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ZIF-8: NOVEL CATALYTIC MATERIAL FOR THE CONVERSION OF CO₂ TO CYCLIC CARBONATES

By
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A Dissertation Submitted to the J.B. Speed School of Engineering of the University of
Louisville in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

Department of Chemical Engineering
University of Louisville
Louisville, Kentucky

December, 2013

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ZIF-8: NOVEL CATALYTIC MATERIAL FOR THE CONVERSION OF CO₂ TO CYCLIC CARBONATES

By
Minqi Zhu

A Dissertation Approved on
November 14, 2013

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DEDICATION

Delicated to my parents

Jianlin Zhu and Shengying Huang

and

Friends

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First, I would like to thank my advisor, Professor Moises A. Carreon for helping me pursue my passion in chemical engineering research. He has given freedom at exploring the unknown in research, while providing sufficient guidance to keep me from getting lost. I greatly appreciate his professional training in doing research and academic writing.

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Lastly, I want to thank my family and friends for being there for me and for having faith in me.

ABSTRACT

ZIF-8: NOVEL CATALYTIC MATERIAL FOR THE CONVERSION OF CO₂ TO CYCLIC CARBONATES

Minqi Zhu

November 14, 2013

The effective utilization of CO₂ as a renewable raw material for the production of useful chemicals is an area of great interest. There are several motivations for producing chemicals from CO₂ whenever possible: (1) CO₂ is a cheap, non-toxic and non-flammable feedstock that can frequently replace toxic chemicals such as phosgene or isocyanates; (2) CO₂ is a totally renewable feedstock compared to oil or coal; (3) the production of chemicals from CO₂ can lead to totally new materials such as polymers; (4) new routes to existing chemical intermediates and products could be more efficient and economical than current methods; and (5) the production of chemicals from CO₂ could have a small but significant positive impact on the global carbon balance.

In particular, the catalytic conversion of CO₂ into cyclic carbonates, which are useful chemical intermediates employed for the production of plastics and organic solvents, represents an attractive route for the efficient use of carbon dioxide. The development of superior performance catalysts requires novel materials with fundamentally different structural, compositional, adsorption and transport properties than those of conventional zeolites, metal oxides or metal phases which have been used

in the past for CO₂ conversion to carbonates. In this respect, metal organic frameworks have emerged as a novel type of crystalline porous materials, which combine highly desirable properties, such as uniform micropores, high surface areas, flexible chemistries, and exceptional thermal and chemical stability, making them ideal candidates for catalytic applications.

Particularly, zeolitic imidazolate framework-8 (ZIF-8) is an appealing metal organic framework that could be used as catalyst for the conversion of CO₂ into carbonates. The Lewis acid sites, associated with Zn²⁺ in ZIF-8 structure, are known to catalyze the coupling reaction of CO₂ and epoxides. The basic sites in organic linker attract CO₂ to be trapped in the structure. With the active catalytic site and promoted CO₂ adsorption capacity, ZIF-8 could potentially be an effective catalyst for the conversion of CO₂ to cyclic carbonates. The intellectual thrust of this proposal is the rational design of ZIF-8, which offers the possibility of demonstrating high catalytic performance for CO₂ conversion to cyclic carbonates.

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CHAPTER 1

INTRODUCTION

1.1. Importance of Carbon Dioxide Conversion

It is more of a common sense now than ever that it is important for us to utilize renewable resources to maintain a sustainable society. In the meantime, the combustion of fossil fuels, including coal, petroleum and natural gas for electricity production and transportation, leads to the well-recognized problem of global warming which was believed to be the results from excess carbon dioxide emission. The world energy consumption by fuel types was summarized in Figure 1.1.¹ It is projected that the world consumption of marketed energy from all fuel sources will have an increase through 2040 and fossil fuels will remain the main source of the energy used worldwide. The carbon dioxide emissions from different energy sources derived from fossil fuels are indicated in Figure 1.2.¹ While a total increase of 46 percent was projected, the carbon dioxide emission from coal-burning has the largest increase. With strong economic growth and continued heavy reliance on fossil fuels expected for most non-OECD economies under current policies, much of the projected increase in carbon dioxide emissions occurs among the developing non-OECD nations. In 2010, non-OECD emissions exceeded OECD emissions by 38 percent; in 2040, they are projected to exceed OECD emissions by about 127 percent.

Figure 1.1. World energy consumption by fuel types ¹

Figure 1.2. World energy related carbon dioxide emissions by fuel types ¹

The temperature increase worldwide has brought people's attention to focus on searching for ways to reduce the concentration of carbon dioxide at

atmosphere. The main human activity that emits CO₂ is the combustion of fossil fuels (coal, natural gas, and liquids) for energy and transportation, although certain industrial emissions in the United States are described in Figure 1.3.²

Figure 1.3. US carbon dioxide emissions by source²

Electricity is a significant source of energy in the United States. The production of electricity generated about 38% of total U.S. Carbon dioxide emissions in 2011, which made it the largest source of CO₂ emissions in the nation. Different types of fossil fuel used to generate electricity will emit different amounts of CO₂ and burning coal will produce more CO₂ than oil or natural gas. The combustion of gasoline and diesel to run an automotive vehicle is the second largest source of CO₂ emissions, accounting for about 31% of total U.S. carbon dioxide emissions in 2011. Many industrial processes emit CO₂ through fossil fuel combustion or chemical reactions. Fossil fuel combustion from various

industrial processes accounted for about 14% of total U.S. CO₂ emissions in 2011.²

Many strategies, such as energy efficiency, energy conservation, fuel switching and carbon capture and sequestration, were developed to reduce CO₂ emissions applying to homes, businesses, industry, and transportation.² With the rapid increase of carbon dioxide concentration at atmosphere, more fundamental and effective approaches should be employed to reduce carbon dioxide content in surrounding air. The effective utilization of CO₂ as a renewable raw material for the production of useful chemicals is an area of great interest. There are several more merits for producing chemicals from CO₂ besides environmental purpose: (1) CO₂ is a cheap, non-toxic and non-flammable feedstock that can frequently replace toxic chemicals such as phosgene or isocyanates; (2) CO₂ is a totally renewable feedstock compared to oil or coal; (3) the production of chemicals from CO₂ can lead to totally new materials such as polymers; (4) new routes to chemical intermediates and products could be more efficient and economical than current methods; and (5) contribute to a positive carbon balance.

1.2. Transformation of Carbon Dioxide

Although carbon dioxide is a renewable resource and has the advantages of being nontoxic, abundant, and economical, few industrial processes utilize CO₂ as a raw material. Because CO₂ is the most oxidized state of carbon, it has a very low energy level, therefore, it is hard for industry to establish a process utilizing CO₂ as a raw material. In other words, a large amount of energy is required to transform CO₂. There are four main methodologies to transform CO₂

into useful chemicals: (1) Using high-energy starting materials such as hydrogen, unsaturated compounds, small-membered ring compounds, and organometallics; (2) Choosing oxidized low-energy synthetic targets such as organic carbonates; (3) Shifting the equilibrium to the product side by removing a particular compound; and (4) Providing physical energy such as light or electricity.³

Figure 1.4. Types of CO₂ conversion as a raw material³

Varies of approaches have been developed over the years to convert carbon dioxide to useful chemicals or chemical products with the consideration of reaction efficiency and economic efficiency, as shown in Figure 1.4, such as CO₂ reductions under photo irradiation/electrolytic conditions, or in the production of synthesis gas by reforming natural gas with CO₂.³ CO₂, which is primarily the result of carbonaceous fuel oxidation or combustion is so thermodynamically and kinetically stable, that requires noticeable energy input and catalysis for its reduction. On the other hand, due to the electron deficiency of the carbonyl carbons, CO₂ has a strong affinity toward nucleophiles and electron-donating

reagents, which means that CO₂ can rapidly react with basic compounds. For example, organometallic reagents such as Grignard reagents readily react with CO₂ even at a low temperature.

1.2.1. Chemical CO₂ Transformation

Carbon dioxide transformation through chemical reaction can be achieved by hydrogenation and non-hydrogenation methods. Hydrogen is a high-energy material and can be used for CO₂ transformation as the reagent. The main products of CO₂ hydrogenation can fall into two categories — fuels (CO, CH₃OH and etc.) and chemicals (Hydrocarbons, formic acid and etc.).⁴ Both homogeneous and heterogeneous catalysts have been used to hydrogenate CO₂.⁵⁻⁷ Homogeneous catalysts exhibit desirable activity and selectivity with a problem of the recovery and regeneration of the catalysts. Meanwhile, heterogeneous catalysts are preferable in terms of stability, separation, handling, and reuse, as well as reactor design, which reflects in lower costs for large-scale productions.^{6,8-11} To take the advantages of both catalysts, new processes have been developed including the immobilization of homogeneous catalysts, exploitation of novel heterogeneous catalysts, and the use of green solvents such as ionic liquids and supercritical CO₂.¹³⁻¹⁵ In the past decades, the catalytic hydrogenation of CO₂ to produce HCOOH, CH₃OH, or CH₄ has been considered the promising route of CO₂ utilization.¹² However, the limited hydrogen supply restricted their large-scale application.

Alternatively, chemicals with higher value, such as carbonates and carbamates, can be obtained from CO₂ transformation through non-

hydrogenation route. Both linear carbonates and cyclic carbonates can be obtained through chemical reaction. Detailed introduction will be presented in section 1.2.7.

1.2.2. Photochemical CO₂ Transformation

Photoreduction of CO₂ is one of the most alluring methods for CO₂ conversion due to the abundance and free access of sunlight, which typically requires a photosensitizer, a catalyst and an electron donor. Photochemical carbon dioxide reduction harnesses solar energy to convert CO₂ into higher-energy products. It is a promising future technology since CO₂ can be reduced to useful compounds by solar energy at room temperature and ambient pressure. Possible reduction products including CO, HCOOH, HCHO, CH₃OH or CH₄, have been obtained by photoreduction of CO₂.¹⁶ While there is environmental and economic interest in producing artificial systems that are efficient photocatalysts, the low turn-over rates of current methods have prohibited wide-scale industrial application.

1.2.3 Electrochemical Conversion of CO₂

A number of chemicals were reported as products from CO₂ conversion through different electrochemical approaches, including carbon monoxide, formate, and methane etc.^{17,18} In an electrochemical transforming reaction of CO₂, catalyst design, electrolyte choice and electrode structure are essential to achieve the maximum conversion. The electrocatalyst carries out two important tasks: controlling the transportation of the electrons between electrodes and accelerates the reaction towards to the products.¹⁹ It is important for an effective

electrocatalyst to be fast at both tasks. In addition to activity, the catalyst needs to be highly selective to the desired products while suppressing unwanted reactions. Furthermore, effective removal of products from the catalyst layer to avoid blocking active sites plays an important role in getting continuous conversion. In addition, electrodes and electrolytes that have high conductivity and allow for sufficient mass transport of the reactants and products to/from the catalyst layers are required in order for the reaction to be performed in an efficient manner.²⁰

1.2.4. Biological Conversion of CO₂

Biological CO₂ conversion is the conversion of carbon dioxide to organic compounds by living organisms, the most prominent example of which is photosynthesis. The utilization of algae/microalgae in the conversion of CO₂ to biomass was studied abundantly.²¹⁻²⁶ Algae can be thought of as marine and freshwater plants that have higher photosynthetic efficiencies than terrestrial plants and are more efficient capturing carbon.²¹ It is found that high CO₂ concentrations promote the growth speed of some strains of green algae capable of growing rapidly under²³⁻²⁵ and increase the production of high value biomolecules.²⁶ It is important to select a strain of algae with a high CO₂ fixing rate, a rapid growth rate and easy cultivation on a large scale in order to generate a large biomass yield.²⁷ The produced biomass can subsequently be converted into biofuels, bio-chemicals, food or animal feed. These useful by-products provide revenue to finance the carbon mitigation process.

1.2.5. CO₂ Conversion through Reforming

CO₂ can be converted to synthesis gas (mixture of carbon monoxide and hydrogen) by reforming, in which CO₂ reacts with hydrocarbons, most commonly, methane. Ni-based catalysts,^{28,29} noble metal catalysts,³⁰ transition metals³¹ and the group VI transition metal carbides^{32,33} were reported to effectively catalyze this reaction. In general, the catalyst is a metal and a catalyst support is required for this reaction to happen, which normally is an oxide, such as SiO₂, Al₂O₃, MgO etc. Both of the two components play important roles during the reforming process. While the active sites on metal promote the reaction to happen, it is the oxide where the CO₂ activation step actually took place.³⁴ A novel bimodal catalyst support was proposed,³⁵ where small pores are formed inside large ones. Large pores enhance the mass transfer rate, while small pores provide large surface areas to disperse active metallic nanoparticles. The building materials for small pores can also be used as promoters or cocatalysts to further enhance the total activity and stability. Furthermore, Bi-reforming³⁶ and tri-reforming³⁷ were also used in the CO₂ conversion process.

1.2.6. CO₂ Conversion to Inorganic Chemicals Using Plasma

Plasma-assisted CO₂ conversion has been researched over the past a few years.³⁸⁻⁴¹ To overcome the inert character of CO₂, gas discharges are used to let the electrons activate the molecules, so that the vibrational excitations stimulate the dissociation and the electronic excitations stimulate ionization. The atmospheric pressure dielectric barrier discharge (DBD) was chosen as the experimental setup. Such discharge has a great ease of implementation.

Operating at atmospheric pressure avoids leakage problems due to large pressure differences between the inside and the outside and in practice such discharges can be implemented just as a sophisticated tube.³⁸

Previous research has confirmed that the CO₂ plasmas can generate a plentiful of active oxygen species and other active plasma species for further reaction with other reactants, like methane, low alkanes and others. These reactions lead to a formation of more valuable chemicals, like ethylene, propylene and oxygenates.³⁹ The yield of alkenes achieved has been competitive to that of the conventional catalytic dehydrogenation of low alkanes.³⁹

The effects of discharge frequency, power input, gas temperature and feed flow rates on the formation of CO and O₂ from pure CO₂.⁴⁰ It is shown that the most important parameter affecting the CO₂ conversion levels is the gas flow rate. At low flow rates, both the conversion and the CO yield are significantly higher. In addition, also an increase in the gas temperature and the power input give rise to higher conversion levels, although the effect on the CO yield is limited. The optimum discharge frequency depends on the power input level and it cannot be unambiguously stated that higher frequencies give rise to increased conversion levels.

