IRON(III)-PORPHYRIN IMMOBILIZED ON MESOPOROUS Al-MCM-41 AND POLYMETHACRYLIC ACID AS CATALYSTS FOR THE SINGLE-STEP SYNTHESIS OF PHENOL FROM BENZENE

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Science (Chemistry)

Faculty of Science
Universiti Teknologi Malaysia

SEPTEMBER 2005

Specially Dedicated To my Beloved Mother

To my Husband, Ervan Latuhari

To my parents in law,

To my Family, Brothers and Sisters

ACKNOWLEDGEMENT

First of all, I thank Almighty Allah, The Creator, for Mercy and Guidance in my whole life and giving me the ability to complete this research.

I would like to express my sincere appreciation and deepest gratitude to my supervisor, Assoc. Prof. Dr. Salasiah Endud, Dr. Hadi Nur and Assoc. Prof. Dr. Zainab Ramli for their supervision, guidance, encouragement, advice, critics, motivation, and patience. Without their support and assistance, this thesis would not have been the same as presented here. It has been truly memorable and educative being a researcher under their supervision. I wish to express special appreciation to Prof. Dr. Halimaton Hamdan, Didik Prasetyoko, M.Sc. and Zeolite and Porous Material Group (ZPMG) members for their help support and valuable hints.

I am also indebted to Ministry of Science, Technology and Innovation (MOSTI) for its support in providing the research grant for the IRPA funding 09-02-06-0057-SR0005/09-04. My study would not have been possible without this funding. I must give my special thanks to Ibnu Sina Institute for Fundamental Science Studies, Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia and also my research friends, thank you for your help and support.

My sincere appreciation also extends to all of my dearest family in www.S36chantique.com and all my sisters in H21 who have given me a beautiful friendship. I thank all of them, who are too numerous to mention each of them individually. And last, I would like to give greatest thank to my beloved mother, Andi Djuaeda, my parents in law, my dearest sisters and brothers, and all of my lovely big family, for their support, encouragement, care and love. And especially grateful to someone who is very patience, love, and supportive to me, my husband Ervan Latuhari, thank you so much.

ABSTRACT

Mesoporous molecular sieve Al-MCM-41 with Si/Al=20 and polymethacrylic acid (PMAA) were used as supports for the immobilization of bulky iron(III)-5,10,15,20-tetra-(4-pyridyl) porphyrin (Fe-TPyP). Metalloporphyrin of Fe(III) was encapsulated inside the mesopores of the ordered structure of Al-MCM-41 by sequential synthesis of Fe-TPyP via treatment of $FeCl_3$ with 5,10,15,20-tetra-(4-pyridyl) porphyrin (TPyP), followed by encapsulation of Fe-TPyP. Fe-TPyP complexes were also successfully encapsulated into PMAA by polymerizing methacrylic acid (MAA) with a cross-linker around the Fe-TPyP complexes. The materials obtained were characterized by X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR), Ultraviolet Visible Diffuse Reflectance (UV-Vis DR), Electron Spin Resonance (ESR), Luminescence and ^{13}C CP/MAS NMR spectroscopies, Thermogravimetric Analysis (TGA) and elemental analysis. The powder XRD data confirmed that the ordered structure of mesoporous Al-MCM-41 remained intact after encapsulation process. Characterization of Fe-TPyP composite with Al-MCM-41 and PMAA using FTIR, UV-Vis DR and ESR confirmed that the structure of Fe-TPyP in inorganic and polymer supports is similar with bare Fe-TPyP. The specific interaction of Fe-TPyP in Al-MCM-41 and/or PMAA was studied by ESR, ^{13}C CP/MAS NMR and Luminescence spectroscopies. The ESR spectra of Fe-TPyP/Al-MCM-41 and Fe-TPyP/PMAA composites showed that there is a shift towards a higher g-value confirming the interaction between Fe-TPyP and supports is occurred. By quenching of the luminescence spectra of Fe-TPyP/PMAA with various concentration of Fe-TPyP, it is evidenced that there is some interaction between Fe-TPyP and PMAA. Further evidence of interaction was corroborated by ^{13}C CP/MAS NMR spectra with show that the peak of carboxyl of PMAA is shifted to higher magnetic field. Single-point BET surface area analysis was used to determine specific surface area of the composites. It is revealed that the surface area of Fe-TPyP/Al-MCM-41 composites is decreased with an increase in Fe-TPyP, suggesting the encapsulation of the complex in the pores of Al-MCM-41 has been achieved. With mesoporous molecular sieve (Al-MCM-41) and the polymer (PMAA) as supports, the immobilized iron-porphyrin system has demonstrated excellent activity for the single-step synthesis of phenol from benzene under mild reaction conditions. The effect of reaction time, solvent, amount of Fe-TPyP loading, temperature and the performance of the recovered catalysts have been studied. The immobilized iron-porphyrin in PMAA (Fe-TPyP/PMAA) gives a higher activity compared to Fe-TPyP supported on Al-MCM-41 (Fe-TPyP/Al-MCM-41). However, the product selectivity of Fe-TPyP/PMAA is not as good as that of Fe-TPyP/ Al-MCM-41. Thus, it is reasonable to assume that the hydrophobic nature of Fe-TPyP/PMAA would account for the high activity, while the rigid, ordered structure of Fe-TPyP/Al-MCM-41 would contribute towards the high selectivity in the single-step synthesis of phenol from benzene in the present study.

