

PREPARATION OF ZINC(II) PORPHYRIN WITH A MESOPOROUS  
STRUCTURE AND ITS PHOTOCATALYTIC PROPERTIES FOR THE OXIDATION  
OF AROMATICS

MAHSA KHOSH KHOOY YAZDI

UNIVERSITI TEKNOLOGI MALAYSIA

PREPARATION OF ZINC(II) PORPHYRIN WITH A MESOPOROUS  
STRUCTURE AND ITS PHOTOCATALYTIC PROPERTIES FOR THE OXIDATION  
OF AROMATICS

MAHSA KHOSH KHOUY YAZDI

A project report submitted in partial fulfilment of the  
requirements for the award of the degree of  
Master of Science (Chemistry)

Faculty of Science  
Universiti Teknologi Malaysia

MAY 2011

*Dedicated to my mother, the benevolent source of love and support.*

## ACKNOWLEDGEMENT

This research would not have been possible without the guidance and the help of several individuals who in one way or another contributed and extended their valuable assistance in the preparation and completion of this study.

First and foremost, my utmost gratitude to Prof. Dr. Salasiah Endud, my supervisor whose sincerity and encouragement I cherish and will never forget. Prof. Salasiah has been my inspiration as I hurdle all the obstacles in the completion of this research work. My appreciation also goes to all the lecturers and laboratory officers at both the Department of Chemistry and Ibnu Sina Institute of Fundamental Science Study, University Teknologi Malaysia.

Great gratitude to Ms. Nadirah Zawani bt Mohd Nesfu for knowledge sharing and invaluable assistance, and to Mr. Ali Mohammad Qasim for all his support, encouragement and help during the compilation of this work.

I would like to thank all of my friends especially Pooneh Raisdana for her support and motivational activities that kept me sane along with all the pressure that accompanied this work.

Last but not the least, I want to express my gratitude to my family. First, my mother, the benevolent source of love and support whose endless giving have been truly inspirational at every moment of my life. Her extensive phone calls and worry were indeed a daily positive stimulus till this project was completed. Then, my lovely Guinea-Pig pet Fandogh, who had always been standing on my shoulders while doing my work, filling me with delight and kindness, witnessing every written word in this piece of work, being one of the biggest parts of my life and a reason why I had pleasurable and amusing working moments..

## ABSTRACT

Mesoporous molecular sieve MCM-41 was used as support for the immobilization of bulky zinc(II)-5, 10, 15, 20-tetraphenylporphyrin (ZnTPP). Zinc porphyrin was prepared via the treatment of ZnCl<sub>2</sub> with 5, 10, 15, 20-tetraphenyl-21H, 23H-porphyrin in dimethylformamide (DMF). The product was crystallized and characterized by Ultraviolet Visible spectroscopy (UV-Vis) and Fourier Transform Infrared spectroscopy (FTIR spectroscopy). ZnTPP encapsulated inside the mesoporous of ordered structure of MCM-41 with three different concentrations were prepared by treatment of zinc porphyrin with MCM-41 in DMF in room temperature. The materials obtained were characterized by X-ray Diffraction (XRD), and Ultraviolet Visible Diffuse Reflectance (UV-Vis DR) spectroscopy. The powder XRD data confirmed that the ordered structure of mesoporous MCM-41 remained intact after encapsulation process. Characterization of ZnTPP composite with MCM-41 using UV-Vis DR confirmed that the structure of ZnTPP in the support is similar with bare ZnTPP. Encapsulated ZnTPP as catalyst in a photoexcited system was found to be active and selective in the D-limonene biotransformation under mild condition with hydrogen peroxide as the oxidant. The influence of different concentrations of catalyst was studied for photocatalytic oxidation of D-limonene to carvone. The products were identified by using Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS).