1.2.7. CO₂ Conversion to Carbonates/Carbamates through Chemical Reaction

Organic carbonates are roughly categorized into cyclic and linear carbonates.⁴² Linear organic carbonate can be synthesized by reacting CO₂ with

alcohol or phenols (Figure 1.5 a). However, the equilibrium for this reaction is located on the left side of the equation. In order to avoid this thermodynamic limitation, it is necessary to remove water from the products using an adequate drying agent or to increase the CO₂ concentration by pressurizing CO₂. Cyclic carbonates, commonly used as electrolyte in lithium ion batteries as well as environmentally friendly solvents and degreasers, can be easily obtained by reacting CO₂ and epoxides (Figure 1.5 b). Homogeneous catalysts, such as quaternary ammonium salts,^{43,44} were used to produce cyclic carbonates. However, the reaction in these processes is typically carried out at elevated temperatures in around 180 °C and pressures higher than 8 atm. Additional energy is required to separate the catalyst from the product after reaction. Aluminum and zinc metal complexes, dialkyltin methoxide and organoantimony halides^{42,45} that also catalyze this reaction, are very poisonous, water/air sensitive, causing handling problems and requiring high temperature and pressure. Nontoxic catalysts, such as phthalocyanines,⁴⁶ porphyrines,⁴⁷ and Schiff bases,⁴⁸ require a co-catalyst in this reaction, in order to achieve moderate to high conversion. For Mg/Al oxide based catalysts,⁴⁹ large amounts of catalyst and long reaction time are necessary for reasonable CO₂ conversion. Zeolites^{50,51} and mesoporous ordered oxides⁵² also catalyze this reaction. However, high temperature and high pressure are required for this reaction to achieve desirable carbonates yield. Normally, a co-catalyst and/or solvent is added to get high conversion and selectivity. Metal organic frameworks (MOFs)⁵³⁻⁵⁶ have emerged as a novel class of catalysts with high activity. These materials

are different with conventional zeolites, metal oxides and metal phases in structure, composition, adsorption and transport properties. They are crystalline microporous materials with highly desirable properties, such as uniform micropores, high surface areas and open porous framework structures with large accessible pore volumes, which make them potentially interesting candidates for catalytic applications.

Figure 1.5. Schematic showing the conversion of CO_2 to (a) linear and (b) cyclic carbonate

Carbamates are widely used as intermediates of agrichemical, pesticide, herbicide and pharmaceutical agents,⁵⁷⁻⁵⁹ solvents,⁶⁰ and chiral auxiliaries.^{61,62} They can be easily synthesized by amines, CO_2 and alcohols (or alkyl halides). Both homogeneous and heterogeneous catalysts were reported to be effective in this reaction. Organic and inorganic bases, crown ethers, and cryptands⁶³⁻⁶⁶ catalyze this reaction. However, these homogeneous catalysts will cost extra energy and effort to be separated from the product. Heterogeneous catalysts, such as, zeolite-encapsulated metal complexes and titanosilicates also catalyze

this reaction very efficiently.⁶⁷ However, a solvent was required for the reaction to achieve high carbamate yields. Adenine-modified Ti-SBA-15 solid catalysts⁶⁸ had excellent catalytic performance at low temperature (80 °C) and low pressure (3.4 bar) under solvent-free conditions. However, the procedure to make the catalyst is long and lack of energy efficiency. Therefore, it is important to find a cheap and easy-made catalyst with properties fundamentally superior than the existing ones. MOFs with ordered structure, large surface area and accessible pores, are promising materials for catalysis application.

1.3. Motivation for This Work

Currently, there are several approaches to convert CO₂ to useful chemicals, each of which has its own disadvantages. The chemical conversion of CO₂ to carbonates and carbamates could be the easiest route for carbon dioxide reduction. The major problem is the lack of a catalyst, which is cheap, active at low temperature and pressure with good recyclability. The development for the catalyst to maintain an excellent performance in repeating operation is still a challenge. Herein, we propose a metal organic framework, namely zeolitic imidazolate framework-8 (ZIF-8), for CO₂ conversion to carbonates and carbamates. In particular, the proposed research has practical implications in environmental issues: (1) reducing CO₂ concentration at atmosphere; and (2) eliminate the usage of toxic phosgene during organic carbonates and carbamates production. The proposed work may also have an important economic impact in reducing the operation costs since it is supposed to operate at low temperature and pressure.

1.4. Dissertation Organization

In the first chapter, the importance of CO₂ conversion and different CO₂ transformation approaches are discussed. The motivation and objectives of this work are also stated in this chapter. The organization of this dissertation is outlined.

In the second chapter, a brief introduction of metal organic frameworks (MOFs) is given. The structures of representative porous catalysts (both crystalline and amorphous materials) from different categories and their catalytic performances in the conversion of carbon dioxide to cyclic carbonates are discussed. The introduction of ZIF-8 crystals synthesis and functionalization is presented.

In chapter three, experimental details on the preparation of ZIF-8 crystals by different approaches are described. The experimental procedure to functionalize ZIF-8 is introduced. The characterization of the fresh and used catalysts is discussed. The calculations of the conversion of the epoxide and the selectivity to carbonate are explained.

In chapter four, the formation of ZIF-8 as a function of time at room temperature employing zinc carbonate basic as the metal source is studied. The kinetics of transformation of ZIF-8 is discussed. Furthermore, the synthesis of ZIF-8 using zinc foils as both substrate and reagent is demonstrated. A detailed analysis of the ZIF-8 crystal is presented. A growth mechanism of the crystals is hypothesized.

In the fifth chapter, the catalytic activity of ZIF-8 in the conversions of CO₂ to styrene carbonate and chloropropene carbonate are evaluated. Possible reaction mechanisms of these two reactions are proposed. The performances of the recycled catalysts are portrayed. An improved catalytic performance by the functionalized ZIF-8 is demonstrated.

The last chapter consists of relevant conclusions obtained from the previous study and recommendations for future work to improve the activity of the catalyst, to employ ZIF-8 in the conversion of CO₂ to carbamates, and to explore the catalytic activity of different ZIFs in the conversion of CO₂ to carbonates.

1.5. Objectives of This Work

The ultimate goal of this work is the rational design of a metal organic framework catalyst (ZIF-8), which offers the possibility of converting carbon dioxide into cyclic carbonates. The specific objectives of this work include:

- (1) Rational design of alternative synthesis methods for ZIF-8 catalysts.
- (2) Understand the basic formation mechanism steps directing the synthesis of ZIF-8 crystals.
- (3) Study the catalytic performance of ZIF-8 crystals in the conversion of CO₂ into cyclic carbonates.
- (4) Establish fundamental structure/catalytic relationships of ZIF-8 catalysts in the conversion of CO₂ into cyclic carbonates.

CHAPTER 2

BACKGROUND

Zeolitic imidazolate frameworks (ZIFs) are emerging functional porous materials with various applications, including catalysis. In this chapter, general introduction to ZIFs is presented. The importance of ZIF-8 and a detailed description is also given. The advantage of functionalized porous material is discussed. Then, we compare the catalytic activity of different porous catalysts, including zeolites, MOFs, mesoporous materials and porous polymers.

2.1. Introduction to ZIFs

The demand for an efficient catalyst for CO₂ conversion is arising. MOFs, emerging as a new type of functional materials with desired features, such as ordered crystalline structure, high surface area, etc., have caught the attention of the scientific community. Unlike the rigid inorganic materials, the combination of organic and inorganic building blocks offer enormous flexibility in crystal structure, pore size and pore shape. These materials cover a much larger range of pore sizes than zeolite, even bridging micro and mesoporous materials and they have a larger adsorption capacity than the established porous materials, namely activated carbon and zeolites. More importantly, the unique structure of MOFs provides more opportunities to functionalization and grafting. MOFs can be easily made in an inexpensive approach to obtain crystals with high purity.

There are two main components in a MOF: metal ions or clusters and organic linker, which coordinate with each other to form one-, two, three-dimensional structures that can be porous. The main properties of MOFs are ordered structures, porous crystals with defined shapes and dimensions and large surface areas. MOFs are very attractive materials for gas storage, gas separation, ion exchange, separation, and polymerization, as well as catalysis.

Figure 2.1. Similarity of Zn-Im-Zn bridge in ZIFs and the Si-O-Si bridge in zeolites ⁷⁵

ZIFs are a subclass of MOFs with topologies resembling that of zeolites. The zeolite-type structures of ZIFs: SOD, CAG, MER, CRB, DFT, GIS, RHO, GME and ITA have been reported. ⁶⁹ ZIFs can be synthesized hydrothermally in a solution with a metal source and imidazole linker material. They are microporous materials possessing advantages from both zeolites and MOFs, such as crystallinity, unimodal micropores, high surface areas, polar walls and excellent thermal and chemical stability. ⁷⁰⁻⁷⁴ Typically, ZIFs are composed of Zn, Co or Cu atoms linked through N atoms by ditopic imidazolate (Im) or functionalized Im linkers to form neutral frameworks and to provide tunable nanosized pores. The pores are formed by four-, six-, eight-, and/or twelve-membered rings of ZnN₄, CoN₄ or CuN₄ tetrahedras. ^{70,75,76} Coincidentally, the metal-imidazole-metal angle in ZIFs structure is similar to the 145° Si-O-Si angle

in zeolites, as shown in Figure 2.1.⁷⁶ Emerging functional applications of ZIFs in gas separation,^{77,78} catalysis,^{53,79} and sensing⁸⁰ have been recently reported.

2.2. ZIF-8 Importance and conventional synthesis approaches

ZIF-8, with a molecular formula of $\text{Zn}_6\text{N}_{24}\text{C}_{48}\text{H}_{60}$, is one of the most studied prototypical ZIF compounds⁸¹⁻⁸⁴ due to its distinct properties, which are especially suitable for applications like catalysis, gas separation and storage. It has a sodalite (SOD) zeolite-type structure (Figure 2.2)⁸⁵ with microporous structure formed by four- and six-membered rings of ZnN_4 clusters by connecting zinc tetrahedras and imidazole bridges (Figure 2.3). ZIF-8 framework, displaying larger pores of diameter 11.6 Å and smaller pores of 3.4 Å, has cubic space group (I-43m) with unit cell dimensions of 16.31 Å.^{75,81,82} Interestingly, the kinetic diameter of CO_2 is 3.3 Å, which allows it to easily enter and pass through the smaller 3.4 Å aperture. ZIF-8 has a high CO_2 adsorption capacity due to its highly porous open structure, large accessible pore volume with fully exposed edges and faces of the organic linkers. The basic sites associated with imidazole groups in the ZIF-8 structure tend to attract more CO_2 to be trapped in the vacant space inside the pores. Studies have shown that the linker in ZIF-8 leads to the high adsorption selectivity of CO_2 when mixed with methane, nitrogen or oxygen. Lewis acid sites (associated with zinc atoms) are known to catalyze the reaction of CO_2 with epoxides to give cyclic carbonates and other precursors of polycarbonate.^{50,52,68}

Figure 2.2. Optimized three-dimensional views of the ZIF-8 structure. Nitrogen, carbon and hydrogen atoms are shown in blue, light grey and white, respectively; (a) viewed along axis [001], (b) viewed along axis [111], (c) ZIF-8 sodalite-type cage, (d) SOD topology, and (e) 6-membered-ring window.⁸⁵

Figure 2.3. Schematic representative of ZIF-8 formation. ZnN_4 tetrahedra are blue, C, and N atoms are black and green spheres. H atoms are omitted for clarity. The yellow sphere represents the largest sphere that occupies the cavity without contacting the interior van der Waals surface.

Based on the superior properties of ZIF-8, such as high surface area, unimodal pore size, high CO₂ adsorption capacity and the appearance of Lewis acid sites and basic sites, it could be a very promising candidate in the application of catalysis. So far, ZIF-8 has been reported to be active for many catalytic reactions including the dehydrogenation of dimethylamine borane,⁸⁶ transesterification of vegetable oil,⁸⁷ the Knoevenagel reaction,⁸⁸ the Friedel-Crafts acylation⁸⁹ the coupling reaction of CO₂ and the epoxides.^{53,90}

ZIF-8 was first synthesized solvothermally by Park et. al. in 2006, by combining zinc nitrate tetrahydrate and 2-methylimidazole in dimethylformamide (DMF) solution under conventional heating.⁷⁵ Since then, a great number of researches have been done to explore the possibilities of ZIF-8 synthesis in respect to further application. Other than conventional heating, Bux and coworkers⁹¹ reported the synthesis of ZIF-8 using microwave heating and Li et. al.⁹² introduced the method employing ultrasound in ZIF-8 synthesis. Different solvents, such as methanol⁹¹ and water⁹³, have been employed in ZIF-8 synthesis. Different precursors, including zinc chloride, zinc acetate, zinc sulfate⁹⁴ and zinc carbonate basic⁹⁵ were reported to be able to synthesize ZIF-8. The molar ratio of Zn and imidazole determines the crystallinity of the final product. It is found that an excess of 2-methylimidazole is necessary for achieving highly crystalline ZIF-8. The synthesized crystals have particle sizes ranging from 50 nm⁸² to ~150 μm⁷⁵ and a large surface area varying from 900 – 1600 m²/g⁷⁵. Although, a lot of effort has been made on the research of ZIF-8, it is still challenging to consistently produce ZIF-8 crystals with small crystal size

and narrow particle size distribution, which may lead to a larger accessible surface area, reduced diffusion resistance and increased adsorption capacity phases. It will be very likely to have a positive impact on its catalytic performance.