ABSTRAK

Penapis molekul mesoliang Al-MCM-41 dengan nisbah Si/Al = 20 dan asid polimetakrilik (PMAA) telah digunakan sebagai penyokong untuk pemegunan kompleks ferum(III)-5, 10, 15, 20-tetra-(4-piridil) porfirin (Fe-TyP). Ferum-porfirin telah dikapsulkan di dalam mesoliang Al-MCM-41 secara sintesis berturutan Fe-TPyP melalui tindak balas $FeCl_3$ dengan 5, 10, 15, 20-tetra-(4-piridil) porfirin (TPyP), dan diikuti pengkapsulan Fe-TPyP. Kompleks Fe-TPyP juga telah berjaya dikapsulkan ke dalam PMAA melalui proses pempolimeran asid metakrilik (MAA) dengan perangkai silang di sekitar kompleks. Sampel yang terhasil dicirikan dengan menggunakan kaedah XRD, spektroskopi FTIR, UV-Vis DR, ESR, pendarcahaya dan ^{13}C CP/MAS NMR, TGA dan analisis unsur. Data XRD menunjukkan bahawa struktur mesoliang Al-MCM-41 yang teratur masih wujud setelah proses pengkapsulan. Pencirian komposit Fe-TPyP dengan Al-MCM-41 dan PMAA dengan kaedah FTIR, UV-Vis DR dan ESR, menunjukkan bahawa struktur Fe-TPyP di dalam penyokong tak organik dan polimer adalah serupa dengan kompleks asal Fe-TPyP. Interaksi spesifik Fe-TPyP dalam Al-MCM-41 dan/atau PMAA dikaji dengan kaedah spektroskopi ESR, pendarcahaya dan ^{13}C CP/MAS NMR. Spektrum ESR bagi komposit Fe-TPyP/Al-MCM-41 dan Fe-TPyP/PMAA memperlihatkan anjakan ke arah nilai-g yang lebih tinggi, menunjukkan adanya interaksi antara Fe-TPyP dan penyokong. Pelindapan spektrum pendarcahaya bagi Fe-TPyP/PMAA dengan pelbagai kepekatan Fe-TPyP membuktikan terjadinya interaksi antara Fe-TPyP dan PMAA. Bukti interaksi tersebut juga turut disokong dengan spektrum ^{13}C CP/MAS NMR yang menunjukkan anjakan puncak karboksil bagi PMAA ke medan magnet yang lebih tinggi. Analisis luas permukaan BET titik tunggal telah digunakan untuk penentuan luas permukaan spesifik komposit. Luas permukaan komposit Fe-TPyP/Al-MCM-41 didapati menurun dengan pertambahan kandungan Fe-TPyP, menunjukkan bahawa Fe-TPyP telah terkapsulkan di dalam liang Al-MCM-41. Sampel penapis molekul mesoliang (Al-MCM-41) dan polimer (PMAA) sebagai penyokong, sistem ferum-porfirin yang dikapsulkan dalam penyokong telah digunakan untuk sintesis langkah tunggal fenol dari benzena pada keadaan tindak balas yang sederhana. Pengaruh masa tindak balas, pelarut, jumlah kandungan Fe-TPyP, suhu dan penjanaan semula mangkin bagi tindak balas tersebut juga telah dikaji. Ferum-porfirin yang terkapsulkan di dalam PMAA (Fe-TPyP/ PMAA) menunjukkan keaktifan yang lebih tinggi berbanding Fe-TPyP/Al-MCM-41. Manakala kepilihan hasil tindak balas menggunakan mangkin Fe-TPyP/PMAA adalah tidak sebaik dengan Fe-TPyP/Al-MCM-41. Maka, adalah dianggapkan bahawa sifat kehidrofobik Fe-TPyP/PMAA mungkin berperanan meningkatkan keaktifan mangkin, manakala struktur tegar dan teratur Fe-TPyP/Al-MCM-41 pula menghasilkan kepilihan yang tinggi dalam sintesis langkah tunggal fenol dari benzena dalam kajian ini.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	TITLE	i
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENTS	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF SCHEMES	x
	LIST OF TABLES	xi
	LIST OF FIGURES	xii
	ABBREVIATIONS	xv
	LIST OF APPENDICES	xvii
1	**INTRODUCTION**	
	1.1 Research Background and Problem Statement	1
	1.2 Research Objectives	8
	1.3 Scope of Study	9
	1.4 Outline of Research	10
	1.5 Outline of Thesis	11
2	**LITERATURE REVIEW**	
	2.1 Introduce to Metalloporphyrins Complexes	12
	2.2 Heterogenization of Metalloporphyrins	14