## ABSTRAK

Bahan mesopori penapis molekul MCM-41 telah digunakan sebagai penyokong bagi memengunkan zink(II)-5, 10, 15, 20-tetrafenilporfirin (ZnTPP). Zink porfirin telah disediakan melalui tindak balas  $\text{ZnCl}_2$  dengan 5, 10, 15, 20-tetrafenil-21H, 23H-porfirin dalam dimetilformamid (DMF). Produk telah dihablurkan dan dicirikan menggunakan spektroskopi Ultra lembayung Nampak (UV-Vis) dan spektroskopi Inframerah Transformasi Fourier (FTIR). ZnTPP dipegunkan dalam struktur mesopori MCM-41 menggunakan tiga kepekatan yang berbeza telah disediakan secara tindak balas zink(II) porfirin dengan MCM-41 dalam DMF pada suhu bilik. Bahan yang diperolehi dicirikan menggunakan pembelauan sinar-X (XRD) dan spektroskopi difusi pemantulan Ultra lembayung (UV-VisDR). Data XRD mengesahkan keseragaman struktur mesopori MCM-41 masih utuh selepas proses pemegungan. Pencirian komposit ZnTPP dengan MCM-41 menggunakan spektroskopi UV-VisDR mengesahkan struktur ZnTPP berpenyokong adalah serupa dengan ZnTPP asal. Mungkin ZnTPP terenkapsulasi dalam dibawah sistem fotopemangunan didapati aktif dan selektif dalam biotransformasi D-limonin keadaan sederhana dengan kehadiran hidrogen peroksida sebagai pengoksida. Pengaruh perbezaan kepekatan mungkin telah dikaji bagi fotopemangkinan pengoksidaan D-limoni kepada karvon. Hasil tindak balas telah dikenalpasti menggunakan kromatografi gas (GC) dan kromatografi gas-spektrometri jisim (GC-MS).

## TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	<b>DECLARATION</b>	ii
	<b>DEDICATION</b>	iii
	<b>ACKNOWLEDGEMENT</b>	iv
	<b>ABSTRACT</b>	v
	<b>ABSTRAK</b>	vi
	<b>TABLE OF CONTENTS</b>	vii
	<b>LIST OF TABLES</b>	ix
	<b>LIST OF FIGURES</b>	x
	<b>LIST OF ABBREVIATIONS</b>	xii
	<b>LIST OF SYMBOLS</b>	xv
	<b>LIST OF APPENDICES</b>	xvii
<b>1</b>	<b>INTRODUCTION</b>	1
	1.1 Background of Study	1
	1.2 Problem Statement	7
	1.3 Research Objectives	7
	1.4 Scope of Study	8
	1.5 Project Outline	9
<b>2</b>	<b>LITERATURE REVIEW</b>	10
	2.1 Introduction to Metalloporphyrins	10
	2.2 Synthesis of Metalloporphyrins	10
	2.3 Heterogenization of Metalloporphyrins	18
	2.4 Immobilization of Metalloporphyrins into MCM-41	19
	2.4.1 Introduction on MCM-41	19
	2.4.2 Immobilization Strategies	21
	2.5 Catalysis Reaction	22
	2.5.1 Introduction on D-limonene and Carvone	22
	2.5.2 Conversion of Limonene to Carvone	23

<b>3</b>	<b>THE RESEARCH METHODOLOGY</b>	<b>26</b>
3.1	Preparation of materials	26
3.1.1	Preparation of Zinc(II) porphyrin	26
3.1.2	Synthesis of Purely Siliceous Si-MCM-41	27
3.1.3	Encapsulation of Zinc(II) porphyrin into MCM-41	27
3.2	Characterization Methods	28
3.2.1	Ultraviolet-Visible spectroscopy (UV-Vis)	28
3.2.2	Fourier Transform Infrared Spectroscopy (FTIR)	29
3.2.3	UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DR)	30
3.2.4	X-ray Powder Diffraction (XRD)	31
3.3	Photocatalytic activity of D-limonene	34
3.3.1	Catalytic testing	34
3.3.2	Analysis of reaction products	34
	3.3.2.1 Gas chromatography- Flame Ionization detector (GC-FID)	34
	3.3.2.2 Gas Chromatography-Mass Spectrometry (GC-MS)	35
<b>4</b>	<b>RESULT AND DISCUSSION</b>	<b>37</b>
4.1	Physical properties of porphyrin and zinc(II) porphyrin	37
4.1.1	Physical properties of Zinc(II) tetraphenylporphyrin encapsulated in MCM-41	39
4.2	Photocatalytic activity of D-limonene	41
<b>5</b>	<b>CONCLUSION AND RECOMMENDATIONS</b>	<b>46</b>
5.1	Conclusion	46
5.2	Recommendations	48
	<b>REFERENCES</b>	<b>49</b>
	Appendices A – B	55 – 60



**LIST OF TABLES**

<b>TABLE NO.</b>	<b>TITLE</b>	<b>PAGE</b>
4.1	Main FTIR bands of porphyrin and zinc(II) porphyrin.	38
4.2	Catalytic activity of H <sub>2</sub> TPP, ZnTPP and different concentrations of ZnTPP in ZnTPP-MCM-41 after UV-Vis light.	44

## LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
1.1	Generic potential energy diagram showing the effect of a catalyst.	2
1.2	Porphyrin and Pyrrole rings.	3
1.3	The structure of heme.	4
1.4	Outline of main research activities.	9
2.1	Rhenium porphyrins.	13
2.2	Possible intermediates of metalloporphyrins.	13
2.3	Direct synthesis of Palladium porphyrin.	17
2.4	MCM-41 structure.	20
2.5	Synthesis of MCM-41 using templating method.	20
2.6	The structure of D-limonene.	23
2.7	The structure of R-(-)-carvone and S-(+)-carvone.	24
2.8	Limonene to carvone transformation.	25
3.1	Synthesis of ZnTPP.	26
4.1	The structure of Zinc(II) tetraphenylporphyrin.	37
4.2	FTIR bands of free porphyrin and zinc(II) porphyrin.	38
4.3	UV-Vis spectra of free porphyrin and zinc(II) porphyrin.	39
4.4	UV-Vis DR spectra of free porphyrin and zinc(II) porphyrin.	40
4.5	XRD patterns of zinc(II) porphyrins encapsulated in MCM-41.	41
4.6	Products of limonene photo transformation in the presence of ZnTPP catalyst.	42
4.7	A possible mechanism for limonene photo-oxidation by ZnTPP.	43
A1	GC/FID plot for ZnTPP-MCM-41 with 25 $\mu$ M concentration of ZnTPP.	55
A2	GC/FID plot for ZnTPP-MCM-41 with 50 $\mu$ M concentration of ZnTPP.	56
A3	GC/FID plot for ZnTPP-MCM-41 with 100 $\mu$ M concentration of ZnTPP.	57

A4	GC/FID plot for ZnTPP.	58
A5	GC/FID plot for uncatalyzed reaction.	59
B1	GC-MS plot for the sample with no catalyst.	60
B2	GC-MS plot for the sample with ZnTPP catalyst.	61
B3	GC-MS plot for the sample with 100 $\mu$ M ZnTPP encapsulated in MCM-41 catalyst.	62

**LIST OF ABBREVIATIONS**

A	–	Absorbance
acac	–	Acetylacetonate
AlCl <sub>3</sub>	–	Aluminium Trichloride
AlH <sub>3</sub>	–	Aluminium Hydride
ATR	–	Attenuated Total Reflectance
C <sub>6</sub> H <sub>5</sub> OH	–	Hydroxybenzene - Phenol
C <sub>6</sub> H <sub>5</sub> CN	–	Benzonitrile
cm	–	Centimeter
CO	–	Carbon Monoxide
Cr(CO) <sub>6</sub>	–	Hexacarbonylchromium
CrCl <sub>2</sub>	–	Chromium(II) Chloride
CTABr	–	Cetyltrimethylammonium Bromide
DMF	–	Dimethylformamide
DNA	–	Deoxyriboneucleic Acid
E <sub>a</sub>	–	Activation Energy
EtOH	–	Ethyl Alcohol (Ethanol)
Fe(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	–	Iron(II) Acetate
FTIR	–	Fourier Transform Infrared
GC-FID	–	Gas Chromatography - Flame Ionization Detector
GC-MS	–	Gas Chromatography - Mass Spectrometry
H <sub>2</sub>	–	Hydrogen molecule
H <sub>2</sub> O	–	Water
H <sub>2</sub> O <sub>2</sub>	–	Hydrogen Peroxide

H <sub>2</sub> TPP	–	Free base tetraphenylporphyrin
HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	–	Acetic acid
HCl	–	Hydrochloric Acid
Hpor-M	–	Metalloporphyrin
IUPAC	–	International Union of Pure And Applied Chemistry
JCPPS	–	Joint Committee on Powder Diffractions Standards
KBr	–	Potassium Bromide
KOH	–	Potassium Hydroxide
LCT	–	Liquid Crystal Templating
M	–	Metal
MCM-41	–	Mobile Composition of Matter No. 41
MoCl <sub>2</sub>	–	Molybdeum Chloride
N	–	Nitrogen
NMR	–	Nuclear Magnetic Resonance
O <sub>2</sub>	–	Oxygen molecule
Pd	–	Palladium
PorH <sub>2</sub>	–	Porphyrin
R•	–	Hydrocarbon Radical
RHA	–	Rice Husk Ash
SBU	–	Secondary Building Unit
TBHP	–	tert-Butyl hydroperoxide
THF	–	Tetrahydrofuran
UV-Vis DR	–	Ultraviolet Visible Diffuse Reflectance
ZnCl <sub>2</sub>	–	Zinc Chloride
ZnTPP	–	Zinc(II) Tetraphenylporphyrin
ZnTPPM25	–	Zinc(II) Tetraphenylporphyrin encapsulated in MCM-41 with 25 μM concentration of zinc
ZnTPPM50	–	Zinc(II) Tetraphenylporphyrin encapsulated in MCM-41 with 50 μM concentration of zinc