2.3. Functionalization of ZIF-8

It is essential for a catalyst to have a high carbon dioxide uptake in the CO₂ conversion reaction. The high surface area, accessible large pores and the polar nature of the pore walls lender a high CO₂ adsorption capacity of ZIF-8. The increase of CO₂ uptake in ZIF-8 can possibly lead to a maximum efficiency of ZIF-8 as a catalyst. One of the industrially established methods of CO₂ capture involves basic aqueous solutions of alcoholic amines, such as, monoethanolamine and triethanolamine etc.⁹⁶, known as CO₂ scrubbing. Inspired by this technology, amine groups have been incorporated into a number of solid supports, including zeolites,⁹⁷ MOFs^{98–101} and mesoporous silica⁵², to improve their CO₂ adsorption capacity by exploiting the efficient amine-CO₂ interactions for different applications, such as gas separation⁹⁸⁻¹⁰⁰ and catalysis^{68,101}. Porous materials have the potential to tailor their pore systems, including pore size, volume and connectivity, and to incorporate functional groups into their linkers, which makes them attractive materials that can be exploited as catalysts for CO₂ conversion. For example, the amine-functionalized Ti-SBA-15 was found to be very effective in the coupling reaction of CO₂ and epoxides to cyclic carbonates, while unmodified Ti-SBA-15 is only slightly active in the same type of reactions.⁶⁸ A big increase of carbonate yield occurred when amine-functionalized ZIF-8 was

employed in the reaction to synthesis chloropropene carbonate from carbon dioxide.⁹⁰

2.4. Different Porous Materials for CO₂ Conversion to Cyclic Carbonates

Cyclic carbonates are important intermediates for the synthesis of useful chemicals, which are currently manufactured with the highly toxic phosgene. A green alternative route for the synthesis of cyclic carbonates is the insertion reaction of CO₂ into the CAO bond of an epoxide (Figure 1.5b). Different catalysts were studied for this type of reaction as introduced in Chapter 1. However, It stills remains a challenge to find an effective and cheap catalyst with high carbonates yield and easy recycling. Porous materials, including zeolites, MOFs, mesoporous silica and porous polymer are emerging new catalysts found to be effective for catalyzing these cycloaddition reactions. They possess many desirable properties, which make them appealing for cycloaddition reactions. In general, these porous materials are chemically and thermally stable and have moderate to high CO₂ uptakes with an open porous structure for improved mass transfer. They have acid sites, which are known as actives sites for cycloaddition reactions inside their structures and high specific surface areas. Figure 2.4 shows representative structures of zeolites, MOFs, and mesoporous oxides. In the following paragraphs, representative examples with decent catalytic performance of each of these porous materials will be discussed regarding their structures and catalytic performances. Then, the fundamental structure/catalysis relationships of these porous phases in the conversion of CO₂ into cyclic carbonates are highlighted.

Figure 2.4. Typical structures of the (a) zeolite, (b) MOF, and (c) mesoporous oxide.

2.4.1. Zeolites Catalysts

Zeolites (microporous crystalline aluminosilicate or silica polymorphs forming three-dimensional frameworks with uniformly sized pores of molecular dimensions) are promising materials for the catalysis of the conversion of CO_2 into cyclic carbonates.^{50,51,102} For example, zeolite beta was found to have high catalytic activity in the cycloaddition reaction of CO_2 to epoxides to form cyclic carbonates.⁵⁰ Zeolite beta is a type of aluminosilicate molecular sieve consisting of a three-dimensional channel system composed by straight and zigzag channels with 12-membered rings as the minimum constricting apertures.¹⁰³ It has a large surface area of at least $600 \text{ m}^2/\text{g}$,¹⁰⁴ and the 12-membered ring has dimensions of $0.66 \times 0.67 \text{ nm}^2$ (straight channel) and $0.56 \times 0.56 \text{ nm}^2$ (tortuous channel), shown in figure 2.5.¹⁰⁵

Figure 2.5. Illustration of zeolite beta framework. ¹⁰⁵

Zeolite beta exhibited high activity for catalyzing different oxiranes, such as epichlorohydrin, propene oxide, styrene oxide, and n-butene oxide, to cyclic carbonates with CO₂ as a raw material. More importantly, this reaction did not require any cocatalyst or solvent. High yields of cyclic carbonates were obtained under mild reaction conditions (120 °C and 6.9 bar). The zeolite beta catalyst maintained its excellent catalytic activity even after eight cycles; this confirmed the typical remarkable zeolite chemical and thermal stability. Researchers found that in the case of the as-synthesized catalyst, the template ion Et₄N⁺ (which is an active alkyl group in one of the homogeneous quaternary ammonium halide catalysts) may have been responsible for the superior catalytic activity of the as-synthesized zeolite beta. In addition, the as-synthesized zeolite beta also had a high adsorption of oxirane and a high amount of activated CO₂. Hence, the greater availability of activated reactant molecules could have also been another

possible reason for the superior activity of the as-synthesized form of zeolite beta. Interestingly, when the organic template was removed by calcination, both the catalytic activity and selectivity for cyclic carbonates were drastically reduced.

2.4.2. Mesoporous Silica Catalysts

Several ordered mesoporous materials, exhibiting pore sizes in the 2–50 nm range, were reported to catalyze the cycloaddition of CO₂ and epoxides to yield cyclic carbonates.^{49,106} MCM-41 is one of these that achieve decent conversion.¹⁰⁶ It was first synthesized by Kresge et. al. by a liquid-crystal templating mechanism in 1992, as shown in Figure 2.6.¹⁰⁷ In its structure, amorphous silica forms hexagonal tubes with uniformly sized mesopores (pore diameter 3 nm). The width of the tubes can be controlled to be within 2 to 10 nm with template molecules of different lengths.¹⁰⁸ The tubes connect to each other through the sharing of the silica walls. MCM-41 has properties such as a high thermal and hydrothermal stability, uniform size and shape of the pores, and large surface area (1000 m²/g).¹⁰⁹ It is an interesting candidate for use as a catalyst for its thermal and hydrothermal stability, uniform size and shape of the pores, and large surface areas.¹¹⁰⁻¹¹³

Figure 2.6. Scheme of the liquid-crystal templating mechanism. Silica source and surfactant form hexagonal arrays of cylindrical micelles. Then the silicate species occupy the space between the cylinders. The final calcination step removes the surfactant leaving hollow cylinders.

For the cycloaddition reaction, it was found that when MCM-41 was used as a catalyst, the carbonate yield increased with increasing temperature and pressure until it reached a maximum. The optimal conditions for higher carbonate yield were found to be 120 °C and 6.9 bar. Noticeably, this reaction achieved high carbonate yields with less catalyst than most reported heterogeneous catalysts. The catalytic ability of MCM-41 decreased after the fifth cycle. According to X-ray diffraction patterns of recycled MCM-41, the catalyst started to lose its crystallinity after the fifth cycle; this could have been the reason for the reduced catalytic performance. It is also important to highlight that the catalyst was not calcined. The as-synthesized MCM-41 contained cetyltrimethylammonium cations as the template, which was likely to act as active sites for the

cycloaddition reaction.

2.4.3. MOF Catalysts

Several MOFs have been effectively used as catalysts in the cycloaddition of CO₂ into epoxides to form cyclic carbonates.^{54,56,114-118} Most of them exhibit moderate to high yield to desired carbonates. For example, the catalytic activity of Cu₃(BTC)₂ was demonstrated in the synthesis of chloropropene carbonate from CO₂ and epichlorohydrin.⁵⁴ Cu₃(BTC)₂ has a three-dimensional twisted boracite framework composed of binuclear copper paddle-wheel units bridged by three-connecting btc ligands (Figure 2.7).¹¹⁹ The framework contains three different types of pores. One unit cell includes eight such small pores. The octahedral holes of a face-centered cubic (FCC) structure are a little larger, the inner surface of which is constructed from benzene rings of the trimesic acid with the six-fold axis of the rings pointing toward the pore center. The third type of pore is even larger, having the hydrogen atom of the trimesic linker pointing toward the pore center. Only the third type of pores has open copper coordination sites pointing into the pore. The pore diameters for these three types of pores are 4.9, 10.5, and 12.2 Å, respectively.¹²⁰ This MOF has a high BET surface area in the 1200–2100 m²/g range.¹²¹

No solvents or cocatalysts were required for this cycloaddition reaction. The catalysts displayed moderate epoxide conversions and moderate selectivities to chloropropene carbonate at 100 °C. Cu₃(BTC)₂ was catalytically selective to chloropropene carbonate only at 100 °C. Only diols of the epoxide and dimers of epichlorohydrin were observed below 100 °C. The chloropropene

carbonate yield at 100 °C was about 33%. The yield to chloropropene carbonate decreased from about 33% to about 23% when it was reused after the first reaction. The X-ray diffraction of the recycled catalyst showed that the $\text{Cu}_3(\text{BTC})_2$ structure was preserved; however, its framework had a greater degree of local structural disorder. Therefore, the reduced activity of recycled catalyst could be attributed, in part, to this local structural disorder and to active site/pore blocking by residual carbonaceous deposits formed during the reaction.

Figure 2.7. Front view and side view of $\text{Cu}_3(\text{BTC})_2$

We proposed that the Lewis acid copper(II) sites played an important role in catalyzing the cycloaddition of CO_2 to epichlorohydrin. In addition, the partial positive charges on the unsaturated copper metal sites of $\text{Cu}_3(\text{BTC})_2$ promoted the binding and activation of the polar carbon–oxygen bonds of carbon dioxide; this resulted in high CO_2 adsorption capacities. In fact, unsaturated copper metal sites have been identified by theoretical and experimental investigations as CO_2 adsorption sites.¹²² The CO_2 adsorption capacities for $\text{Cu}_3(\text{BTC})_2$ ranged from 8.0 to 12.7 mol/kg at room temperature and 15 bar.¹²³⁻¹²⁵ Therefore, the copper

acid sites promoted the adsorption of carbon dioxide on the solid surface and its further conversion to the carbonate. Although some MOFs showed to be catalytically active in the CO₂ cycloaddition reaction to cyclic carbonates, there are still important challenges remaining unsolved, such as the synthesis cost and stability.

2.4.4. Porous Polymer Catalysts

It is important to mention that conjugated microporous polymers (CMP) (porous materials with an extended π -conjugation in an amorphous organic framework) are effective catalysts for the conversion of CO₂ into cyclic carbonates.¹²⁶ Different from the previously mentioned catalysts, the microporous polymers are amorphous. For instance, cobalt- and aluminum-coordinated conjugated microporous polymers were reported to catalyze the CO₂ conversion to cyclic carbonates.¹²⁶ Figure 2.8 shows the structure and NMR spectrum of Co-CMP.

These polymers showed exceptional catalytic activity in the conversion of propylene oxide to propylene carbonate under mild experimental conditions. In the absence of co-catalyst nBu₄NBr (TBAB), the PO/CO₂ coupling reaction catalysed by Co-CMP yields only 6.7% PC after 48 h. However, catalysts that combined Co-CMP with a co-catalyst TBAB promoted the coupling reaction with an 81.5% yield at room temperature and atmospheric pressure. This is notably better than the 77.1% yield already described for the homogeneous catalyst Salen-Co-OAc. Enrichment of CO₂ concentrations near the catalytic centers

located in the pore structures of the CO₂-capturing heterogeneous catalyst likely explains enhanced performance of Co-CMP compared with Salen-Co-OAc.

Figure 2.8. (a) Three-dimensional view of Co-CMP in an amorphous periodic cell. (b) Solid-state ¹H-¹³C CP/MAS NMR spectrum of Co-CMP recorded at a spinning speed of 10 kHz.¹²⁶

Al-CMP also exhibited excellent catalytic activity under the same experimental conditions and catalyzed the coupling reaction with a yield of 78.2%. The catalytic performances of Co/Al-CMP and the catalysts currently used in industry for PO/CO₂ coupling, such as KI and KI/β-CD,¹²⁷ were compared. At atmospheric pressure and room temperature, KI and KI/β-CD exhibited poor catalytic activities with yields of 3.8% and 3.9%, respectively. Co-CMP and Al-CMP were much more active than the industrially available KI/β-CD and KI. High surface areas (800–965 m²/g, with an average pore size of 0.5 nm) and huge CO₂ uptakes were associated with the improved catalytic performance.¹²⁶

Although decent conversion can be achieved by using the above-

mentioned porous catalysts, there are several limitations making them less desirable materials to use as catalysts. They normally require high reaction temperature, high reaction pressure, long reaction times, and the presence of solvents and/or cocatalysts, etc. On the other hand, ZIF-8 can overcome these limitations based on its promising properties. Despite the high surface area, unimodal pore size and large carbon dioxide adsorption capacity, the bifunctional nature of ZIF-8 potentially could lead to highly active catalysts requiring lower reaction temperatures.

CHAPTER 3

EXPERIMENTAL APPROACHES AND METHODS

One of the main goals of this work is to find alternative approaches to synthesize ZIF-8 with more desirable features, such as small crystal sizes and narrow size distribution. In principle, catalysts with small crystal size will be more efficient in catalyzing the reaction since it enhance the surface area and accelerates the mass transfer rate. We explored two different methods to synthesize ZIF-8: synthesis employing zinc carbonate basic and synthesis at the liquid-solid interface. The two novel synthesis methods follow different crystal growth mechanisms. Another goal of this project is to explore the catalytic activity of ZIF-8 in the conversion of CO₂ to carbonates/carbamates and to improve its performance by the functionalization of the crystals with ethylenediamine. In this chapter, we describe in detail the different synthesis procedures of ZIF-8 and the techniques and equipments employed to characterize and evaluate the fresh and used ZIF-8 crystals.

3.1. Synthesis of ZIF-8 Crystals Using Conventional Approaches

ZIF-8 crystals can be synthesized both at room temperature or solvothermally at 150 °C, as shown in Figure 3.1. Zinc nitrate hexahydrate, (Zn(NO₃)₂·6H₂O, Fluka Analytical, ≥99%) was used as inorganic precursor, 2-methylimidazole (C₄H₆N₂, Sigma Aldrich, 99%) was used as organic linker, and

methanol (CH_3OH , Acros Organics, 99+%) was used as solvent. We carried out the synthesis of ZIF-8 using different synthesis approaches described in the next paragraphs.

Figure 3.1. Synthesis of ZIF-8 crystals at room temperature or solvothermally.

3.1.1. Room Temperature Synthesis

In a typical synthesis, 0.3 g of zinc nitrate hexahydrate was dissolved in 11 g of methanol. A solution consisting of 0.66 g of 2-methylimidazole and 11 g of methanol was added to the Zn-containing solution, and the mixture was vigorously stirred for 24 h to form a homogeneous mixture. The gel composition is $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}:\text{C}_4\text{H}_6\text{N}_2:\text{CH}_3\text{OH}=1:8:700$, as reported earlier.⁸² The resultant solid particles were separated from the solvent by centrifugation at 3000 rpm for 10 min and washed with methanol. The washing was repeated three times. The resultant ZIF-8 crystals were dried overnight at 100 °C.

3.1.2. Solvothermal Synthesis

The synthesis gel, the zinc – 2-methylimidazole – alcohol solution for the solvothermal synthesis of ZIF-8 crystals had the same composition as above. It was loaded in a teflon lined Parr stainless steel autoclave and heated under

autogenous pressure in a conventional oven at 150 °C for 5 hours. The resultant solid particles were separated from the solvent by centrifugation at 3000 rpm for 10 min, washed with methanol and dried overnight at 100 °C.