2.2.1 Metalloporphyrins Supported on Molecular Sieves 16

2.2.2 Metalloporphyrins Supported on Polymer Matrix 21

2.3 Oxidation of Benzene to Phenol 23

2.4 Characterization Techniques 25

2.4.1 X-ray Powder Diffraction (XRD) 26

2.4.2 Fourier Transform Infrared Spectroscopy (FTIR) 27

2.4.3 UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DR) 29

2.4.4 Electron Spin Resonance (ESR) 30

2.4.5 Atomic Absorption Spectroscopy (AAS) 32

2.4.6 Single-Point BET Surface Area Analysis 33

2.4.7 Thermogravimetry Analysis (TGA) 34

2.4.8 Scanning Electron Microscopy (SEM) 35

2.4.9 Luminescence Spectroscopy 36

2.4.10 ^{13}C CP Magic-Angle-Spinning NMR Spectroscopy (^{13}C CP/MAS NMR) 37

3 ENCAPSULATION OF IRON(III)-PORPHYRIN WITHIN ORDERED MESOPOROUS Al-MCM-41

3.1 Direct Synthesis of Mesoporous Molecular Sieve Al-MCM-41 39

3.2 Preparation of Iron(III)-Tetra (4-Pyridyl) Porphyrin (Fe-TPyP) 40

3.3 Preparation of Fe-TPyP/Al-MCM-41 40

3.4 Results and Discussion 42

3.4.1 Characterization of Al-MCM-41 42

3.4.2 Characterization of Iron(III)-Tetra (4-Pyridyl) Porphyrin 47

3.4.3 Characterization of Fe-TPyP/Al-MCM-41 50

4 IMMOBILIZATION OF IRON(III)-PORPHYRIN IN POLYMETHACRYLIC ACID

4.1 Polymethacrylic acid as Organic Support 64
4.2 Synthesis of Polymethacrylic acid (PMAA) 65
4.3 Synthesis of Fe-TPyP/PMAA 65
4.4 Results and Discussion 66
4.4.1 Characterization of Polymethacrylic acid (PMAA) 66
4.4.2 Characterization of Fe-TPyP/PMAA 70

5 SINGLE-STEP SYNTHESIS OF PHENOL FROM BENZENE OVER Fe-TPyP/Al-MCM-41 AND Fe-TPyP/ PMAA CATALYSTS

5.1 Reaction Mechanism of Benzene Oxidation to Phenol 82
5.2 The Single-Step Synthesis of Phenol from Benzene 83
5.3 Analysis of Reaction Products 85
5.3.1 Gas Chromatography (GC) 85
5.3.2 Gas Chromatography – Mass Spectrometry Analysis (GC-MS) 86
5.3.3 High Performance Liquid Chromatography (HPLC) 87
5.4 Results and Discussion 89
5.4.1 Catalytic Activity 89
5.4.2 The Selectivity of Products 91
5.4.3 Regenerability of Catalysts 92
5.4.4 Optimization of Reaction Condition 94

6 CONCLUSION AND RECOMMENDATION 98

REFERENCES 101

APPENDICES 109

LIST OF SCHEMES

SCHEME NO	TITLE	PAGE
1.1	Basic features of the cytochrome P-450 oxidation mechanism	2
5.1	The probable products of benzene oxidation (phenol, hydroquinone, catechol, resorcinol and benzoquinone)	83
5.2	Proposed reaction path for the oxidation of benzene	84

LIST OF TABLES

TABLE NO.	TITLE	PAGE
3.1	XRD data and lattice parameter of the Al-MCM-41 samples	46
3.2	Assignment of FTIR bands of TPyP and Fe-TPyP complexes	49
3.3	XRD data of iron-containing Al-MCM-41 catalysts	55
3.4	Iron content (%Fe) of Fe-TPyP/Al-MCM-41 with different amount of Fe-TPyP loading	60
3.5	Surface properties of Al-MCM-41-supported Fe-TPyP with different amount of Fe-TPyP loading	60
4.1	Assignment of ^{13}C CP/MAS NMR spectrum of PMAA	69
4.2	Assignment of chemical shift of ^{13}C CP/MAS NMR spectra of as-synthesized PMAA and Fe-TPyP/PMAA with various of amount of Fe-TPyP loading	79
4.3	Iron content (%Fe) of Fe-TPyP/PMAA with different amount of Fe-TPyP loading determined by AAS	79
4.4	Surface properties of PMAA-supported Fe-TPyP with different amount of Fe-TPyP loading	81
5.1	GC-FID oven-programmed setup for identifying phenol	86
5.2	Catalytic activity of single-step synthesis of phenol from benzene	89
5.3	The catalytic activity of Fe-TPyP supported in Al-MCM-41 and polymethacrylic acid (PMAA) during the recycling in single-step synthesis of phenol from benzene	93

LIST OF FIGURES

FIGURE NO	TITLE	PAGE
1.1.	Commercial routes to synthesize phenol from benzene (with cumene as an intermediate)	6
1.2.	Oxidation reaction of benzene to phenol with dioxygen	8
2.1.	Structure of iron(III) tetra-(4-pyridyl)-porphyrin (Fe-TPyP)	14
2.2.	Structure of zeolite NaX (I) and iron(III) porphyrins (FeP)	17
2.3.	M41S family of mesoporous materials: (a) hexagonal MCM-41; (b) cubic MCM-48; (c) lamellar MCM-50	19
2.4.	Horväth-Kawazoe pore size distribution for MCM-41, zeolite Y and amorphous silica	20
2.5.	Schematic of the structure of the mesoporous material MCM-41 with cylindrical mesopores packed in a hexagonal array and amorphous siliceous pore walls	20
2.6.	Polymer immobilized rhodium catalyst, $P_{RH.}$ P_{RH} was prepared from the copolymerization of [(^{i}dppe)Rh(nbd)]BF_4 (2 mol%) into an ethylene dimethacrylate-based polymer (98 %)	23
2.7.	One-step benzene to phenol conversion using N_2O in the gas phase	25
2.8	Bragg reflection diagram	26
2.9	Optical layout of the Michelson interferometer (S = IR source, D = detector)	28
2.10	The IUPAC classification of adsorption isotherms	33
3.1	Reaction of TPyP with $FeCl_3$ in ethanol in the synthesis of iron-porphyrin complexes	41
3.2	Theoretical encapsulation of Fe-TPyP within ordered mesoporous Al-MCM-41	42
3.3	FTIR spectra of (a) as-synthesized and (b) calcined samples of Al-MCM-41	43