- ZnTPPM25 – Zinc(II) Tetraphenylporphyrin encapsulated in MCM-41 with  
100  $\mu$ M concentration of zinc
- ZnTPP• – Zinc(II) Tetraphenylporphyrin Radical

**LIST OF SYMBOLS**

$\text{\AA}$	–	Angstrom $10^{-10}$ meters
$\theta$	–	Theta
$^{\circ}$	–	Degree
$\mu$	–	Mue
$\lambda$	–	Wavelength
$\varepsilon$	–	Wavelength-dependent molar absorptivity
$\sigma$	–	Head to head overlap of two orbitals
$\bullet$	–	Radical
$h$	–	Plank's constant
$c$	–	Speed of light
$E_0$	–	Ground State energy
$E_1$	–	First excitation state
$n$	–	Diffraction order from $n=1,2,3, \dots$
$a_0$	–	Unit cell parameter
$V$	–	Volt
$A$	–	Amper
$d$	–	Interplanar spacing
$I$	–	Intensity of light
$I_0$	–	Intensity of incident light
$k$	–	Kilo
$K$	–	Kelvin
$h$	–	Hour
$g$	–	Gram

m	–	Milli
min	–	Minute
mL	–	Millilitre
M	–	Mole
$\mu\text{M}$	–	Micromole
nm	–	Nanometer
R	–	Reflectance



**LIST OF APPENDICES**

<b>APPENDIX</b>	<b>TITLE</b>	<b>PAGE</b>
A	GC-FID RESULTS	55
B	GS-MS RESULTS	60

## CHAPTER 1

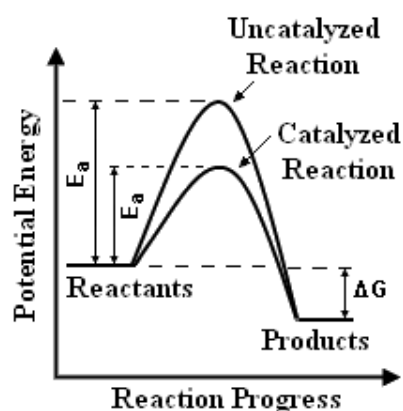
### INTRODUCTION

#### 1.1 Background of Study

A catalyst is a substance that can change the rate of a reaction. A catalytic reaction is a kind of reaction that has a different activation energy with none catalytic reaction. There are different kinds of catalysts that can change the rate of a reaction, whether increasing or decreasing it. There are two types of catalysts, homogeneous and heterogeneous ones. A homogeneous catalyst is in the same phase with the reactants while the heterogeneous catalyst is in a different phase with the reactants. Catalysts are crucial entities in many chemical reactions. Different types of catalysts can be used in different types of reactions depending on the need. The effects of the presence of a catalyst on reactions can be well noticed in the reactions with very high activation energies. In the absence of a catalyst, these kinds of reactions can impossibly take place (Shriver *et al.*, 1999).

The knowledge of the catalytic reactions mechanism has improved dramatically in recent years because of the availability of isotopically labeled molecules, improved methods for determining reaction rates and improved spectroscopic and diffraction techniques (Shriver *et al.*, 1999). Due to the findings, the catalyst itself is not consumed by the reaction though it may participate in various chemical transformations. A catalyst introduces a new pathway to the reaction, an alternative one with a different transition state. The important fact is that it does not have any effect on the chemical equilibrium because it changes the rate of both forward and reverse reactions, as shown in Figure 1.1. Catalysts affect the rate of a reaction by making a change in the transition state. When they work as accelerators, the reaction will possess a different transition state with lower activation energy. On the other hand, when they slow up a reaction, the transition state will possess higher activation energy. They usually participate in the rate determination step of a reaction. They generally

react with one or more reactants to form the intermediates that lead to the products with regenerate catalysts included (Robertson, 1970; Shriver *et al.*, 1999)



**Figure 1.1:** Generic potential energy diagram showing the effect of a catalyst.

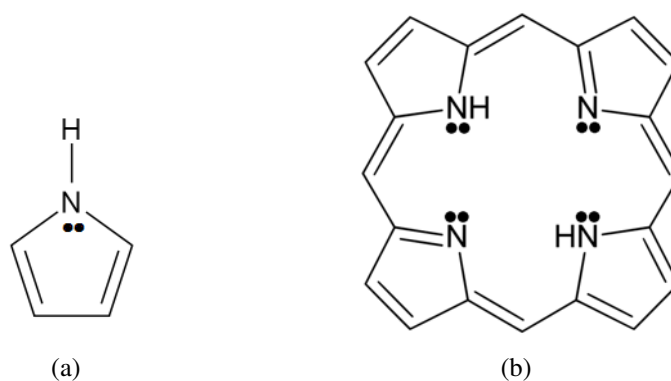
The catalytic reaction must be thermodynamically favorable and it should run at a reasonable rate, also the catalyst must have a proper selectivity toward the desired product and it must have a long life, enough to be considered economical. A selective catalyst produces a high proportion of the desired product with a minimum amount of side products. In industry, there is a substantial economic stimulus to develop selective catalysts (Shriver *et al.*, 1999).