3.2. Synthesis of ZIF-8 Crystals Using Zinc Carbonate Basic

An alternative approach to prepare ZIF-8 crystals is as follows: 2.8 mmol of zinc carbonate basic ($[\text{ZnCO}_3]_2 \cdot [\text{Zn}(\text{OH})_2]_3$, Sigma Aldrich) were dissolved in 1.4 mol of methanol. A solution consisting of 64.4 mmol of 2-methylimidazole and 1.4 mol of methanol was added to the Zn based solution and vigorously stirred for different times. Finally, this solution was centrifuged at 3000 rpm, washed thoroughly with methanol and dried overnight at 100 °C.

3.3. Synthesis of ZIF-8 Crystals at the Liquid-Solid Interface

ZIF-8 can be grown from zinc foil in the presence of concentrated 2-methylimidazole alcohol solutions. The solution pH and reducing environment were identified as key parameters in the formation of a pure ZIF-8 phase. In a typical synthesis, 11*11 mm, 0.25 mm thick zinc metal foils (Fisher Scientific Company) (as shown in figure 3.2a) were used as both a reagent and a substrate for the direct growth of ZIF-8 crystals. Prior to the synthesis, the zinc foils were cleaned with ethanol and deionized water, respectively, for 5 minutes in an ultrasound bath.

For the synthesis of ZIF-8, a solution containing 0.66 g of 2-methylimidazole in 22 ml of methanol, or 2-propanol (Sigma-Aldrich) was loaded together with a zinc foil in a 250 ml stainless steel high pressure Parr reactor (Model 4576A) (Figure 3.3). The reactor was sealed and H_2 pressurized at 100

psia to create a reducing environment. The synthesis was carried out under stirring at 150 °C for 5 h. After reaction, the reactor was cooled down to room temperature, the foil was taken out, rinsed gently with the corresponding solvent and a white to yellowish layer formed on the surface of the zinc foil, as shown in Figure 3.2b. The foil will be dried overnight in the oven at 75 °C. Alternatively, the 2-methylimidazole – alcohol solution and the zinc foil were loaded in a teflon lined Parr stainless steel autoclave and heated under autogenous pressure in a conventional oven at 150 °C for 4 days. After this time, the autoclave was cooled down to room temperature, the foil was taken out, rinsed gently with the corresponding solvent and dried overnight.

Figure 3.2. (a) Pure zinc foil and (b) Zinc foil with a layer of ZIF-8 crystals

Figure 3.3 Stainless steel high pressure Parr reactor (Model 4576A)

3.4. Functionalization of ZIF-8 Crystals

The procedure to functionalize ZIF-8 crystals is as follows: 2 g of dry ZIF-8 was suspended in 30 ml anhydrous toluene (extra dry, water < 30 ppm, Acros). To this suspension, 0.75 mmol of ethylene diamine ($C_2H_8N_2$, Sigma Aldrich) were added, and the mixture was refluxed for 20 hours in the apparatus as seen in Figure 3.4. The functionalized crystals then was taken out, and dried overnight in the oven at 75 °C.

Figure 3.4. Reflux apparatus used to functionalize ZIF-8

3.5. Cycloaddition reaction: Synthesis of Cyclic Carbonates from CO₂ and Epoxides

3.5.1. Synthesis of Chloropropene Carbonate

In a typical cycloaddition reaction, 18 mmol of epichlorohydrin (Fluka Analytical, $\geq 98\%$) and 100 mg of ZIF-8 was placed in the same batch reactor described in section 3.3 (Figure 3.3). The reactor was pressurized with CO₂ (Welders Supply) at 7 bar, and the reaction was carried out at 70-100 °C for 4 h. After the reaction, the reactor was cooled to room temperature, the unreacted CO₂ was vented out, and the catalyst was separated by centrifugation. In the recycle experiments, the catalyst, after use in the cycloaddition reaction, was washed with ethanol and acetone, centrifuged and air dried before reuse.

3.5.2. Synthesis of Styrene Carbonate

Styrene oxide (SAFC, $\geq 97\%$) was used as a substrate to synthesize styrene carbonate. The molar ratio of styrene oxide and ZIF-8 and the procedure

of the experiment were similar to the one described in section 3.4. However, the reaction condition was different. After it was loaded with styrene oxide and ZIF-8 catalyst, the reactor was pressurized with CO₂ to 7 or 10 bar, and the reaction was carried out at 50–100 °C for 0.5-10 h. After the reaction, the reactor was cooled, the unreacted CO₂ was vented out, the catalyst was separated from reactants and washed with acetone for reuse.

3.6. Characterization of Fresh and Recycled ZIF-8 Crystals

Powder X-ray diffraction patterns were collected using a Bruker D8-Discover diffractometer at 40 kV and 40 mA with Cu K α radiation. The morphology of the ZIF-8 crystals was determined with a Field Emission Scanning Electron Microscope (SEM) (FEI Nova 600) with an acceleration voltage of 6 kV. Transmission electron microscopy (TEM) studies, including TEM imaging, selected area electron diffraction (SAED), and energy-dispersive X-ray spectroscopy (EDS), were performed using a FEI Tecnai F20 transmission electron microscope. A field emission gun (FEG) was used for the electron source and the studies were performed at the accelerating voltage of 200 keV. Samples for TEM analysis were prepared by dispersing the powders onto lacey-carbon coated copper TEM grids. The surface area and adsorption–desorption isotherm measurements were carried out on a Micromeritics Tristar 3000 porosimeter at 77 K using liquid nitrogen as coolant and the samples were degassed at 150 °C for 3 h before the measurements. Fourier transform infrared spectroscopy (BX FTIR, Perkin-Elmer) was used to determine the lattice vibrations in the ZIF-8 framework. The acidic and basic properties of fresh and

spent ZIF-8 catalysts were determined using NH_3 and CO_2 as probe molecules, respectively. In temperature-programmed desorption of ammonia (NH_3 -TPD; Micromeritics Auto Chem 2910 instrument), 0.1 g of the catalyst was taken in a U-shaped, flow-through, quartz sample tube. Prior to measurements, the catalyst was pretreated in He (30 ml/min) at 250 °C for 1 h. A mixture of NH_3 in He (10 vol%) was passed (30 ml/min) at 40 °C for 1 h. The sample was, then, flushed with He (30 ml/min) for 1 h. TPD measurements were carried out by raising the temperature from 40 to 250 °C at a heating rate of 5 °C/min. In the temperature-programmed desorption of carbon dioxide (CO_2 -TPD; Micromeritics Auto Chem 2910 instrument), a mixture of CO_2 in He (10 vol%) was passed (30 ml/min) over the activated catalyst for 1 h at 40 °C. The sample was, then, flushed with He (30 ml/min) for 1 h. The CO_2 -TPD measurements were carried out in the range 40 to 250 °C at a heating rate of 10 °C/min. From the areas of the desorption peaks and from the calibration curves generated prior to the analyses of the catalyst samples, the amount of acidic and basic sites present in the catalysts were determined. The quantitative analysis of elemental carbon, hydrogen, and nitrogen were carried out at Midwest Microlab. LLC, Indianapolis, IN. In diffuse reflectance infrared Fourier transform (DRIFT) spectral measurements, the samples were initially activated at 350 °C for 1 h in a flow of nitrogen. The temperature was brought down to 50 °C and pyridine was adsorbed. Then, prior to spectral measurements, any loosely bound pyridine was removed by flushing the sample with nitrogen for 0.5 h (spectral resolution = 2 cm^{-1} , number of

scans = 400). Difference FTIR spectra were obtained by subtracting the spectrum of the catalyst from that of the sample adsorbed with pyridine.

3.7. Evaluation of the Catalytic Activity of ZIF-8

The products from the catalytic reaction were analyzed by GC–MS (HP 5890 gas chromatograph equipped with 5970 mass selective detector, 30 m × 0.32 mm HP-5 column coated with 5% phenyl polysiloxane stationary phase) (Figure 3.5) to determine the conversion of the epoxide in terms of weight percentage. The temperature ramp rate during the gas chromatographic analysis was 70–220 °C at 15 °C/min.

Figure 3.5. GC/MS used to analyze product composition.

After analysis, a report with data of the composition will be obtained, which the percentage of each reactant and each product will be listed. The conversion and selectivity can be calculated from these data. The conversion of the epoxide can be calculated by the following equation,

$$C = 1 - x$$

where C is the conversion of epoxide and x is the percentage of the unreacted epoxide in the products mixture. The selectivity can be calculated as follows,

$$S = \frac{y}{1 - x}$$

where S is the selectivity and y is the percentage of the desired carbonate in the final mixture.

CHAPTER 4

ZIF-8 CRYSTALS: RESULTS AND DISCUSSIONS

Here we follow the formation of ZIF-8 as a function of time at room temperature employing zinc carbonate basic as the metal source and demonstrate the synthesis of ZIF-8 at the solid-liquid interface using zinc foils both as substrate and reagent. We found that at short to moderate synthesis times, ZIF-8 crystals and ZnO nanoneedles coexist. Long synthesis times promoted the complete crystallization of ZIF-8. ZIF-8 crystals were able to grow from zinc foils in a batch reactor under hydrogen environment at 150 °C for 5 hours and in a teflon lined Parr stainless steel autoclave at 150 °C for 4 days. A layer of ZIF-8 crystals formed homogeneously at the surface of the zinc foil. We hypothesize that the nucleation of ZIF-8 crystals takes place heterogeneously from the grain boundaries at the metallic surface. A reducing environment and a decrease in pH during synthesis favored the formation of pure ZIF-8 phase, as a minor impurity presented in the samples synthesized in the air environment. To the best of our knowledge, it is the first time of growing metal organic frameworks at the liquid-solid interface using the metal sources as both substrates and reagents.

4.1 Room Temperature Synthesis of ZIF-8: The Coexistence of ZnO Nanoneedles

Different from other counterions, the use of zinc carbonate basic leads to the coexistence of ZIF-8 crystals and ZnO nanoneedles at short to moderate synthesis times. The presence of carbonate basic in the synthesis gel led to a rich hydroxyl species solution environment. The condensation of these hydroxyl species resulted in the formation of ZnO nanoneedles. In addition, we demonstrate that the kinetics of transformation of ZIF-8 is governed by Avrami's classic model. A basic understanding on the formation mechanisms of zeolitic imidazolate frameworks presented here is relevant and important to rationally develop metal organic frameworks with tailored properties.

4.1.1 Crystal Structure of ZIF-8 and Kinetic of Crystal Formation

Figure 4.1. XRD patterns of ZIF-8 as a function of synthesis time: a) 10 min; b) 30 min; c) 2 h; d) 6 h; e) 24 h; f) 48 h and g) 120 h.

Figure 4.2. Area under the curve for (0 1 1) plane of ZIF-8 synthesized at: a) 10 min; b) 30 min; c) 2 hrs; d) 6 hrs; e) 24 hrs; f) 48 hrs; g) 120 hrs

The XRD patterns of the ZIF-8 samples synthesized in the presence of zinc carbonate basic at different synthesis times were shown in Figure 4.1. All XRD patterns correspond to the sodalite structure, which is a typical structure of ZIF-8. The peak position and intensity are in agreement with previously reported ZIF-8 XRD spectra.^{75,82,128}

The area under the curve of each peak was quantified using origin software, after baseline correction, to determine the relative crystallinity curve of ZIF-8 phase. Figure 4.2 shows the representative calculation of the area under the curve for (011) plane of ZIF-8. The calculation of areas under all curves was summarized in Table 4.1. From the table, we observed that the reflections of higher order for ZIF-8 corresponding to the planes (011), (022), (112), (022), (013) and (222) increased as time progressed. This curve can be directly related to the phase transformation rate. As shown in Figure 4.1, the presence of defined XRD peaks at 10 minutes indicates that ZIF-8 forms even at this short synthesis time.

Table 4.1. Area under the curve for the higher order XRD reflections of ZIF-8

Time (min)	Area under the curve						Total
	(0 1 1)	(0 0 2)	(1 1 2)	(0 2 2)	(0 13)	(2 2 2)	
0	0	0	0	0	0	0	0
10	746	151	896	65	55	70	1983
30	1110	154	1067	59	82	94	2566
120	1528	201	1178	63	91	119	3180
360	1950	266	1331	81	102	184	3914

1440	3086	433	1516	103	158	305	5601
2880	3434	550	1726	185	181	433	6509
7200	5210	653	1902	187	228	522	8702

The relative crystallinity of each peak was obtained by calculating the ratio of the area under current curve to the area under the curve with maximum crystallinity with the data in Table 4.1. For example, the relative crystallinity of the 10 min sample is 0.228, which is 1983/8702. By plotting the relative crystallinity of each sample with its reaction time, the crystallization rate curve of ZIF-8 and the data points represent the total measured intensity of the six primary XRD reflections of ZIF-8 were shown in Figure 4.3.

Figure 4.3. Crystallization rate curve of ZIF-8. Inset shows that the growth regime follows Avrami's kinetics.

The relative crystallinity of ZIF-8 increased linearly during the first 2h from ~20% to ~40%. Then the rate of crystallization increased slowly from 2h to 24h

from ~40 % to ~60 %. Finally, after 48h the relative crystallinity of ZIF-8 remained ~80%, reaching a maximum of 100% at 120h. Interestingly, in the growth regime, the kinetics of transformation followed Avrami's model ¹²⁹⁻¹³¹ (inset of Figure 4.3). Therefore, the relative crystallinity of ZIF-8 as a function of time in this region can be expressed as $y(t)=1-\exp [-ktn]$; where t is synthesis time, $y(t)$ is the relative crystallinity of ZIF-8 as a function of time, k is a scaling constant, and n is the Avrami's constant. The Avrami's constant can be calculated by obtaining the linearized Avrami's equation first,

$$\ln (-\ln[1-y(t)]) = \ln K + n \ln t$$

then plotting $\ln(-\ln[1-y(t)])$ with $\ln t$. By linear regression, we can obtain the values of K and t . For our case, $k=0.14$, and $n\sim 0.27$. Although typical values of Avrami's n constant are in the 1-4 range, this constant can adopt different values, including fractional numbers below 1. ¹³² Values of the Avrami exponent below 1 have been typically attributed to both decreasing nucleation and growth rates.