3.4	XRD patterns of the as-synthesized and calcined Al-MCM-41 samples	45
3.5	TGA thermograms of (a) as-synthesized and (b) calcined samples of Al-MCM-41	46
3.6	FTIR spectra of (a) TPyP and (b) Fe-TPyP complexes	48
3.7	UV-Vis DR spectra of (a) TPyP and (b) Fe-TPyP	50
3.8	FTIR spectra of (a) Fe-TPyP complexes, (b) Al-MCM-41 and (c) Fe-TPyP/Al-MCM-41	51
3.9	FTIR spectra of Fe-TPyP/Al-MCM-41 with various of Fe-TPyP loadings	53
3.10	XRD patterns of Al-MCM-41 and Fe-TPyP/Al-MCM-41 with various of Fe-TPyP loadings	54
3.11	UV-Vis DR spectra of (a) Fe-TPyP and (b) Fe-TPyP/ Al-MCM-41	56
3.12	UV-Vis DR spectra of Fe-TPyP/Al-MCM-41 with various of amount of Fe-TPyP loading	57
3.13	ESR spectra of (a) Fe-TPyP and (b) Fe-TPyP/Al-MCM-41	58
3.14	ESR spectra of Fe-TPyP and Fe-TPyP/Al-MCM-41 with various amount of Fe-TPyP loading	59
3.15	TGA thermograms of (a) calcined Al-MCM-41, (b) Fe-TPyP/Al-MCM-41 and (c) Fe-TPyP complexes	61
3.16	Scanning electron micrographs of (a) Al-MCM-41 and (b) Fe-TPyP/Al-MCM-41	62
3.17	Proposed mechanism of Fe-TPyP complex-Al-MCM-41 supports interaction	63
4.1	Structure of polymethacrylic acid (PMAA)	65
4.2	Schematic representation of the procedure of synthesis of composite Fe-porphyrin-polymethacrylic acid. Methacrylic acid (MAA) monomers assemble with the metallo-porphyrin, followed by cross-linking polymerization	66
4.3	FTIR spectrum of as-synthesized polymethacrylic acid (PMAA)	67
4.4	TGA thermograms of as-synthesized polymethacrylic acid (PMAA)	68
4.5	The luminescence excitation and emission spectra of as-synthesized polymethacrylic acid (PMAA) (λ_{ex} = 333 nm , λ_{em} = 574 nm)	68
4.6	^{13}C CP/MAS NMR spectrum of as-synthesized polymethacrylic acid (PMAA)	69
4.7	FTIR spectra of (a) Fe-TPyP complexes, (b) as-synthesized PMAA and (c) Fe-TPyP/PMAA	71

4.8	UV-Vis DR spectra of (a) Fe-TPyP and (b) Fe-TPyP/ PMAA	72
4.9	UV-Vis DR spectra of Fe-TPyP/PMAA with various of amount of Fe-TPyP loading	73
4.10	ESR spectra of Fe-TPyP and Fe-TPyP/PMAA (containing 50 and 100 µmol Fe-TPyP)	74
4.11	The luminescence emission spectra of (a) as-synthesized PMAA, (b) Fe-TPyP/PMAA and (c) Fe-TPyP (λ_{ex} = 333 nm)	75
4.12	The luminescence emission spectra of as-synthesized PMAA and Fe-TPyP/PMAA with different of amount of Fe-TPyP loading (λ_{ex} = 333 nm)	76
4.13	The Stern-Volmer kinetics: the dependence of the ratio of the luminescence intensities (I_0/I) on the Fe-TPyP concentration	77
4.14	^{13}C CP/MAS spectra of Fe-TPyP/PMAA with various of amount of Fe-TPyP loading (a) 100 µmol, (b) 50 µmol, (c) 25 µmol, (d) 5 µmol and (e) as-synthesized PMAA	78
4.15	TGA thermograms of (a) Fe-TPyP complexes, (b) Fe-TPyP/PMAA and (c) as-synthesized polymethacrylic acid (PMAA)	80
5.1	Block diagram of a gas chromatograph	86
5.2	Effect of the difference catalyst on the phenol yield for 20 hours reaction	90
5.3	The product selectivity of single-step synthesis of phenol in aqueous hydrogen peroxide using Fe-TPyP/Al-MCM-41 and Fe-TPyP/PMAA catalysts	91
5.4	The percentage conversion of benzene to phenol in aqueous hydrogen peroxide using Fe-TPyP/Al-MCM-41 and Fe-TPyP/PMAA	92
5.5	Effect of reaction time on the phenol yield in the single-step synthesis of phenol from benzene over Fe-TPyP/ Al-MCM-41 and Fe-TPyP/PMAA catalysts	95
5.6	Effect of different solvent on phenol yield using Fe-TPyP/ Al-MCM-41 and Fe-TPyP/PMAA as catalysts at 70 °C	95
5.7	Effect of amount of Fe-TPyP loading on the phenol yield in free-solvent at 70 °C for 20 hours reaction time over Fe-TPyP/Al-MCM-41 and Fe-TPyP/PMAA catalysts	96
5.8	Effect of reaction temperature on phenol yield in free-solvent for 20 hours reaction time over Fe-TPyP/ Al-MCM-41 and Fe-TPyP/PMAA catalysts	97

