملك فهد للبترول والمعادن
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Final Report

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Department	Chemistry, Physics	Research Topic	Synthesis and Characterization of Metal Organic Frameworks
Level	Senior		

Date:

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Student's Signature

Advisor's Signature

1 Introduction

Metal-Organic Frameworks (MOFs) are coordination compounds that have an extended three-dimensional crystalline structure composed of metal ions or metal clusters that are linked by polydentate organic ligands, called linkers. In the last three decades, this subclass of crystalline materials has risen to become one of the most promising research fields to offer solutions to countless challenges ranging from energy storage, carbon capturing and conversion, heterogenous catalysis to drug delivery, chemical sensing, electrochemical, photonics, etc. The chemical modularity and tunability of MOFs combined with their structural properties such as high porosity, surface area, and crystallinity provide a sound pretext for the increased interest in this field of research for countless areas of application.

The reason for the diversity of the prospective applications and the growing interest in MOFs rests on two aspects, structural and chemical. Structurally, MOFs are crystalline and possess ultrahigh porosity in most cases. This is significant because any application occurring on the surface, such as gas separation and storage, and heterogenous catalysis, will be greatly amplified as the area of an entire football field could be equated to the internal surface of about one gram of a MOF. However, what sets apart from other classes of porous materials is their chemical tunability and modularity that is produced by the different possible topologies, various functionalized organic linkers and inorganic Secondary Building Units (SBUs). The contrasting disciplines of organic and inorganic molecular chemistry could be both applied to construct crystalline materials that are bestowed with targeted structural, physical, and chemical properties. Thus, through functionalization coupling of different properties within MOF, unique and sophisticated functions may be achieved. An example of such coupling is the capture of carbon dioxide within the MOF pores coupled with catalytic conversion of it to economically more valuable chemicals.

2 Literature Review

Prior to my involvement in research with Dr. Aasif in Uxplore, I have only had a modest background about the subject from sections from [1, 2]. Prior to applying to Uxplore, I have read the editorial to the “2012 Metal-Organic Frameworks” special issue of *Chemical Reviews* [3].

Initially, my advisor provided me the following literature: The MOF5 paper [4], a historically important landmark in the field; A review paper for carbon dioxide capture in MOFs [5]; A paper

on defect introduction to a MOF for catalyzing carbon dioxide fixating synthesis of a bioactive compound that was authored by himself [6]; Another was a new MOF which works as a chemosensor for Palladium in water, which was also authored by himself [7]. Aside from the scientific findings, the MOF5 paper was important because it motivated interest in MOFs highlighted the merits and prospects of MOFs. The MOF5 itself demonstrated a one of the first chemically and thermally stable MOF, this could be reasoned by the rational choice of linker, which has strong carboxylate-metal coordination, and the large length dimension with limited flexibility due to the carboxylate being connected and conjugated with the phenyl ring.

Seeking better understanding, I found the excellent book by Omar Yaghi (arguably the most prominent chemist in the field), “Introduction to Reticular Chemistry” [8]. The chapters on Determination and Design of Porosity (Ch.2) and Zeolitic Imidazolate Frameworks (Ch.20) were the ones I had most interaction with, the latter is a subclass of MOFs. In addition, [9] was also helpful in explaining ZIFs. The 2012 Chemical Reviews special issue had the invaluable paper regarding the deconstruction of MOF structures using their underlying topological nets [10]. I have also, partially, read a more recent article on carbon dioxide capture and conversion [11]. Moreover, an important review paper on MOFs in heterogeneous catalysis was published in the “2020 Porous Framework Chemistry” special edition of “Chemical Review”[12].

3 Problem Statement and Research Objectives

3.1 ZIF Project

Zeolitic Imidazolate Frameworks are a subclass of MOFs with a structure resembling zeolite, having tetrahedral metal nodes linked by imidazoles that have an angle similar to that between silicon linking oxygen atoms in zeolite. Unlike zeolites and MOFs, ZIFs are hydrophobic so they are more stable in and their performance is not affected by humid conditions. This makes them a better material for carbon capture applications.