4.1.2. Surface Properties and Morphology of Synthesized ZIF-8 Samples

The specific BET surface areas of all samples correlated with the ZIF-8 relative crystallinity (Figure 4.4). For example, surface areas increased linearly at short synthesis times and remained practically constant in the 48h - 120h range. It is important to mention that the apparent surface area was evaluated using the BET method and taking the data in the $0.01 < P/P_0 < 0.3$ range. The relatively low observed surface areas may indicate that the synthesized ZIF-8 still contains some unreacted 2-methylimidazole linker that was not desorbed from the framework.

Figure 4.4. ZIF-8 BET specific surface area as a function of synthesis time.

Figure 4.5 shows TEM images of selected samples synthesized at different synthesis times. Interestingly, the presence of a second phase in nanoneedle form was observed for samples synthesized from 10 minutes to 48 hours. At 30 minutes, ~30 nm ZIF-8 crystallites, some of them already faceted coexist with nanoneedles displaying ~10-20 nm diameter and lengths in the ~100-150 nm range (Figures 4.5a,b). As time progressed, the size of the ZIF-8 crystals increased to ~50-60 nm, with no evident size growth of the nanoneedle-like phase (Figures 4.5c,d).

Figure 4.5. Representative TEM images of ZIF-8 as a function of synthesis time: a, b) 30 min; c, d) 24 h; e, f) 120 h. In a-d, arrows indicate ZIF-8 phase. e and f are pure ZIF-8 crystals.

Finally, at 120 hours, only well faceted ~80-90 nm hexagonal and cubic like crystals corresponding to pure ZIF-8 phase were observed (Figures 4.5e,f). It is important to mention that only for the sample synthesized at 120 hours, pure ZIF-8 crystals were present (no nanoneedles), suggesting that at this time the complete crystallization of the microporous framework takes place. The TEM

images revealed that increasing the crystallization time led to an increase in ZIF-8 crystal size due to Ostwald ripening, a well-known thermodynamically-driven process, in which small crystals disappear at the expense of the formation of larger crystals.

4.1.3. Identification of ZnO Nanoneedles

SAED and EDS study were carried out to identify the composition and crystal structure of the nanoneedles. A typical SAED ring pattern obtained from a sample with high density of nanoneedles is shown in Figure 4.6a. The radial intensity distribution profile, measured from this pattern to improve sensitivity and ring detection, is plotted in Figure 4.6b (black line) after background subtraction. The profile is superimposed with a literature x-ray diffraction (XRD) pattern of wurtzite ZnO (JCPDS pattern 01-075-0576). It can be seen that majority of the SAED rings coincide with XRD lines suggesting that nanoneedles consists of wurtzite ZnO. The TEM image shown in Figure 4.6c shows nanoneedles with ~20 nm diameter and lengths in the ~100-200 nm range. The SAED pattern and the radial intensity distribution profile are in agreement with the EDS measurements, which confirms that nanoneedles are composed of zinc and oxygen, as shown in Figure 4.6d, where an EDS spectrum obtained from a single nanoneedle is presented. Elemental quantification of this spectrum yields 49 ± 2 and 51 ± 2 at % of Zn and O, respectively which is in excellent agreement with ZnO. In addition to ZnO rings, the SAED pattern consists of three additional rings at the d-spacing of 0.312, 0.268, and 0.155 nm, respectively. The origin of these rings it is not clear. ZnO nanoneedles coexist with ZIF-8 at low (10 minutes) to moderate (48 hours)

synthesis times and vanish at long synthesis time (120 hours), which suggests that, in this reaction, the amorphous ZnO nanoneedles also act as a Zinc source to promote the formation of ZIF-8 crystals, until all the ZnO nanoneedles are consumed.

Figure 4.6. a) SAED pattern and b) its radial intensity profile measured for sample containing high concentration of nanoneedles. Diffraction rings corresponding to wurtzite ZnO are indexed. c) TEM image of ZnO nanoneedles. d) EDX spectrum measured from one of such nanoneedles.

4.1.4. ZIF-8 Growth Pathway

At the beginning of the reaction, the zinc carbonate part of the reactant ($[\text{ZnCO}_3]_2 \cdot [\text{Zn}(\text{OH})_2]_3$) starts to react with 2-methylimidazole to form ZIF-8 crystals, while the zinc hydroxide part of the reactant begins to form ZnO nanoneedles through hydrolysis under the influence of the organic amino group, as shown in Figure 4.7. Small ZIF-8 crystals and ZnO nanoneedles coexist in the solution. After the zinc carbonate is consumed, the ZnO nanoneedles start to act as a zinc source and react with 2-methylimidazole to form more ZIF-8 crystals.

The amount of ZnO nanoneedles decreases while the amount of ZIF-8 crystals increases. The disappearance of the nanoneedles at long synthesis times, indicates that this is a metastable phase that coexists with ZIF-8 at low (10 minutes) to moderate (48 hours) synthesis times.

Figure 4.7. The coexistence of ZIF-8 crystals and ZnO nanoneedles at short synthesis times.

It is important to mention that ZnO nanoneedles were only observed when Zn carbonate basic was used as the metal source. Other zinc precursors including Zn sulfate, Zn nitrate and Zn chloride led only to hexagonal and cubic faceted crystals, typical morphology of pure ZIF-8 phase, as shown in Figure 4.8. Different from sulfate, nitrate and chloride counterions, the presence of carbonate basic in the synthesis gel leads to a rich hydroxyl species solution environment. It is likely then that the dehydration of these hydroxyl species results in the formation of ZnO nuclei. At this point, the ZnO nanoneedles can grow by condensation of these hydroxyl species.¹³²

Figure 4.8. Representative TEM images of ZIF-8 synthesized with (a) Zinc nitrate hexahydrate, (b) Zinc sulfate monohydrate, and (c) Zinc chloride as zinc source, and methanol as solvent. Sodium formate was employed in this synthesis from zinc chloride to promote precipitation.

The nanorod-like or nanoneedle-like morphology has been observed when organic amino groups are present as additives in the synthesis gel. For instance, zinc oxide nanorods have been synthesized in the presence of ethylenediamine,¹³³ triethanolamine,¹³⁴ diethylenetriamine^{135,136} and hexamethylenetetramine.¹³⁷⁻¹³⁹ In our case, part of the 2-methylimidazole coordinates with Zn to form ZIF-

8, while the unreacted 2-methylimidazole (which is in excess in our prevailing synthesis conditions) may act as the organic amino group catalyst promoting the formation of ZnO nanoneedles. It has been proposed that diverse amino group functionalities with Lewis basic character, can play multiple roles in the formation of ZnO nanorods, including the effective control of the precipitation and passivation of crystal surfaces.^{139,140} The ZnO nanorods perform as a zinc source to grow ZIF-8 crystals.

4.2. Growth of ZIF-8 Crystals at the Solid-Liquid Interface

An alternative approach that we tried to synthesize ZIF-8 crystals was attempting to grow this MOF at the solid-liquid interface. The next paragraphs describe relevant results on the development of these crystals via this novel synthesis methodology.

4.2.1. ZIF-8 Crystals Synthesized under H₂ Environment in a Parr Reactor

The XRD patterns and typical SEM images of two samples synthesized with 2-propanol and methanol at 100 psia were shown in Figure 4.9. The XRD patterns for both samples (Fig 4.9a and 4.9b) correspond to SOD structure, typical structure of ZIF-8. The peak positions of both XRD patterns are in agreement with previous reports,^{75,82,128} confirming the growth of pure ZIF-8 crystals. The difference in peak intensity between the two samples may indicate preferential orientation of the crystals, in particular of the (011) plane for the sample synthesized with 2-propanol and of the (112) plane for the sample synthesized with methanol. This behavior is well known, and has been reported for other metal organic framework films.¹⁴¹⁻¹⁴³

Figure 4.9. XRD and representative SEM images (insets) of ZIF-8 crystals synthesized under H_2 at 100 psia employing (a) 2-propanol and (b) methanol as solvent.

Therefore, a reducing environment favored the formation of pure ZIF-8 phase. The inset of Figure 4.9a shows a representative SEM image for the sample synthesized with 2-propanol. This particular sample shows hexagonal faceted crystals, typical of this topology, displaying a broad size distribution in the ~ 0.5 - $3\ \mu\text{m}$ range. A representative SEM image for the sample synthesized with methanol (inset of Figure 4.9b) shows as well defined hexagonal-like crystals with sizes between ~ 0.5 - $1.5\ \mu\text{m}$.

Figure 4.10. (a) STEM image of a cluster of well-faceted ZIF-8 crystallites. (b) A single crystal SAED pattern measured from one of such crystallites. This $[-421]$ pattern was consistently indexed using ZIF-8 cubic crystal structure. (c) A typical EDS spectrum measured from a single crystallite

TEM studies for the sample synthesized with 2-propanol as solvent under H_2 at 100 psia revealed its highly crystalline form as seen in STEM image in Figure 4.10a showing typical morphology of this sample, consisting of highly-faceted, well-developed crystallites in the size range of 0.5-2 μm . The crystallites are single crystals, as confirmed by the SAED study. An example of a typical, single crystal SAED pattern obtained from one of such crystallites is shown in Figure 4.10b. This and all other patterns measured from this sample were successfully indexed using the ZIF-8 cubic structure and the lattice parameter derived from this analysis agrees very well with the literature value of 16.32 Å reported for ZIF-8.⁷¹ These findings are also consistent with the EDS study *i.e.*,

the EDS spectra from this material (Figure 4.10c) are similar to a typical spectrum of ZIF-8. Specifically, the quantification of EDS spectra from our samples is in agreement with ZIF-8 molecular formula.

4.2.2. ZIF-8 Crystals Synthesized in the Absence of H₂ in a Parr Reactor

Although ZIF-8 formed in the absence of H₂, a minor unknown phase was observed, as shown in Figure 4.11, which suggests that, the reducing environment is critical for the formation of pure ZIF-8 phase.

Figure 4.11. a) XRD and b) representative SEM of a ZIF-8 sample synthesized with 2-propanol as solvent, in the absence of H₂. Synthesis was conducted for 5 hr. XRD shows the formation of ZIF-8 phase and a secondary phase.

4.2.3. Synthesis of ZIF-8 under Autogeneous Pressure

Figure 4.12. (a) XRD, (b) SEM and (c) TEM of ZIF-8 crystals synthesized hydrothermally at 150 °C for 4 days, and employing 2-propanol as solvent.

ZIF-8 crystals were also grown hydrothermally from zinc foils in a teflon lined Parr stainless steel autoclave at 150 °C for 4 days. Interestingly, pure ZIF-8 phase was grown only when 2-propanol was employed as a solvent. 2-propanol can act as hydrogen donor, and therefore as a strong reducing agent.^{144,145} Figure 4.12a shows the XRD pattern of this particular sample, which is in well agreement with ZIF-8 structure. The intensity of the XRD reflections suggests preferential orientation of the (112) plane. As shown in Figure 4.12b, the morphology of this sample consisted of well-defined faceted hexagonal plates displaying different sizes in the 6-12 μm range. Not surprisingly the size of the

crystals was larger than those synthesized under H_2 atmosphere due to the prolonged synthesis time. As shown in Figure 4.12c, detailed morphological inspection by TEM reveals that also nanosized-ZIF-8 hexagonal crystals formed, confirming the presence of a broad crystal size distribution, and suggesting heterogeneous nucleation.

Figure 4.13. a) XRD and b) representative SEM of a ZIF-8 sample synthesized with methanol as solvent. Synthesis was conducted a teflon lined Parr stainless steel autoclave at $150^{\circ}C$ for 4 days. XRD shows the formation of ZIF-8 phase and a secondary phase.

When methanol was used as a solvent, ZIF-8 and a second phase formed, as shown in Figure 4.13. Similarly to the samples synthesized under H_2

atmosphere, the formation of pure ZIF-8 was favored in the presence of a reducing environment.

4.2.4. Proposed Formation Pathway

Figure 4.14. Proposed formation pathway for the growth of ZIF-8 crystals at the solid-liquid interface.

Figure 4.14 shows the basic steps leading to the growth of ZIF-8 crystals at the solid-liquid interface. The surface of the zinc foil consists of grain boundaries (a). At moderate to alkaline conditions the predominant Zn species in organic solvents such as methanol and dimethylformamide are solvated Zn^{2+} ions.¹⁴⁶ Since the neutral imidazole undergoes deprotonation at moderate to basic pH¹⁴⁷ it is likely that the formation of ZIF-8 nuclei takes place via coordination or assembly of Zn^{2+} ions with the deprotonated imidazole (Im^-) (b). The concentration of protons at high pH is lower, and therefore the degree of surface linker deprotonation increases as pH increases¹⁴⁸ favoring the formation of ZIF-8. The grain boundaries represent potential sites in which heterogeneous

nucleation¹⁴⁹ of ZIF-8 may take place. Due to the discontinuous nature of the grain boundaries, in principle, both the critical nuclei radius and nucleation rate will not be the same throughout the surface of the foil resulting in a broad nuclei size distribution (c), and consequently leading to ZIF-8 crystals displaying different sizes (d).

4.2.5. The Importance of Synthesis Basic Conditions

Figure 4.15. a) XRD and TEM (inset) and b) EDS of a sample synthesized with 2-propanol as solvent at pH=4.8. Synthesis was conducted under H₂ at 100 psia for 5 hr. XRD and EDS suggest the formation of layered Zn(OH)₂.

The reduction in pH for the methanol and 2-propanol based solutions from 9.4 to 8.9 and 9.2 to 7.5 respectively promoted the crystallization of the framework. Previously, our group and independent groups^{82,128,150} have

concluded that pH plays a critical role in the crystallization of ZIFs. When acidic pH was used in the synthesis solution, ZIF-8 phase did not form, instead layered Zn(OH)_2 was observed (Figure 4.15). At acidic conditions, the poor deprotonation of the linker limited the formation of ZIF-8.

CHAPTER 5

CATALYTIC PERFORMANCE OF ZIF-8 CRYSTALS

Here we demonstrate the catalytic activity of the ZIF-8 in the synthesis of styrene carbonate from carbon dioxide and styrene oxide (shown in Figure 5.1) even at low temperatures, such as 50 °C. The styrene carbonate yields increase to ~54 mol % at 100 °C. The catalytic activity of ZIF-8 and amine-functionalized ZIF-8 catalysts in the synthesis of chloropropene carbonate from CO₂ and epichlorohydrin is also presented, as shown in Figure 5.8. ZIF-8 catalysts displayed high epoxide conversions and moderate to high selectivities to chloropropene carbonate at reaction temperatures as low as 70 °C. In contrast to many prior-art catalysts, solvents or co-catalysts were not required in either of the reactions.