ABBREVIATIONS

λ	wavelength
2θ	Bragg angle
AAS	Atomic Absorption Spectroscopy
Al-MCM-41	Aluminium Mobil Crystalline Materials-41
CuK_α	X-ray diffraction from copper K_α energy levels
CP/MAS NMR	Cross-Polarization Magic-Angle-Spinning Nuclear magnetic Resonance
UV-Vis DR	Ultraviolet Visible Diffuse Reflectance
Fe-TPyP	iron(III)-tetra-(4-pyridyl)porphyrin
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
GC-MS	Gas Chromatography – Mass Spectrometry
h	hour
HPLC	High Performance Liquid Chromatography
IR	Infrared
KBr	Potassium bromide
MAS NMR	Magic-angle-spinning nuclear magnetic resonance
MCM-41	Mobil Crystalline Materials-41
Fe-TPyP/Al-MCM-41	iron(III)-porphyrin supported on Al-MCM-41
OH	hydroxyl
PMAA	Polymethacrylic acid
EGDMA	ethylene glycol dimethacrylate
AIBN	2.2'-azobis (2-methyl) propionitrile
Fe-TPyP/PMAA	iron(III)-porphyrin supported on polymethacrylic acid
SEM	Scanning Electron Microscopy
Si/Al	silicon-to-aluminium ratio

TGA	Thermogravimetric Analysis
TO_4	Tetrahedral unit where T = Al or Si
TPyP	Tetra-(4-pyridyl)-porphyrin
TS-1	Titanium silicalite
XRD	X-ray Diffraction technique
ESR	Electron Spin Resonance
TON	Turnover Number

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-Vis DR)	109
B	Luminescence Spectroscopy (LS)	110
C	Scanning Electron Microscopy (SEM)	111
D	Gas Chromatography (GC)	113
E	Gas Chromatography-Mass Spectrometry (GC-MS)	118
F	High Performance Liquid Chromatography (HPLC)	124
G	Reaction Path for the Oxidation of Benzene to Phenol	126
H	List of Publications	128

CHAPTER 1

INTRODUCTION

1.1 Research Background and Problem Statement

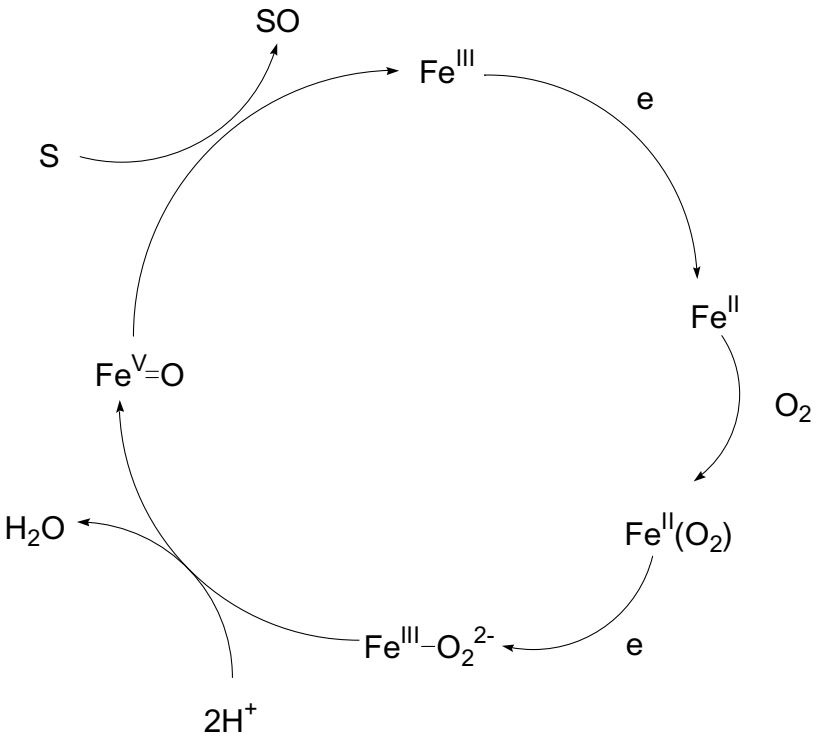
Selective catalytic oxidation of hydrocarbons under mild conditions is of academic interest and industrial importance [1]. In synthetic organic chemistry, oxidation represents one of the most important methods for substrate functionalization and functional group transformation. In the chemical industry, oxygenated products of petroleum namely, alcohols, aldehydes or acids, are important feedstocks for various industrial processes.

Traditionally, oxidation of hydrocarbons are performed with stoichiometric amounts of inorganic oxidants such chromium chloride and potassium permanganate [2]. The use of these oxidants for oxidation reaction leads to a big environmental problem because of the generation of numerous amounts of by-products.

In recent years, as a result of increasing environmental constraints, “clean” oxidants such as dioxygen (or air), hydrogen peroxide, and alkyl hydroperoxides, which are inexpensive, is becoming more important both in industry and academia, and chemical processes based on cleaner technologies are expected to increase significantly in the next few years.

In biological systems, nature has its unique way for doing selective O_2 oxidation, which is accomplished by certain enzymatic systems. Some enzymes of the mono- and dioxygenase types incorporate one or both oxygen atoms of O_2 respectively into a substrate.