The objective of our ZIF project is to synthesize mixed metal ZIFs at mild conditions. This approach to design in which one targets replacement of the metal cluster with mixed metal while retaining the structure and topology of the framework is known as *Isorecticular design*. Once this is obtained we should test their gas adsorptive and related properties, as well their catalytic activity. Lastly, a pyrolysis procedure is carried out to produce MOF-driven materials that contain metallic

centers, electron-rich nitrogen, with highly conjugated aromatic systems. We suspect this could have enhanced catalytic activity.

The framework in the study to which we seek to form isorecticular structures is ZIF-8, a cobalt-based ZIF. Isostructural design with a series of metals in 1:1 ratio with cobalt. The XRD plots are found in **Figures 2**.

My tasks include carrying out the (1) synthesis and (2) separation procedures for different doping metals and (3) carrying out XRD scans for the obtained samples **Figure 1**.

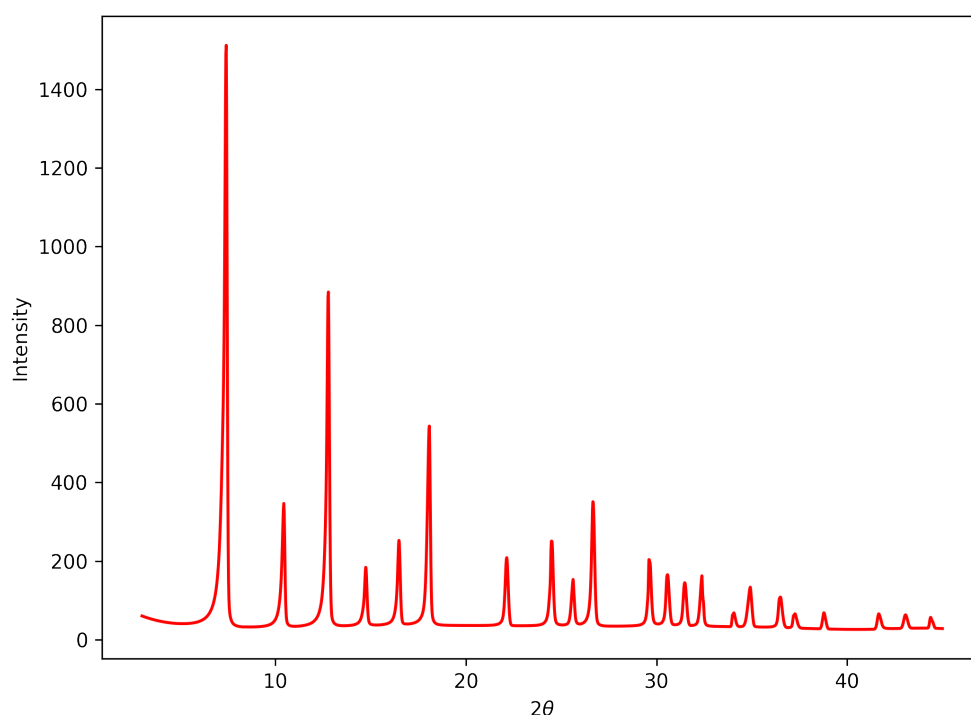


Figure 1 P-XRD of a ZIF Sample

Beside P-XRD, another crystallinity-related experiment was Field Emission Scanning Electron Microscopy (FESEM) which provides topographical information. It was carried for the ZIF-8 sample seen in **Figure 3**.