5.1. ZIF-8 crystals as catalysts in the Synthesis of Styrene Carbonate

The Zn²⁺ acid sites are known to catalyze the cycloaddition reaction of CO₂ and epoxides. The nitrogen basic moieties from the imidazole linker in ZIF-8 promoted the adsorption of the CO₂ on the solid surface. The simultaneous presence of both elevated further conversion to the cyclic carbonate. The simultaneous presence of both the acid sites and the nitrogen basic moieties from the imidazole linker in ZIF-8 promoted the adsorption of the CO₂ on the solid surface and its further conversion to the cyclic carbonate. Pyridine and

ammonia were used as probe molecules to estimate the type and density of acid sites in fresh and reused ZIF-8 catalysts. DRIFT spectroscopy of adsorbed pyridine revealed the presence of both Brönsted (B) and Lewis (L) acid sites. The B-sites have nearly vanished in the case of recycled ZIF-8 catalysts. The ZIF-8 catalysts could be recycled and reused without significant loss in catalytic activity. The ZIF-8 catalysts could be recycled and reused without significant loss in catalytic activity.

Figure 5.1. Cycloaddition of CO₂ to styrene oxide to form styrene carbonate,

5.1.1. Catalytic Performance of Fresh and Recycled ZIF-8 Catalysts

The cycloaddition of carbon dioxide to styrene oxide yielded styrene carbonate as the only product. Controlled blank experiments under our reaction conditions confirmed that the reaction did not proceed to a significant extent in the absence of the ZIF-8 catalyst. Figure 5.2a shows the catalytic performance of fresh and samples of recycled ZIF-8 at 80 °C and 7 bar for 5 hours. It is likely that Lewis acid sites, associated with Zn ions in the ZIF-8 framework play an important role in catalyzing the cycloaddition of carbon dioxide to styrene carbonate. In addition, the presence of basic nitrogen atoms of the imidazole ligand, probably, favors the adsorption and binding of CO₂ as well as activation of the carbon-oxygen bonds in CO₂. The spent ZIF-8 catalysts were reused in

several recycling experiments with no significant loss in catalytic activity (yield to styrene carbonate decreased slightly from ~39.4% (fresh) to ~ 37% (recycled). Interestingly, the yield to styrene carbonate correlated with the surface area of the samples (Figure 5.2b). The decrease in surface area suggests partial pore blockage of the recycled ZIF-8 by carbonaceous material formed during the reaction. We have observed this phenomenon previously.⁹⁰

Figure 5.2. (a) Catalytic performance of fresh and recycled ZIF-8 catalysts in the synthesis of styrene carbonate from carbon dioxide and styrene oxide. Reaction conditions: 80 °C, 7 bar for 5 hours. (b) Correlation between yield (mol%) to styrene carbonate and ZIF-8 specific surface area.

5.1.2. Crystal Structures and Morphology of the Fresh and Recycled ZIF-8 Catalysts

Figure 5.3. XRD patterns of ZIF-8 catalyst: (a) fresh, (b) first recycle (c) second recycle and (d) third recycle. Reaction conditions: 80 °C, 7 bar for 5 hours.

Figure 5.3 shows the XRD patterns of the fresh and recycled ZIF-8 catalysts. Both the intensities and positions of the XRD peaks of all catalysts correspond to sodalite structure, which is the typical known topology of ZIF-8,⁷⁵ confirming that the structural stability of ZIF-8 is preserved for all recycled catalysts. Figure 5.4 shows the morphological features (hexagonal-faceted crystals) of the fresh and recycled ZIF-8 catalysts obtained from scanning electron microscopy. The fresh catalyst (Figure 5.4a) and the first recycled catalyst (Figure 5.4b) displayed average crystal sizes in the ~200-270 nm range. This average size increased, slightly, to ~230-320 nm range for the second and

third recycled catalysts (Figure 5.4c and 5.4d). The slight increase in crystal size for the recycled catalysts is likely related to Ostwald ripening and/or recrystallization.¹²⁸ The basic hexagonal, morphological features of the ZIF-8 catalyst were, however, still preserved in the recycled catalysts.

Figure 5.4. SEM images of ZIF-8 catalyst: (a) fresh, (b) first recycle (c) second recycle and (d) third recycle. Reaction conditions: 80 °C, 7 bar for 5 hours.

5.1.3. Reaction Kinetics

Figure 5.5a shows the catalytic performance of ZIF-8 (% yield of styrene carbonate) as a function of temperature. ZIF-8 was catalytically active even at 50 °C. Over zeolite-based and mesoporous solid acid catalysts, this reaction usually occurs only at temperatures above 100 °C.^{50,52, 67,68,82,106, 150-153} The yield to styrene carbonate increased as temperature was increased, reaching a maximum of ~53.5 mol % at 100 °C. Even at 100 °C, the recycled ZIF-8 catalyst

maintained its catalytic activity (~53% for the first recycle). At higher temperatures the yield of styrene carbonate decreased due to its further polymerization. We followed the kinetics of the reaction at 100 °C and estimated the reaction rate constant. The order of reaction is calculated with respect to styrene oxide. From the concentration (yield) fraction (which corresponds to the normalized concentration) vs. time plot (Figure 5.5b), we extracted the slope of the line, which corresponds to the rate constant (slope = $0.0458 \text{ hr}^{-1} = 7.7 \times 10^{-4} \text{ min}^{-1}$). The linear correlation factor (R^2) is larger than 96%, which is statistically acceptable.

Figure 5.5. Catalytic performance of ZIF-8 in the synthesis of styrene carbonate from carbon dioxide and styrene oxide: (a) as a function of temperature. Reaction conducted at 7 bar for 5 hours; (b) as a function of time. Reaction conditions: 100 °C, 7 bar.

5.1.4. Identification and Quantification of Acid Sites and Basic Sites in the Fresh and Recycled ZIF-8 Catalysts

Fig.5.6. DRIFT spectra of adsorbed pyridine for fresh and recycled ZIF-8 catalysts.

ZIF-8 is a bi-functional catalyst containing both acidic and basic sites associated with the Lewis acid Zn^{2+} ions and the basic imidazole groups, respectively. Pyridine and ammonia were used as probe molecules to estimate the type and density of acid sites in fresh and reused ZIF-8 catalysts. DRIFT spectroscopy of adsorbed pyridine revealed the presence of both Brønsted (B) and Lewis (L) acid sites (Figure 5.6). The IR peaks arising from B-sites appeared at 1634–1670 and 1546 cm^{-1} and the peaks from the L-sites appeared at 1575 and 1475–1499 cm^{-1} . H-bonded pyridine showed IR peaks at 1590 and 1435 cm^{-1} .⁶⁸ The B-sites have nearly vanished in the case of recycled ZIF-8 catalysts. The concentrations of acid and basic sites of fresh and recycled ZIF-8 catalysts

were determined using NH_3 and CO_2 as probe molecules, respectively. Figure 5.7 shows the NH_3 -TPD and CO_2 -TPD profiles of fresh and recycled (3rd recycled) ZIF-8 catalyst. The TPD peak around 45 °C is probably due to the desorption of physically adsorbed NH_3 .

Figure 5.7. (a) NH_3 -TPD and (b) CO_2 -TPD profiles of fresh and recycled (3rd recycle) ZIF-8 catalysts.

Table 5.1 summarizes the concentration of acid and basic sites of the fresh and recycled catalyst (3rd recycle). The amount of NH_3 adsorbed on ZIF-8 is reduced significantly after the third recycle, indicating a significant decrease in the concentration of acidic sites upon reuse. On the other hand, only a slight decrease in basicity was observed for the recycled catalyst. The slight decrease in activity of the recycled catalysts may suggest that basic sites may play a more relevant role (as compared to acid sites) in catalyzing the conversion of styrene oxide into its carbonate. In earlier studies,^{52,68} we had found that some of the

most active solid catalysts for the conversion of carbon dioxide and styrene oxide into styrene carbonate were those based on mesoporous SBA-15. Yields to styrene carbonate were as high as ~89% and ~95% for adenine modified Ti-SBA-15⁶⁸ and Al-SBA-15,⁵² respectively. However, the temperature required for achieving these higher yields was 120 °C. The ZIF-8 catalysts of the present investigation were active at as low a temperature as 50 °C.

Table 5.1. Acid and basic properties of fresh and recycled ZIF-8 catalysts

Catalyst	Acidic sites (mmol/g; NH ₃ -TPD) ^a	Basic sites (μmol/g; CO ₂ -TPD)
Fresh ZIF-8	0.675	4.375
Recycled ZIF-8 (3 rd recycle)	0.066	3.750

^aArea of NH₃ desorption peak in the temperature range 40–180 °C.

Other metal organic frameworks have been used as catalysts for the synthesis of styrene carbonate from CO₂ and styrene oxide.^{114,115,117} For instance, MOF-5 effectively catalyzed this cycloaddition reaction, however a quaternary ammonium salt was needed to observe high catalytic activity of MOF-5.¹¹⁷ Co-MOF-74¹¹⁴ and Mg-MOF-74¹¹⁵ displayed high yields to styrene carbonate, at relatively high temperature of 100°C. Interestingly, the high CO₂ adsorption capacity of Co-MOF-74 and Mg-MOF-74 correlated with the superior observed catalytic performance of these catalysts.

5.1.5. Reaction Mechanism

The reaction mechanism is expected to be similar to that of the conventional cycloaddition reactions.⁶⁸ The epoxide (styrene oxide, in the

present case) is activated on the acidic sites and CO₂ on the basic sites. The activated CO₂ is then inserted into the epoxide ring forming the cyclic carbonate. CO₂ adsorption and activation are a crucial step in this cycloaddition reaction. In bimolecular, cycloaddition reactions involving CO₂, the concentration of adsorbed CO₂ will influence, crucially the rate of the reaction, especially at temperatures above the boiling point of CO₂ when physical adsorption of CO₂ is not expected to be significant. While Lewis acid sites associated with Zn atoms are needed for catalyzing the reaction, the basic sites, associated with the N atoms of the imidazole rings of ZIF-8 are needed to adsorb the CO₂, increase the surface concentration of adsorbed CO₂ and, thereby, increase the rate of the cycloaddition reaction. Below 100 °C, the concentration of adsorbed styrene oxide, the other reactant in this cycloaddition reaction, is expected to be high. With high concentrations of both the reactants (styrene oxide and CO₂) the rates of this bimolecular reaction are high. This is probably, one of the reasons for the high catalytic activity of ZIF-8 even at lower temperatures. ZIF-8 with high CO₂ uptake capacity at ambient conditions, large pore size and simultaneous presence of both acidic and basic sites, therefore, is a highly efficient catalyst for the production of cyclic carbonates even at temperatures as low as 50 °C.

5.2. ZIF-8 Catalysts in the Conversion of CO₂ to Chloropropene Carbonate

The catalytic activity of ZIF-8 and amine-functionalized ZIF-8 catalysts in the synthesis of chloropropene carbonate from CO₂ and epichlorohydrin is demonstrated, as shown in Figure 5.8. In contrast to hitherto known catalysts, ZIF-8 catalysts displayed high epoxide conversions and moderate to high

selectivities to chloropropene carbonate at reaction temperatures as low as 70 °C. No cocatalysts or solvents were required during the reaction. The incorporation of ethylenediamine in ZIF-8 enhanced its catalytic performance as a result of the higher CO₂ adsorption capacity of the amine- functionalized samples. The ZIF-8 catalysts, however, lost their distinctive crystalline structure and superior catalytic performance when attempts were made to recycle them after use.

Figure 5.8. Cycloaddition of CO₂ and Epichlorohydrin to form Chloropropene Carbonate.

5.2.1. Crystal Structure and Surface Properties of Fresh ZIF-8 Catalysts

The XRD pattern of the as-synthesized ZIF-8 catalyst, shown in Figure 5.9a, corresponds to a sodalite structure, which is the typical, known structure of ZIF-8.⁷⁵ The morphological features of ZIF-8 crystals were investigated by transmission electron microscopy, which shows sharp, hexagonally faceted ZIF-8 crystals of 500 nm (Figure 5.9b). Scanning electron microscopy (SEM) also confirmed the presence of 400–500 nm crystals displaying a relatively narrow size distribution and hexagonal morphology (Figure 5.10 and 5.11). The CHN analysis revealed that the carbon, hydrogen, and nitrogen contents in the ZIF-8 framework are C, 42.0%; H, 4.3%; and N, 24.4% (theoretical values for ZIF-8: C, 42.2%; H, 4.4%; and N, 24.6%).⁸²

Figure 5.9. a) XRD and b) TEM of ZIF-8 solids employed as catalysts in the synthesis of chloropropene carbonate from CO_2 and epichlorohydrin.

Figure 5.10. SEM of ZIF-8 catalysts employed as catalysts in the synthesis of chloropropene carbonate from CO_2 and epichlorohydrin.

Figure 5.11. N₂ adsorption-desorption isotherms of ZIF-8 catalysts employed as catalysts in the synthesis of chloropropene carbonate from CO₂ and epichlorohydrin.

5.2.2. Performance of Pure ZIF-8 Catalysts

The cycloaddition of CO₂ to epichlorohydrin yielded chloropropene carbonate as the main product. Diols and dimers of epichlorohydrin were the other products. Controlled experiments under our reaction conditions confirmed that the reaction did not proceed to a significant extent in the absence of the ZIF-8 catalyst. Figure 5.12 shows the catalytic performance of ZIF-8 as a function of temperature. ZIF-8 was catalytically active, even at reaction temperatures as low as 70 °C. Over zeolite-based and mesoporous solid acid catalysts, this reaction usually occurs at temperatures above 100 °C.^{50,51,67,68,102,150,152-156} The conversion of epichlorohydrin increased as the temperature was increased, reaching a maximum of 100% at 100 °C, while the selectivity to chloropropene carbonate decreased. The highest chloropropene carbonate yield was observed at 80 °C.

Figure 5.12. Catalytic performance of ZIF-8 as a function of temperature in the synthesis of chloropropene carbonate from CO₂ and epichlorohydrin.