A well-known monooxygenase, iron porphyrin-based cytochrome P-450, has been the subject of intensive study [3] largely because of their ability to catalyze a wide variety of oxidation transformations, such as alkenes epoxidation and alkanes hydroxylation with molecular oxygen. The key steps in the catalytic cycle is reductive activation of O_2, whereby one oxygen atom is reduced to H_2O and the other oxygen atom becomes available to form a high-valent iron oxo species for the oxidation process (see Scheme 1.1) [4]. In the last two decades, therefore, increasing attention in catalytic oxidation has been focused on the reactivity and oxidation properties of biomimetic systems based on Fe(II), Ru(II) and Mn(II)[5-7].



Scheme 1.1 Basic features of the cytochrome P-450 oxidation mechanism [4]

Synthetic metalloporphyrins are widely used as homogeneous catalysts for hydrocarbon oxidation, as well as model for cytochrome P-450 [8-9]. Metalloporphyrin complexes of iron [10], manganese [11] and ruthenium are known to be active catalysts for alkenes epoxidation. There are, however, several disadvantages in using metalloporphyrins as catalysts in homogeneous oxidation processes. The difficulty in separating the catalysts from the product substantially increases the cost of using homogeneous catalysis in commercial processes.

Heterogeneous catalysts, on the contrary, can be easily separated from the reaction products simply by filtration. Yet most heterogeneous catalysts are less selective in complex reactions. Therefore, it is highly desirable to develop materials based on metalloporphyrin, which possess both the high selectivity of homogeneous catalysts and the convenience of heterogeneous catalysts. One approach to achieve this goal is to immobilize homogeneous catalysts on porous solid supports, which simultaneously has the advantages of tuning the liquid phase oxidation from homogeneous into heterogeneous.

Microporous materials with regular arrays of internal channels and uniform pores such as zeolite [12] have been extensively studied as inorganic support. Immobilization of metalloporphyrin catalysts on microporous zeolite appears to be a good way to render these materials active for organic substrate oxidation.

Zeolites have large internal surfaces and specific sites available for active metal substitution thus allowing the preparation of materials for selective processes. Furthermore, the uniform pore sizes provide both size- and shape-selectivity towards the reactant and product molecules. Based on isomorphous substitution approach a number of materials of potential industrial usage have been developed. A typical example is TS-1, a titanium modified silicalite that catalyses olefin epoxidation, alcohol oxidation and phenol hydroxylation with 30% hydrogen peroxide [13]. In addition, metalloporphyrin complex such as *cis*-$Mn(bypy)_3$ [14] encapsulated in zeolite Y have been reported to be active catalysts towards cyclohexene oxidation.

Supporting metalloporphyrins on zeolite also provides a physical separation of active sites, thus minimizing catalyst self-destruction and dimerization of unhindered metalloporphyrins [15]. Although this approach has been demonstrated to be very successful, the main problem is the pore sizes of zeolites are very small (<13 Å) which limit their applications to reactions in which large molecules are involved [16].

In 1992, Beck *et al*. [17] reported the preparation and characterization of a new family of crystalline mesoporous molecular sieves, which are designated as M41S. MCM-41 is a member of this family associated with unique pores (20-100 Å) and large well-defined internal surface areas (>1000 m^2 g^{-1}). Due to the large pores of these mesoporous molecular sieves, high molecular mass organic molecules can easily gain access into the pores.

Transition metal complexes and organometallic compounds can be immobilized onto the mesoporous MCM-41 supports by physical adsorption or covalent linkage. Titanocene dichloride was anchored to MCM-41 by Maschmeyer *et al*. [18]. Copper-salen and iron-salen complexes encapsulated in the channels of Al-MCM-41 have been reported to be an active catalyst towards polymerization of bisphenol-A at room temperature using hydrogen peroxide as oxidant and dioxane as solvent [19]. More recently, much effort was focused on the immobilization of metalloporphyrins onto the silica MCM-41 surface.

Che and co-workers [20] have immobilized a ruthenium porphyrin on modified MCM-41. It was reported that the derived catalyst gives higher turnover numbers (TON) in the epoxidation of olefins than the free ruthenium porphyrin. It is interesting to note that in the oxidation of *cis*-stilbene with the modified MCM-41 material, the major product was *trans*-stibene oxide. In contrast, oxidation of *cis*-stilbene catalyzed by free ruthenium porphyrin gave a 1:1 mixture of *cis*- and *trans*-stilbene oxides. The high selectivity to give *trans*-stilbene oxide was attributed to the steric constraint imposed by the uniform channels of the MCM-41 support. This example demonstrated the potential of mesoporous MCM-41 materials as size and shape selective catalysts.

Stimulated by these works, we are interested in modifying the MCM-41 materials with metalloporphyrin as catalysts for selective oxidation reactions. MCM-41 can serve as a support for the metalloporphyrin species by providing a large surface area and uniform surface for catalytic reaction. The larger pore dimensions would allow processing of bulky chemicals of interest.

In this research, iron porphyrin has been immobilized within ordered mesoporous Al-MCM-41. It is well known that iron porphyrin complexes is effective catalyst for the conversion of olefins into *trans*-diols or *trans*-diol *mono*-ethers by using H_2O_2 [21]. In order to tune the activity of the supported catalysts the knowledge on the microenvironment of the immobilized complexes is essential. However, there are few reports on correlation between the structure of the immobilized catalysts and the catalytic activities. It is anticipated that immobilization of the metalloporphyrins in inorganic or organic support will stabilize and/or modify the catalytic performance by influencing the chemoselectivity, regioselectivity and shape selectivity of the reaction.