Catalysts are important in chemical laboratories, chemical and pharmaceutical industry as well as in biology. The important role of catalysis is underlined by the fact that approximately ninety percent of all nowadays products in these areas are being produced by processes that require at least one catalytic step. At the same time, using the hydrocarbons as the main stock for goods and fine chemicals needs at least one oxidation step that is usually carried out with transition metals. Therefore oxidation catalysis is a main research field in academic and industrial chemistry. In most of these processes, species with metal-carbon bonds are formed as important intermediates. Using organic ligands, and therefore organometallic complex metal fragments, is the best way to achieve efficient oxidation catalysis (Meyer and Limberg, 2007).

Porphyrins are abundant organic compounds. They are ring shaped, and can be used as organic ligands to generate organometallic complexes. A porphyrin has four pyrrole rings. A pyrrole has four carbon atoms and a nitrogen atom shaped like a pentagon ring ( $C_4H_5N$ ) as shown in Figure 1.2. Porphyrin can act as a bi, tri or hexadentate ligand as well as the normal tetradentate ligand (Ostfeld and Tsutsui,

1974). Porphyrins as macrocycle molecules have highly conjugated systems. The porphyrin ring has a total of twenty six pi electrons. The macrocycles have intense absorption bands in the visible region that contribute to its strong color (Fleischer, 1970).

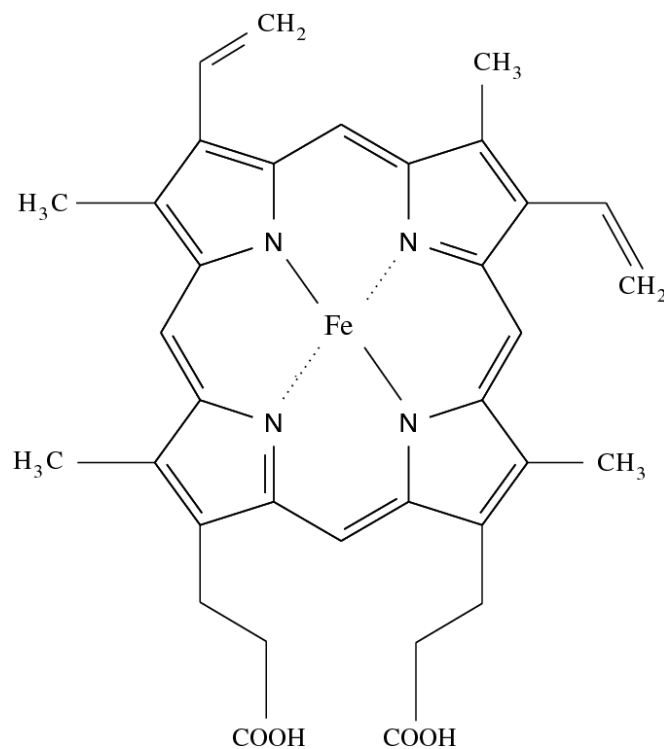
Different transition metals can be bound inside the porphyrin ring, which consequently forms various organometallic complexes. The four nitrogens in the middle of the porphyrin ring can make bonds with transition metals like iron (Fe), copper (Cu), cobalt (Co) and Zinc (Zn). Each of these organometallic complexes can be used as a source of catalysts for different reactions especially the redox reactions (Kadish *et al.*, 2000).



**Figure 1.2:** (a) Pyrrole ring, (b) Porphyrin ring.

There are different types of porphyrins that can be used as a ligand. They can be substituted by both organic and inorganic groups. These substituents can give various characteristics to the porphyrin ring. Therefore, a large group of ligands can be produced for specific needs (Chou *et al.*, 2003).