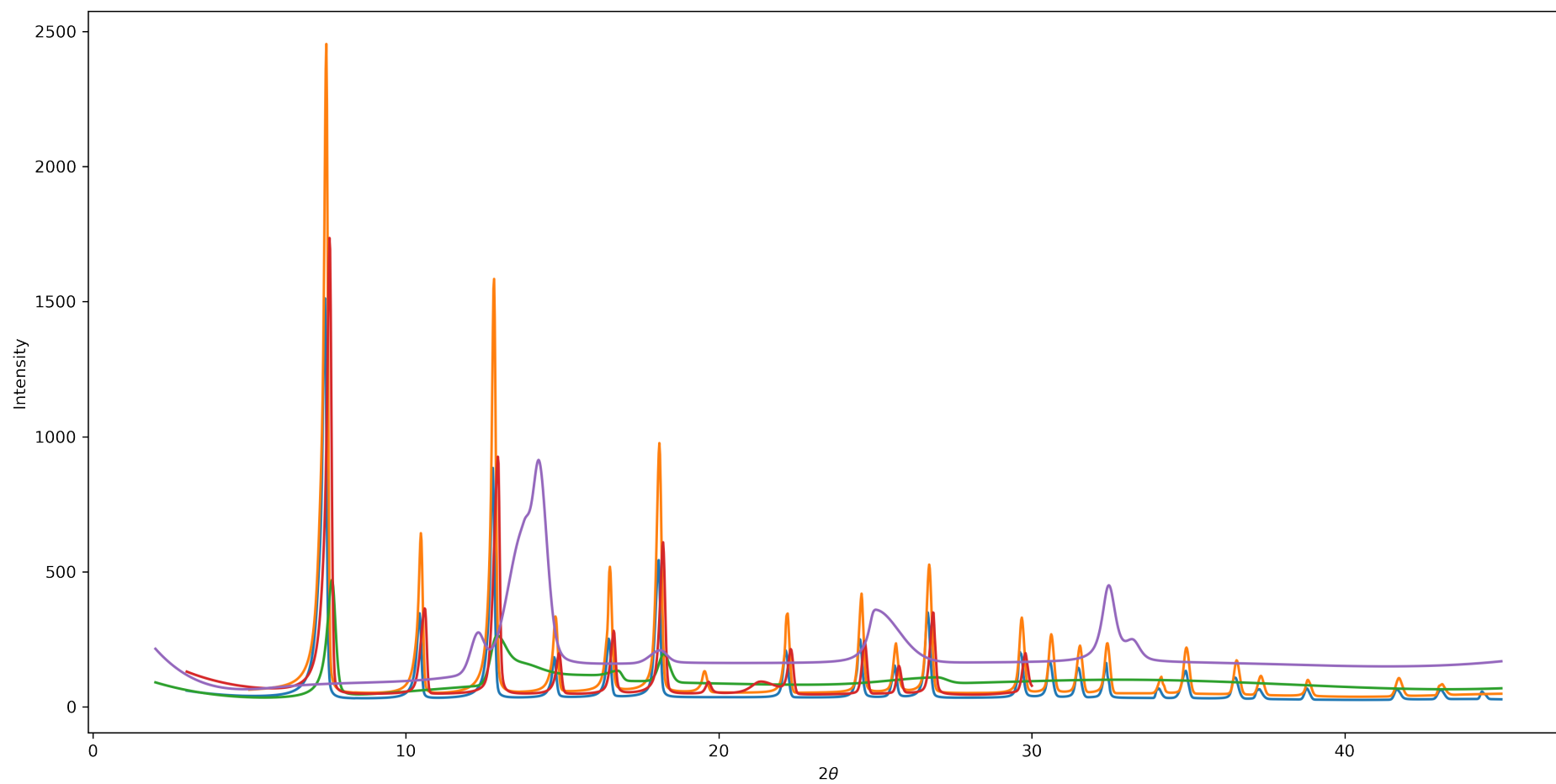


Figure 2 XRD of Attempted ZIF-8 with Co 1:1 Metal isorecticular structures.