Supported catalysts are also often plagued by leaching of the metal into solution. Our approach to this problem is to radically change the nature of the support. The even distribution of large, regular pores and extremely high surface area that characterizes mesoporous molecular sieve MCM-41 makes them ideal supports. This support has the added benefit that the silica structure has stability to chemical reagents. Also, easy separation of the products from the separation medium, along with the recovery and reuse of the expensive catalyst provide an attractive advantage over homogeneous catalysts.

The key feature of the MCM-41, which separates it from currently used zeolite support, is its extreme porosity. However, the MCM-41, an inorganic material, is hydrophilic and rigid. In this research, we also propose a procedure to immobilize iron porphyrin on the polymer support, namely polymethacrylic acid (PMAA). One expects that the flexibility and hydrophobicity of the polymer as support give certain advantages in oxidation of organic compounds. The production of porous polymers containing large aromatic moieties or transition metal complexes such as the iron porphyrin complexes is considered to be useful, since they are in

high demand for a variety of applications ranging from catalysis, chromatography, diagnostics and sensors [1]. To the best of our knowledge, iron porphyrin complexes supported on PMAA has not yet been reported.

Phenol is produced globally on the scale of 17 billion pounds/year [22] due to demand for bisphenol A (polycarbonate resins), phenolic resins, coprolactam (nylon 6.1), xylenols, aniline, alkylphenols and others. It is used in the manufacture of plywood, construction, automotive and appliance industry. It is also used as a raw material in the production of nylon and epoxy resins, disinfectant and slime-killing agent.

Phenol has been mainly manufactured using the cumene method by which the selectivity for the phenol is high. However, this cumene process consists of three steps and produces acetone as a byproduct (Figure 1.1) [23]. The efficiency of the three-step cumene process strongly depends on the price of the by-product acetone, which is considerably varying.

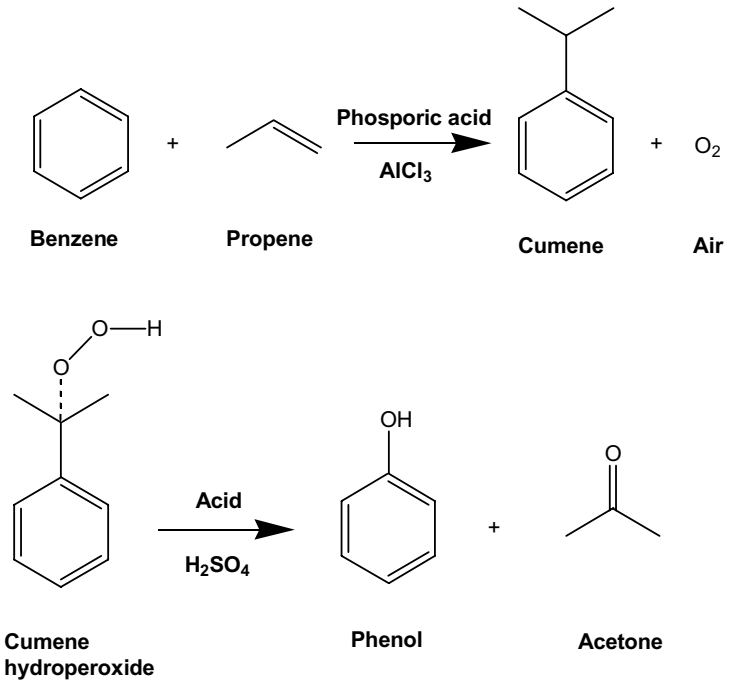


Figure 1.1 Commercial routes to synthesize phenol from benzene (with cumene as an intermediate) [23]

The cumene method has several significant shortcomings: it is a multistage synthesis; the intermediate cumene hydroperoxide is explosive; there are ecological problems and the production rate of the co-product acetone exceeds market demand. Therefore, both industry and academia are intensively searching for new routes to phenol based on direct benzene oxidation. The single-step synthesis of phenol from benzene would be an alternative.

The single-step production of phenol by direct insertion of oxygen into the benzene ring is an attractive and challenging method, not only from a practical point of view but also from a synthetic chemical point of view, because the direct oxygenation of the energetically stable benzene to produce phenol has been one of the most difficult oxidation reactions [24].

The gas-phase oxidation of benzene to phenol by nitrous oxide has been widely studied over Fe-ZSM-5 [25]. In the presence of Fe-ZSM-5, the selectivity of benzene and N_2O for phenol exceeded 98 and 95%, respectively, but the conversion of benzene to phenol is very low. The oxidation of benzene to phenol over $H_6PMo_9V_3O_{40}$ and palladium acetate in VPI-5 and MCM-41 has been reported in the presence of molecular oxygen [26]. Over $H_6PMo_9V_3O_{40}$, after 4 hours at 130 ^oC the benzene conversion is 15% and the selectivity for phenol is above 70%.

Phenol synthesis by liquid-phase oxidation of benzene with hydrogen peroxide has been also studied using iron-heteropoly acid [27]. Furthermore, Miyahara *et al.* has studied the liquid-phase oxidation of benzene to phenol catalyzed by Cu catalysts supported on zeolites [28], and MCM-41 [29], and also supported CuO catalysts ($CuO-Al_2O_3$) [24]. In the presence $CuO-Al_2O_3$, the phenol yield is very low (< 1%) and the leaching of Cu is less than 10%.

An attractive alternative route is the direct oxidation of benzene to phenol using molecular oxygen and a suitable catalyst. A one-step process such as this would require less energy and generate zero waste, while producing only phenol. This reaction model of hydroxylation of benzene with oxygen is presented in Figure 1.2.