One of the most famous porphyrins is ferroporphyrin or heme that has iron (Fe) bonded with its nitrogens inside. The structure is shown in Figure 1.3. The hemoglobin in red blood cells that transfers the oxygen all over the body has four subunits and each of these subunits has a heme group. Amino acids are attached to these heme groups to make hemoproteins. A Heme is the prosthetic group of these metalloproteins. In a heme, Iron (II) is responsible for the oxygen transportation in the body. The sixth position around the iron in the heme will be occupied by the oxygen ( $O_2$ ) and the fifth one is coordinated with the histidin residue. While the oxygen is attached to the iron, the porphyrin ring has a planar shape but when the oxygen is released, the porphyrin will adopt the domain configuration (Lever and Gray, 1989).



**Figure 1.3:** The structure of heme.

Chlorophyll that is responsible for capturing the sun's energy in plants is another example. The central metal of the chlorophylls porphyrin is magnesium (Mg). Photosynthesis is the most important process in green plants in which light's energy is converted to chemical energy, stored in carbohydrates. Magnesium in the porphyrin center absorbs a photon and one of its 3s electrons get excited to a higher energy state. Consequently, the electron will be ejected out of the magnesium when more photons are absorbed. The magnesium is oxidized in this situation and it gets its electron back from the photolysis of water. The magnesium's electron enters a chain called electron transport chain, after which the energy storage process starts (Gray, 1981).

Vitamin B<sub>12</sub> is also a good example to show the important roles of porphyrin rings. This compound has cobalt (Co) as a central metal. Vitamin B<sub>12</sub> is a water soluble vitamin that is normally involved in the metabolism of every cell of human body. Also, it affects DNA synthesis and regulation, fatty acid synthesis and energy production (Banerjee and Ragsdale, 2003; Eschenmoser and Wintner, 1977). Besides all the work that has been done on metalloporphyrins in biological systems, metalloporphyrins have been studied for other reasons as well, for example, the search for superconductors (Adler, 2007), anti-cancer drugs (Macquet and Theophanides, 1972), catalysis (Hansen and Drenth, 1993) and chemical shift reagents (Gianferrara *et al.*, 2007).

Much work has been done on the catalytic activity of metalloporphyrins. Different metalloporphyrins have been selected for catalysis of different reactions. For example, researches show that Manganese porphyrins have uncommonly high reactivity toward olefin epoxidation and alkane hydroxylation (Campestrini and Meunier, 1992). Also, ruthenium porphyrins have been found to catalyze the aerobic epoxidation of olefin under mild conditions (Groves and Quinn, 1985). In substituted metalloporphyrins, for example, researches have been done in catalytic activity of halogenated iron porphyrins in alkene and alkane oxidation by iodosylbenzene and hydrogen peroxide (Guedes *et al.*, 2005).

In addition, researches have been done on metalloporphyrins extracted from natural sources like heme fragment in cytochrome c or magnesium porphyrin in chlorophyll. For these non-synthetic metalloporphyrins, the mechanism of their catalytic activity in the body or in plants has been found. In other cases, these metalloporphyrins have been used as a catalyst in other reactions. For example, copper porphyrin extracted from the feather of certain birds was used to study the mechanism of oxidation of ascorbic acid in human body. In this research, they found that ascorbic acid in the body is oxidized in the presence of copper porphyrin and iron porphyrin together since copper porphyrin alone is insufficient for the oxidation to take place (Keilin, 1951).

Metalloporphyrins as catalysts for oxidation reactions are highly selective as well as being able to operate in mild conditions (Haber *et al.*, 2004). Besides all the advantages of using metalloporphyrins in the oxidation of hydrocarbons there are some disadvantages in using them as homogeneous catalysts. The difficulty of separating the product from the catalyst increases the cost of using homogeneous catalysis in the commercial process. Due to this fact, heterogenization of metalloporphyrins by using porous solid supports can be a good solution to keep their properties besides solving the separation issues. There are three classes of materials that are used as heterogeneous catalysts and adsorption media. One of them is microporous inorganic solids with pore diameter of 20 Å and less and the other is mesoporous inorganic solids with pore diameter of 20 to 500 Å. The third one is macroporous materials which its pore diameter is greater than 500 Å (Rouquerol *et al.*, 1994).

Zeolites as a member of microporous materials with regular arrays of internal channels have been extensively studied as an inorganic support. They are hydrated, crystalline tectoaluminosilicates that are constructed from  $TO_4$  tetrahedra (T = tetrahedral atom, e.g., Si, Al); each apical oxygen atom is shared between two adjacent

tetrahedral giving a framework ratio of O/T = 2. They have specific sites available for active metal substitution which gives them the ability to be prepared for selective processes (Davis and Lobo, 1992). Different Zeolites have been used for different purposes. For example, zeolite Y was used for encapsulation of metalloporphyrins such as cis-Mn(bypy)<sub>3</sub> to be active catalysts toward cyclohexane oxidation (Skrobot, 2003). Zeolites have been used as supports for metalloporphyrins that provide a physical separation of active site, therefore catalyst self-destruction and dimerization of unhindered are minimized (Li, 2002). However, due to the small pore size of the Zeolites, their application in reactions involved with large molecules is limited (Thomas, 1998).