It is known that Lewis acid sites catalyze the reaction of CO₂ with epoxides to give propylene carbonates and other precursors of polycarbonates.^{52,64} Recently, Chizallet et al. identified Zn^{II} (strong Lewis acid sites) as one of the species that coexist on the surface of ZIF-8 crystals.⁸⁷ It is likely that these Lewis acid sites (associated with Zn ions) play an important role in catalyzing the cycloaddition of CO₂ to epichlorohydrin. In addition, the polar nature of ZIF-8 (i.e., the presence of the basic nitrogen atoms of the imidazole ligand)⁷⁶ favors the binding and activation of the polar carbon-oxygen bonds of CO₂. The presence of both the Zn^{II} acid sites and the N basic moieties (in adjacent locations) from the imidazole linker in ZIF-8 probably facilitates the adsorption of the CO₂ on the

solid surface and its further conversion to the carbonate. As mentioned earlier, the high adsorption capacity of CO₂ is well-known.

5.2.3. Performance of functionalized ZIF-8 catalysts

Organic cations containing amino group functionalities have high affinity for CO₂. Therefore, the incorporation of amino groups in the surface of ZIF-8 should promote CO₂ adsorption and, in principle, should improve catalytic performance. Recently, our group has demonstrated the successful surface functionalization of zeolite SAPO-34 with ethylenediamine.¹⁵⁷

5.2.4. Comparison of the Performances of Pure and Amine-Functionalized ZIF-8 Catalysts

Table 5.2. Catalytic performance of ZIF-8 and functionalized ZIF-8 in the cycloaddition of CO₂ to epichlorohydrin reaction.

Catalyst/Temperature (°C)	Epichlorohydrin Conversion (%)	^c Selectivity (%)		
		Chloropropene carbonate	Diol	Dimer
^a ZIF-8 (70)	65.5	63.4 [41.5]	36.6	0.0
^a ZIF-8 (80)	84.1	52.0 [43.7]	23.7	24.3
^a ZIF-8 (100)	98.2	33.4 [32.8]	29.8	36.8
^b ZIF-8-f (70)	74.6	71.8 [53.6]	28.2	0.0
^b ZIF-8-f (80)	100	73.1 [73.1]	26.9	0.0
^b ZIF-8-f (100)	100	49.1 [49.1]	50.9	0.0

^a Pure ZIF-8; ^b Functionalized ZIF-8; ^c Numbers in square brackets indicate respective yields

Table 5.2 summarizes the catalytic performance of ZIF-8 in the cycloaddition of CO₂ to epichlorohydrin reaction. In another set of controlled

experiments, the activity for zinc nitrate hexahydrate, ethylene diamine, and 2-methylimidazole for carbonate formation in the absence of added ZIF-8 catalysts, was evaluated at 80 °C and 7 bar for 4 h. Zinc nitrate hexahydrate, 2-methylimidazole and ethylene diamine displayed yields to diol corresponding to only 20%, 100%, and 19%, respectively.

5.2.5. Structure and Properties of Amine-Functionalized ZIF-8 Catalysts

Figure 5.13. XRD pattern of functionalized (ethylene diamine) ZIF-8

The XRD pattern of the ethylenediamine-functionalized ZIF-8 (Figure 5.13) shows that the crystalline structure of ZIF-8 was preserved even after the amine functionalization. The surface area of the functionalized ZIF-8 slightly decreased to 1096 m²/g (1173 m²/g for the nonfunctionalized ZIF-8). The grafting of ethylenediamine in the ZIF-8 framework was confirmed by FTIR (Figure 5.14) which shows $\nu(\text{NH})$ and $\nu(\text{CH})$ stretching vibrations corresponding to ethylenediamine. The CHN analysis for the ZIF-8-functionalized sample corresponded to C, 47.5%; H, 4.8%; and N, 25.2%. As shown in Figure 5.15, for

reaction temperatures in the 70–100 °C range, both the conversion and yield to chloropropene carbonate were enhanced on functionalization of the ZIF-8 surface with ethylenediamine.

Figure 5.14. FTIR of a) non-functionalized and b) amine-functionalized ZIF-8

Figure 5.15. Catalytic performance of functionalized ZIF-8 as a function of temperature in the synthesis of chloropropene carbonate from CO₂ and epichlorohydrin.

5.2.6. Comparison of Pure and Amine-functionalized ZIF-8 Catalysts

CO₂ adsorption isotherms (Figure 5.16) were collected for the nonfunctionalized and the amine-functionalized ZIF-8. Higher CO₂ uptakes were observed for the functionalized phase. Therefore, the improved catalytic performance of the amine-functionalized ZIF-8 as compared with the nonfunctionalized ZIF-8 may be due, at least in part, to the higher CO₂ adsorption capacity of the former, since it is well-known that active catalysts for the insertion of CO₂ into epoxides are those exhibiting high CO₂ uptakes.¹⁵³

Table 5.2 summarizes the catalytic performance of ZIF-8 and amine-

functionalized ZIF-8 in the cycloaddition of CO₂ to epichlorohydrin reaction. The yield of the carbonate was maximum at 80 °C. Zeolite beta is an efficient catalyst for the synthesis of cyclic carbonates.⁵⁰ The catalytic performance of zeolite beta (BET surface area 343 m²/g) in the cycloaddition of CO₂ to epichlorohydrin reaction was compared with that of ZIF-8. At 70 °C, no chloropropene carbonate was formed over zeolite beta. Only the diol was observed. At 80 °C, the yield of chloropropene carbonate was 61.1%, and finally, at 100 °C, the yield of chloropropene carbonate increased to 82.2%.

Figure 5.16. CO₂ adsorption isotherms of non-functionalized and amine-functionalized ZIF-8. Adsorption isotherms were measured at room temperature using water as the coolant.

5.2.7. Comparison of Pure/Amine-functionalized ZIF-8 Catalysts and Zeolites Catalysts

At 70 °C, ZIF-8 (both the nonfunctionalized and amine-functionalized forms) exhibited better catalytic performance than zeolite beta. At 80 °C, functionalized ZIF-8 displayed the best catalytic performance. Zeolite beta performed better at 100 °C. Other catalysts that have been employed for this reaction are zeolite TS-1, HY, and SBA-15. We evaluated the activity of these catalysts at 80 °C and 7 bar for 4 h. The only observed product for zeolite TS-1 and HY was diol. The yield to diol was 17% and 23% for TS-1 zeolite and HY zeolite, respectively. For SBA-15, the yield to chloropropene carbonate was only 37%.

5.2.8. Recyclability of ZIF-8 Catalysts

Recyclability is an important and essential feature of any catalyst to be considered for use in industrial applications. We have investigated the influence of catalyst recycle on the catalytic properties of ZIF-8 in the cycloaddition reaction. In the recycle experiments, the catalyst after use in the cycloaddition reaction was washed with acetone, centrifuged, and air-dried before reuse. The catalytic activity of the recycled catalysts (both nonfunctionalized and amine-functionalized) was evaluated at a reaction temperature of 80 °C. The yield of chloropropene carbonate decreased from 43.7% (fresh) to 22.7% (recycled) for the nonfunctionalized ZIF-8 and from 73.1% (fresh) to 30.6% (recycled) for the amine-functionalized ZIF-8. The XRD and FTIR of the recycled ZIF-8 catalysts (both pure and functionalized) after the reaction at 80 °C (as shown in Figure

5.17 and 5.18) and suggest that the ZIF-8 structure is preserved after the first cycle. However, the apparent BET surface area decreased from 1173 to 772 m²/g for the nonfunctionalized ZIF-8 and from 1096 to 915 m²/g for the functionalized ZIF-8. This may suggest pore blockage of the recycled ZIF-8 by carbonaceous material formed during the reaction and may explain in part the lower activity of the recycled catalysts. In fact, for other solid catalysts, such as SBA-15, the loss in activity of recycled catalysts has been attributed to active site pore blocking by residual carbonaceous deposits.⁶⁸ The recycled catalysts (after the second cycle) lost their structural features after reaction, as confirmed by XRD. The latter revealed the presence of an amorphous phase, indicating that the ZIF-8 framework collapsed during the recycle experiments.

Figure 5.17. XRDs of recycled (a) non-functionalized and (b) amine-functionalized ZIF-8.

5.2.9. Investigation of the Cause of the Loss of Activity in Recycled Catalysts

To investigate the loss of crystallinity of the ZIF-8 framework in greater detail, we carried out the following experiments: (1) we measured the changes in the pH of the reaction mixture during the reaction. The pH remained unchanged (7–7.2) during the reaction, thus ruling out enhanced acidity of the reaction mixture (from HCl formed from epichlorohydrin) as the cause of the crystalline collapse. We found that at acidic pH, the ZIF-8 framework was unstable. In fact, pH ~5 led to the formation of layered $\text{Zn}(\text{OH})_2$. At acidic conditions, the poor deprotonation of the linker may limit the formation of ZIF-8. (2) The H_2O content of epichlorohydrin was measured to be below 0.2%. Although this may account for the small amount of diols sometimes observed in the products, it is not enough to cause crystalline collapse. ZIF-8 is known to be chemically stable in the presence of water and aromatic hydrocarbons⁷⁵ as well as thermally stable up to ~200 °C.⁸² (3) ZIF-8 was heated in toluene at 100 °C for 6 h at low pressures. There was no change in the XRD pattern, even after the above experiment was repeated twice. There was no formation of carbonaceous matter. (4) ZIF-8 was heated in epichlorohydrin at 100 °C for 6 h. Diols were observed as products. Conversion was low, and there was no significant formation of carbonaceous matter. Significantly, there was no change in the XRD pattern, even after the above experiment was repeated twice.

These results suggest that the synergistic effect of the presence of CO_2 at high pressures (and temperatures) and the poisoning/blocking of the active sites

by carbonaceous matter in the pores are the probable reasons for the observed catalytic deactivation and crystalline instability of ZIF-8. It may be noted that the instability of the ZIF-8 at high pressures is already well-known.⁸³

Figure 5.18. FTIRs of (a) fresh ZIF-8, (b) recycled non-functionalized and (c) amine-functionalized ZIF-8.

In summary, we demonstrate the high catalytic activity of ZIF-8 and amino-functionalized ZIF-8 catalysts in the synthesis of chloropropene carbonate from CO₂ and epichlorohydrin. In contrast to hitherto known catalysts, the ZIF-8 catalysts displayed high epoxide conversions and moderate to high selectivities to chloropropene carbonate at reaction temperatures even as low as 70 °C. No cocatalysts or solvents were required for the reaction to proceed. The incorporation of ethylenediamine in the ZIF-8 framework enhanced its catalytic performance as a result of the higher CO₂ adsorption capacity of the amine-functionalized samples. The ZIF-8 catalysts, however, lost their distinctive

crystalline nature and superior catalytic performance when attempts were made to recycle them after use.

5.2.10. Proposed Reaction Mechanism

Figure 5.19. Suggested reaction mechanism for the catalytic conversion of CO₂ and epoxides to cyclic carbonates over MOFs: (a) adsorption steps, (b) nucleophilic attack, (c) ring opening, (d) ring closure.

The suggested reaction mechanism for the conversion of CO₂ and epoxides to cyclic carbonates over ZIF-8 is illustrated in Figure 5.19. First, CO₂ is adsorbed on a basic site and the epoxide is adsorbed on an adjacent acid site (typically Lewis acid sites). The nucleophilic attack of the δ^- charge of CO₂ should lead to a high ring strain in the epoxide promoting ring opening. Finally, when CO₂ is desorbed from the basic site, ring-closure takes place and the cyclic carbonate is formed. This mechanism is in agreement with that reported

recently.¹⁵⁸ The reaction mechanism over mesoporous oxides has been reported earlier^{52,68}, and similar to the mechanism over ZIF-8, involves activation of the epoxide on the acid sites, and activation of CO₂ on basic sites. The activated CO₂ is then inserted into the epoxide ring leading to the cyclic carbonate.

CHAPTER 6

CONCLUDING REMARKS AND FUTURE DIRECTIONS

6.1 Concluding remarks

We have demonstrated the synthesis of ZIF-8 crystals using two different approaches from the conventional room temperature and solvothermal methods. Two crystal growth mechanisms were proposed. ZnO nanoneedles were found to coexist with ZIF-8 crystals at short to moderate synthesis time when zinc carbonate basic was employed as the zinc source. Pure ZIF-8 crystals were obtained when we extend the synthesis time, for example, to 120 hours. High quality ZIF-8 crystals were fabricated on a piece of zinc foil. To our best knowledge, it is the first time that a MOF structure was synthesized at the liquid-solid interface using the metal source as both substrate and reagent. Moreover, we present the catalytic performance of the as-synthesized ZIF-8 and the amine-functionalized ZIF-8 in the synthesis of styrene carbonate and chloropropene carbonate. The catalyst exhibited moderate to high activity at low temperatures. In contrary to the conventional catalysts, cocatalysts and solvent were not required in both reactions. The specific deliverables from this work are:

1. ZIF-8 was synthesized at room temperature employing zinc carbonate basic as the metal source. The formation of ZIF-8 crystals as a function of time was investigated. ZIF-8 crystals and ZnO nanoneedles coexisted at short to moderate synthesis times. Only pure ZIF-8 crystals presented in the final product after long

synthesis times. Larger crystal size (~80-90 nm) was obtained due to the prolonged reaction time (120 hrs), by comparing to the ~30 nm size obtained after 30 minutes. Surface area of the crystals increased from ~100 m²/g to ~600 m²/g when the reaction time was extended from 30 minutes to 120 hours. In addition, the kinetics of transformation of ZIF-8 is governed by Avrami's classic model. A basic understanding on the formation mechanisms of zeolitic imidazolate frameworks presented here is relevant and important to rationally develop metal organic frameworks with tailored properties.

2. ZIF-8 was synthesized at the solid-liquid interface using zinc foils both as substrate and reagent. Pure ZIF-8 phase formed when a decrease of PH occurred. ZIF-8 with high crystallinity was obtained only at a reducing atmosphere. The nucleation of ZIF-8 crystals took place most likely from the grain boundaries at the metallic surface. The heterogeneous nature of the grain boundaries resulted the wide distribution of crystal sizes from 0.5-3 μ . The direct growth of ZIF-8 crystals from metallic substrates demonstrated in this study, may have relevant implications in the formation of continuous and well intergrowth films/membranes with potential use in diverse functional applications.