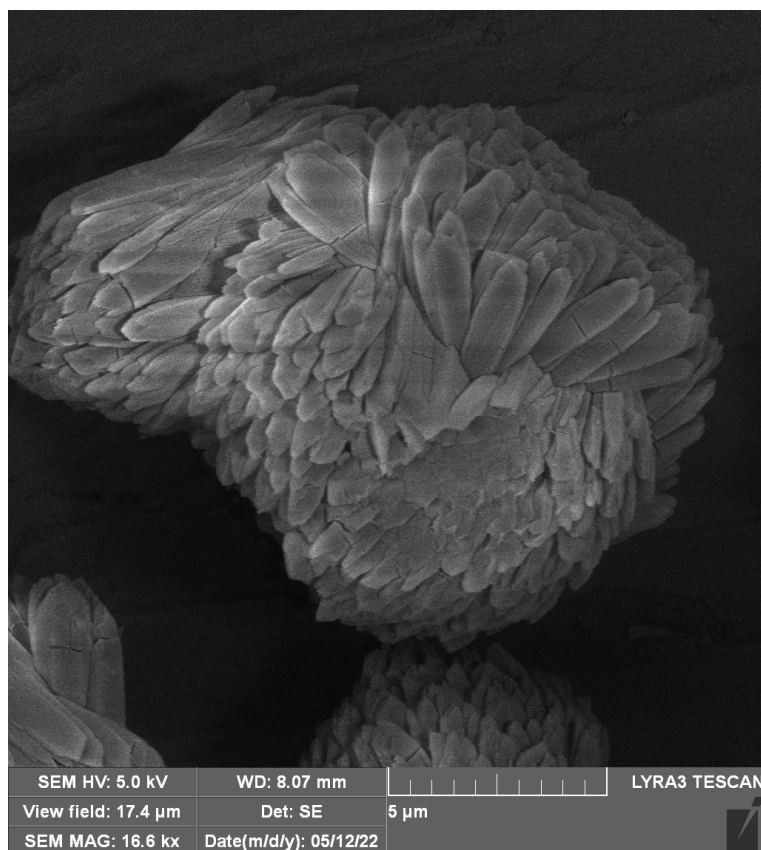


Figure 3 FESEM of ZIF-8 Crystals

For gas adsorption applications, Brunauer–Emmett–Teller analysis is of principal importance as it assess the gas adsorption as well as porosity of a solid surface based on the specific surface area. This results of this experiment can be seen in **Figure 4**.