MCM-41 is a mesoporous material from the M41S family which has unique pores and large well-defined internal surface area (Beck *et al.*, 1992). Due to its pore size, high molecular mass organic compounds can be fitted into the pores. Recently, much effort was focused on immobilization of metalloporphyrins into the silica MCM-41 surface. Fe, Mn and Co tetraphenylporphyrin complexes were immobilized in MCM-41 and used as catalysts for cyclohexene oxidation by peroxide. The study showed that the interaction between the support and metalloporphyrins causes modifications in MCM-41 chemical environment and these materials appear to be good catalysts for reported reaction (Costa *et al.*, 2008). Ruthenium meso-tetrakis-(2, 6-dichlorophenyl)porphyrin complex were immobilized into MCM-41 to catalyze selective alkene epoxidations in order to easy catalysts recycling. The research showed that Ru supported catalyst is effective toward norbornene and cyclooctene oxidations, where zeolite-based TS-1-catalyzed condition is unsuccessful in transformation (Liu *et al.*, 1998).

In this research the same interest in using modified MCM-41 with metalloporphyrins as catalysts for selective oxidations is followed. The oxidation of D-limonene to carvone is studied by using zinc tetraphenylporphyrin immobilized on MCM-41 as a catalyst.

Porphyrin-based photocatalytic system for biotransformation of D-limonene was first reported by Trytek *et al.* in 2005. In their work, some porphyrin complexes such as zinc tetraphenylporphyrin and cobalt tetraphenylporphyrin were used as catalysts in the presence of dioxygen as an oxidant. The aim of this work was to study the photochemical excitation as a clean and an appropriate strategy of porphyrin-based biomimetic catalysis. Their result showed that in the absence of light limonene, oxidation by using porphyrin complexes as catalysts does not take place and in the

absence of catalysts using the light, the result does not give observable oxidation. Cobalt tetraphenylporphyrin did not show any result of oxidation where zinc porphyrin catalyzed the reaction (Trytek *et al.*, 2005). The same method is used to catalyze the oxidation of D-limonene to carvone in this research.

## 1.2 Problem Statement

Photocatalytic reaction based on zinc(II) tetraphenylporphyrin for oxidation of D-limonene to carvone was done by (Trytek *et al.*, 2005). Zinc(II) tetraphenylporphyrin was used as a homogeneous catalyst, but the separation of the catalyst from the product in this method is rather difficult. Moreover, homogeneous catalysts are not recyclable and not reusable. Therefore, in this research, zinc(II) tetraphenylporphyrin immobilized into MCM-41 is used as heterogeneous catalysts to provide an easier method to separate and recycle the catalyst.

The photocatalytic reaction which was reported before carried out at room temperature (Trytek *et al.*, 2005). Hence, the same way is adopted in this study since providing the appropriate conditions for the reaction is easy, and it does not need extra energy to be used. As D-limonene can be obtained from citrus peel oil with an amount of up to 50 kg as a byproduct annually it can be used as cheap and ready to use starting material to produce more valuable fragrance compounds such as carvone (Trytek *et al.*, 2005).

## 1.3 Research Objectives

The main objectives of this research are:

- i) To synthesize zinc(II) tetraphenylporphyrin and to characterize it by Ultraviolet Visible spectroscopy (UV-Vis) and Fourier Transform Infrared spectroscopy (FTIR spectroscopy).
- ii) To immobilize zinc(II) tetraphenylporphyrin and tetraphenylporphyrin into MCM-41 and characterize the products by X-ray Diffraction (XRD), and Ultraviolet Visible Diffuse Reflectance (UV-Vis DR).



- iii) To study and optimize the catalytic activity of encapsulated zinc porphyrin and porphyrin in the photocatalysis of limonene to carvone using Gas Chromatography (GC) and Gas Chromatography-Mass Spectroscopy (GC-MS).