3. We have demonstrated the novel catalytic activity of ZIF-8 catalysts in the synthesis of styrene carbonate from carbon dioxide and styrene oxide. In contrast to hitherto known catalysts, ZIF-8 catalysts displayed catalytic activity even at temperatures as low as 50 °C. Styrene carbonate yields as high as ~54% at 100 °C were observed for the ZIF-8 catalysts. Lewis acid Zn²⁺ sites and the nitrogen basic moieties from the imidazole linker in the ZIF-8 framework

promoted the adsorption of carbon dioxide on the solid surface and its further conversion to the carbonate. The spent ZIF-8 catalysts were reused in several recycling experiments. After a slight initial loss, there was no further significant loss in catalytic activity. The slight decrease in the concentration of basic sites for the recycled catalysts and considerable decrease in the concentration of acid sites suggests that both acid and basic sites are relevant in catalyzing the conversion of styrene oxide into its carbonate.

4. We demonstrate the high catalytic activity of ZIF-8 and amino-functionalized ZIF-8 catalysts in the synthesis of chloropropene carbonate from CO₂ and epichlorohydrin. In contrast to hitherto known catalysts, the ZIF-8 catalysts displayed high epoxide conversions, and moderate to high selectivities to chloropropene carbonate at reaction temperatures even as low as 70°C. No co-catalysts or solvents were required for the reaction to proceed. The incorporation of ethylenediamine in the ZIF-8 framework enhanced its catalytic performance due to the higher CO₂ adsorption capacity of the amine-functionalized samples. The ZIF-8 catalysts however, lost their distinctive crystalline nature and superior catalytic performance when attempts were made to recycle them after use.

6.2. Future Directions

6.2.1. Improving the activity of ZIF-8 in the conversion of CO₂ to carbonates

Our studies demonstrated that ZIF-8 is a promising material for catalyst. It performed much better than most of the existing catalysts. It required less energy input to catalyze the reaction and was easier to be separated from the product. More importantly, ZIF-8 is nontoxic and easy to make. However, further

investigations should be made to improve its catalytic performance, such as searching for the ideal crystal size and best catalyst/reactant ratio for the reaction, the proper activation of the catalyst, as well as the possibilities to improve the reusability of the catalyst. The modification of catalyst using hydrogen, nitrogen and ammonium was reported to increase the surface area of ZIF-8, hence the CO₂ uptake.¹⁵⁹ It might be beneficial if we use the modified ZIF-8 in the cycloaddition reaction of CO₂ and epoxides. Currently, the hydrothermal approaches to synthesize MOFs are more expensive than producing zeolite. Therefore, future work can be focused on reducing the cost of fabricating ZIF-8 to make the catalyst more economically efficient by exploring the effects of impure solvent, different gel composition and cheaper zinc sources. Furthermore, While ZIF-8 is decently active in the conversion of CO₂ to carbonates in the lab using pure carbon dioxide, its performance with CO₂ gas mixture is not clear. It is important to study the catalytic ability of ZIF-8 when using CO₂ mixed with other gases because CO₂ does not come in pure form but rather as in flue gas (mixture of gases).

6.2.2 Investigating the activity of ZIF-8 in the conversion of CO₂ to carbamates

The superior catalytic performance of ZIF-8 has exhibited in the conversion of CO₂ to cyclic carbonates inspired us to further explore its catalytic ability. Based on the fact that, ZIF-8 has a high preferential adsorption of CO₂,¹⁶⁰ we project that ZIF-8 could be active in other CO₂ involved catalytic reactions. The synthesis of carbamates (RNH-CO₂R') is an interesting candidate.

Carbamates are compounds widely used for a number of purposes including pharmaceutical preparation, production of agrochemicals such as pesticides and herbicides, and more generally, production of intermediates of fine and commodity chemicals.^{161,162} Commercially, carbamates are synthesized by aminolysis of chloroformate esters, obtained from phosgene and alcohol¹⁶³ which is a hazardous route. To overcome this drawback, many alternative approaches such as catalytic carbonylation of nitroaromatics and the oxidative carbonylation of amines have been developed.¹⁶⁴⁻¹⁶⁶ The reaction of amines with carbon dioxide in the presence of alkyl halides is the most eco-friendly process for the production of carbamates (Figure 6.1). This reaction is catalyzed by onium salts, basic catalysts, sterically hindered organic bases, crown ethers or solid cesium carbonates.¹⁶⁷⁻¹⁷⁵ Titanosilicates and zeolite-encapsulated metal complexes⁶⁷ is also found to catalyze this reaction. But in all those cases¹⁶⁷⁻¹⁷⁵ the reaction requires a strong donor solvent dimethylformamide (DMF). It is also reported that various carbamates can be synthesized in high yields in the absence of a solvent using an as-synthesized form of zeolite-beta.⁵⁰

Figure 6.1. Schematic showing the catalytic conversion of CO₂ into a carbamate.

The development of superior performance catalysts requires novel materials with fundamentally different structural, compositional, adsorption and transport properties than those of conventional zeolites, metal oxides or metal phases. In this respect, ZIF-8 is a novel crystalline microporous material with

highly desirable properties, such as uniform micropores, high surface areas and open porous framework structures with large accessible pore volumes making it potentially interesting candidates for catalytic applications. Furthermore, the preliminary results obtained in our lab shows that ZIF-8 is active in the conversion of CO₂ to carbamates (Table 6.1).

Table 6.1. Preliminary results of CO₂ conversion to carbamates

Amines	Structures	Conversion to Carbamates
Aniline		10.8%
Hexylamine		12.7%
Benzenelamine		10.8%

Reaction conditions: 10 mmol amine, 12 mmol *n*-butyl bromide and 100 mg ZIF-8 catalyst will be placed in the high pressure reactor. The reactor will be pressurized with CO₂ in the range of 4-10 bar. The reactions will be carried out at 80-100 °C at different times.

6.2.3 Exploring the catalytic activities of more structurally appealing MOFs

ZIFs are genuinely suitable materials as catalysts for the CO₂ conversion reactions because the Zn²⁺ ions inside the ZIFs' structures Lewis acid sites that catalyze the coupling reaction of CO₂ and epoxides. Besides ZIF-8, there are many other ZIFs that have ordered crystalline structures and exhibit interesting properties, such as ZIF-95, ZIF-68, ZIF-82, ZIF-70 have surface areas higher than 1000 m²/g and ZIF-70, ZIF-78, ZIF-82 have CO₂ uptakes larger than 50

cm³/g. ⁷⁴ More information of these ZIFs are indicated in Table 6.2.

Table 6.2. Compositions, topology parameters, surface areas and CO₂ uptakes for several promising ZIFs.^a

Name	Composition ^b	d _a ^c	d _p ^d	BET surface area (m ² /g)	CO ₂ uptake (cm ³ /g)	Ref.
ZIF-68	Zn(bIm)(nIm)	7.5	10.3	1090	37.6	70,71
ZIF-69	Zn(cblm)(nIm)	4.4	7.8	950	40.6	70,71
ZIF-70	Zn(lm) _{1.13} (nIm) _{0.87}	13.1	15.9	1730	55.0	70,71
ZIF-78	Zn(nblm)(nIm)	3.8	7.1	620	51.5	70,71
ZIF-79	Zn(mblm)(nIm)	4.0	7.5	810	33.5	71,73
ZIF-81	Zn(brblm)(nIm)	3.9	7.4	760	38.2	71,73
ZIF-82	Zn(cnlm)(nIm)	8.1	2.6	1300	52.7	71,73
ZIF-95	Zn(cblm) ₂	3.7	24.0	1050	19.7	71
ZIF-100	Zn ₂₀ (cblm) ₃₉ (OH)	3.4	35.6	595	32.6 ^e	71

^a For method of analysis, see Ref. 176. ^b Formula excluding guests. ^c d_a is the diameter of the largest sphere that will pass through the pore. ^d d_p is the diameter of the largest sphere that will fit into the cages without contacting the framework atoms. Pore metrics measurements exclude guests. ^e Measured at 273K, while the others were measured at room temperature.

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176. Method of analysis: The Cambridge Structural Database was searched with the criterion of obtaining all the structures that contain the metal-bi-imidazole; the metal is surrounded by at least four nitrogens, two of which are part of the imidazole ring. Each imidazole is bound to two metals through the nitrogen atoms with no discrimination according to the nature of the bonds. Recently published compounds were obtained from the CCDC deposition number. This search gave a total of 172 structures, which were analyzed with the TOPOS 4.0 package [Blatov, V.A.; Carlucci, L.; Ciani, G.; Proserpio, D.M. "Interpenetrating Metal-Organic and Inorganic 3D Net Works: A Computer-Aided Systematic Investigation. Part I Analysis of the Cambridge Structural Database" *Cryst. Eng. Comm.* **2004**, 6, 377-395]. For each entry, all doubled atoms were eliminated, and the adjacency matrix was calculated using the AutoCN routine with the default parameters and excluding hydrogen bonds, van der Waals, and special contacts. The obtained database was filtered to eliminate all the zero-, one-, and two-dimensional structures; 105 structures were found to be three-dimensional. The adjacency matrix was then simplified by calculating the centroids with the ADS routine for all non-metal atoms, and then all 0-, 1- and 2-connected atoms were eliminated, obtaining a database that includes only the reduced graphs of the nets. The topology

of the reduced structures was obtained using the ADS routine with the default parameters, selecting the “classification” option for only valence bonds. In some cases, the topology was obtained using Systre 1.1.5 [Delgado-Friedrichs, O.; O’Keeffe, M. “Identification of, and Symmetry Computation for Crystal Nets” *Acta. Crystallogr.* **2003**, A59, 351- 360].

CURRICULUM VITAE

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Professional Summary

Chemical engineer with extensive academic and research experience in material science, catalysis, gas separation and gas adsorption. Recognized by several peer-reviewed publications and an award from a national meeting. Possesses good communication skills.

Education

Ph.D. in Chemical Engineering GPA 3.7/4

University of Louisville, Louisville, KY, US (2008.10 – expected 2013.12)

Bachelor of Engineering GPA 78/100

Shandong University, Jinan, Shandong, China (2003.9 – 2007.6)

Experience

Graduate Research Assistant (2010.8 – present)

University of Louisville, USA

- Developed two methods to synthesize zeolitic imidazolate framework-8 (ZIF-8).
- Prepared various zeolites and MOFs with different techniques: hydrothermal and microwave heating.

- Fabricated membranes on different supports for the separation of CO₂ from CH₄.
- Studied the catalytic activity of different nanoporous materials (ZIF-8, SAPO-56, etc.) in the conversion of CO₂ to cyclic carbonates and carbamates in a batch reactor.
- Functionalized ZIF-8 with ethylenediamine and greatly improved its catalytic activity in the conversion of CO₂ to chloropropene carbonate.
- Developed nano-valved sorbent system for reversible natural gas storage.
- Collaborated with Prof. Shamus McNamara, Department of Elec. & Computer Engineering, U of L for a project obtaining the Knudsen pumps (which are based on the thermal transpiration phenomenon that gas molecules drift from the cold end to the hot end of a narrow channel) by the synthesis of porous materials on various substrates (glass fiber, stainless steel and ceramic).
- Extensive experience in characterization of materials using porosimeter, scanning electron microscopy, X-ray diffractionspectroscopy, infrared spectroscopy and gas chromatography.
- Trained new users in the proper use of the lab equipments, including BET, GC, batch reactor etc.
- Mentored an undergraduate student in his co-op research project.

Researcher in R&D Department

(2007.7 – 2007.12)

Shanghai Argus Fine Chemical Co. Ltd., China

- Analysis of different dye samples.
- Maintenance and troubleshooting of HPLC.
- Colored fabric using pad dyeing process and dip dyeing process.
- Tested the colored fabric by analytical methods (such as titration) and machines (like fabric fastness tester).

Undergraduate research

(2005.5 – 2007.6)

Shandong University, China

- Studied the impact of microwave on the electroplating of Ni.
- Analyzed the active ingredients in a Chinese medicine – Sanhuangpian.

Awards

- KOKES award at 23rd NAM conference 2013, Louisville, Kentucky, US. **2013**
- Second place in Technology Innovation Research Competition, **2006**, Shandong University, China

Professional Affiliation American Institute of Chemical Engineers

Publications

1. M. Zhu, M. A. Carreon, "Porous crystals as active catalysts for the synthesis of cyclic carbonates", *Journal of Applied Polymer Science* **2013**.
2. Z. Xie, M. Zhu, A. Nambo, J. B. Jasinski, M. A. Carreon, "Microwave-assisted synthesized SAPO-56 as a catalyst in the conversion of CO₂ to cyclic carbonates", *Dalton Transactions* 2013, 42, 6732-6735.
3. M. Zhu, D. Srinivas, S. Bhogeswararao, P. Ratnasamy, M. A. Carreon, "Catalytic activity of ZIF-8 in the synthesis of styrene carbonate from CO₂ and styrene oxide", *Catalysis Communications* **2013**, 32, 36-40.
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5. M. Miralda, E. E. Macias, M. Zhu, P. Ratnasamy, M. A. Carreon, "Zeolitic Imidazole Framework-8 Catalysts in the Conversion of CO₂ to Chloropropene Carbonate", *ACS Catalysis* **2012**, 2, 180-183.
6. M. Zhu, S.R. Venna, J.B. Jasinski, M.A. Carreon, "Room temperature synthesis of ZIF-8: The coexistence of ZnO nanoneedles", *Chemistry of Materials* **2011**, 23, 3590-3592.

Presentations

1. "Catalytic activity of ZIF-8 in the synthesis of styrene carbonate from CO₂ and styrene oxide" (poster) **23rd NAM conference 2013. Louisville, Kentucky, US.**
2. "Growth of zeolitic imidazolate framework-8 crystals from the solid-liquid interface" (oral) and "Zeolitic imidazolate framework-8 catalysts in the conversion of to chloropropene cabonate" (poster) **AICHE annual meeting 2012. Pittsburgh, Pennsylvania, US.**
3. "Zeolitic imidazolate framework-8 catalysts in the conversion of to chloropropene cabonate" (poster) **Kentucky Innovation and Entrepreneurship Conference 2012. Louisville, Kentucky, US.**
4. "Room temperature synthesis of ZIF-8: The coexistence of ZnO nanoneedles" (poster) **NAMS annual meeting 2011. Las Vegas, Nevada, US.**

Extracurricular Activities

Graduate Teaching Assistant (2010.8 – 2012.8)

University of Louisville

- Gave lectures for both graduate and undergraduate levels of courses.
- Tutored students for homework.
- Conducted labs for undergraduate students at unit operation lab.
- Diagnosed and solved the malfunctioning of the equipment for "cooling tower".

Recruitment officer for Energy Club (2012.8 – 2013.8)

University of Louisville

- Propagation of the club among new students.
- Presentation (posters) of the club in students association fair.
- Enrollment of the new club members.