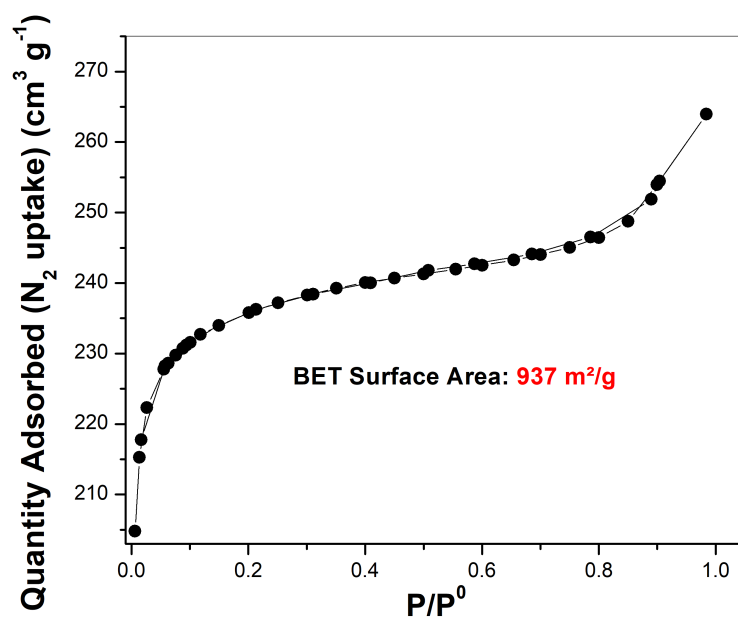


Figure 4 Brunauer–Emmett–Teller of a ZIF-8 sample

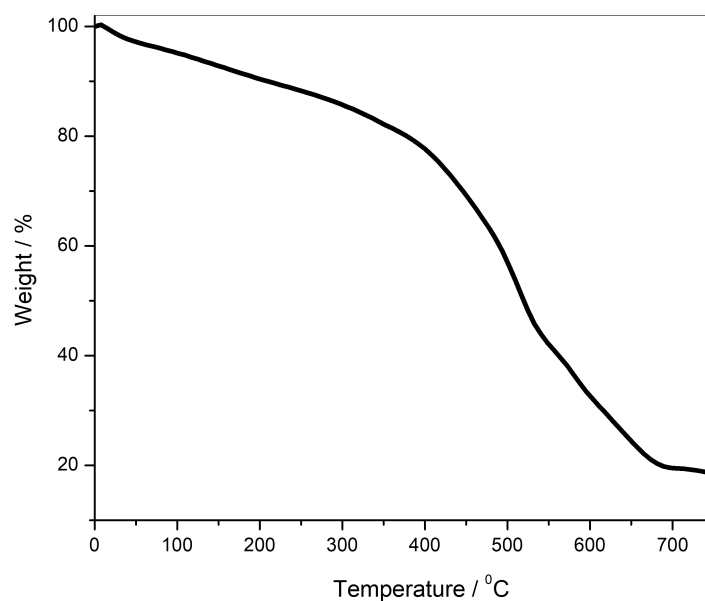


Figure 5 Thermogravimetric Analysis of a ZIF-8 sample

3.2 MOF Project

For the other project, I have also been carrying out (1) synthesis and (2) separation procedures and (3) carrying out XRD scans of UiO-67 MOF **Figure 2**. The goal is to obtain quantitative amounts for to carry out Post-Synthetic Modification, which is a method for fractionalizing the linkers.

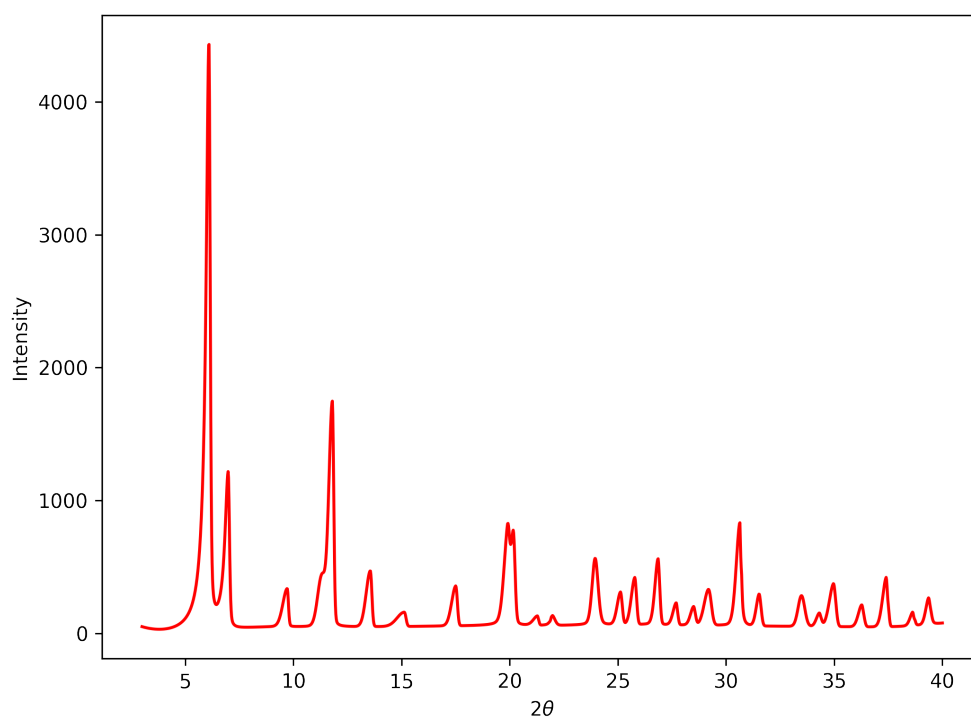


Figure 3 P-XRD of a UiO-67 Sample

4 Conclusion

Prior to this research experience, all what I knew about MOFs did not exceed the three pages or so found in a standard modern inorganic chemistry textbook. I still have a lot to learn. However, a lot has been learned about the solvothermal synthesis, separation, determination of some structural properties of Metal-Organic Frameworks. A little about, defect introduction, catalysis, sensing, MOF design and functionalization strategies. In the future, my aim is the synthesis of more functionalized MOF and carrying out their application in catalysis or sensing and perhaps carry out organic synthesis of sophisticated linkers.

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