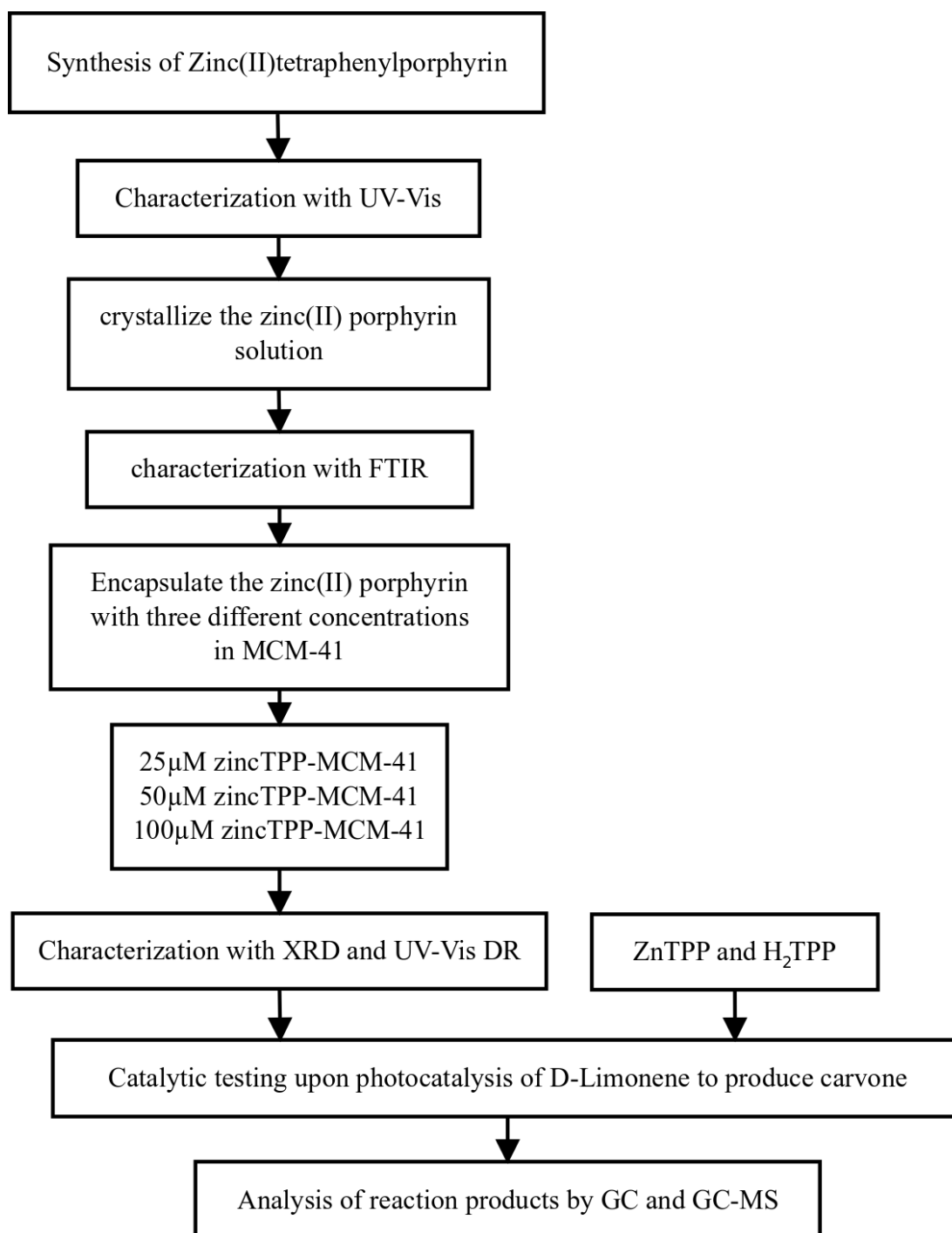
#### 1.4 Scope of Study

This study involves the synthesis of zinc(II) tetraphenylporphyrin via the treatment of  $ZnCl_2$  with 5, 10, 15, 20-tetraphenyl-21H, 23H-porphyrin in dimethylformamide. The synthesized product will be encapsulated in MCM-41. MCM-41 is not synthesized in this research and it is ordered from a third party.

The reactivity of the prepared catalysts will be tested in the photocatalysis of D-limonene to carvone. In this reaction, hydrogen peroxide is used as an oxidant and UV light is used as an excitation agent.

The synthesized zinc porphyrin will be characterized by Ultraviolet Visible spectroscopy (UV-Vis) and Fourier Transform Infrared spectroscopy (FTIR spectroscopy). The encapsulated products in MCM-41 will be characterized by X-ray Diffraction (XRD), and Ultraviolet Visible Diffuse Reflectance (UV-Vis DR). The catalytic properties and the reusability of the prepared catalysts will be tested in the photocatalysis of D-limonene. Optimization of the reaction parameters involves using different concentrations of catalysts. The products will be analyzed using Gas Chromatography (GC) and Gas Chromatography-Mass Spectroscopy (GC-MS).

## 1.5 Project Outline



**Figure 1.4:** Outline of main research activities.