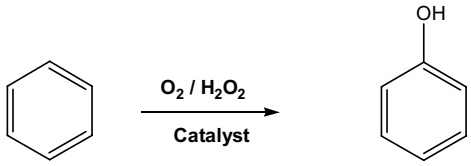


Figure 1.2 Oxidations reaction of benzene to phenol with dioxygen

Recently, the best catalyst for benzene to phenol oxidation by nitrous oxide is Fe-ZSM-5 zeolite, which provides nearly 100% benzene selectivity, but low conversion of benzene [25]. The remarkable catalytic performance of this zeolite was show to be related to the presence of iron and upon high temperature treatment. In these systems, the reaction only occurs in the gas phase (ca. 300º) and there is no report on single-step liquid phase oxidation of benzene to phenol in the literature. For these reasons, in this research, we will study the single-step liquid phase oxidation of benzene to phenol using iron(III)-porphyrin supported on Al-MCM-41 and polymethacrylic acid (PMAA).

1.2 Research Objectives

The main objectives of the research are:

i. To synthesize Al-MCM-41 and polymethacrylic acid (PMAA).

ii. To synthesize iron(III) tetra-(4-pyridyl)-porphyrin (Fe-TPyP) complexes supported on mesoporous Al-MCM-41 and polymethacrylic acid (PMAA) matrix.

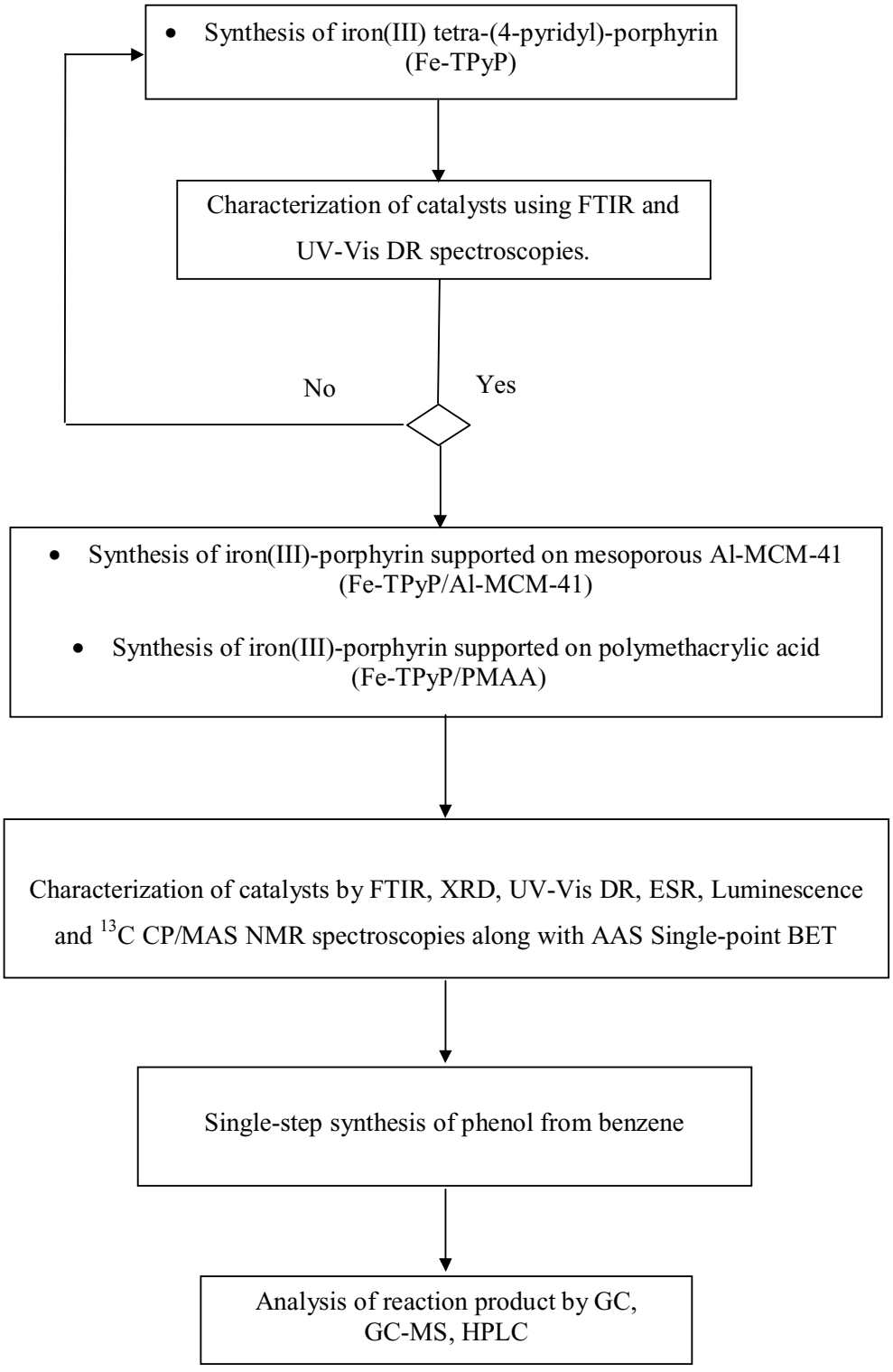
iii. To investigate the physicochemical properties of Fe-TPyP encapsulated in Al-MCM-41 and Fe-TPyP supported on polymer matrix.

iv. To compare the performance of the hybrid catalysts of Fe-TPyP supported on mesoporous Al-MCM-41 and polymethacrylic acid (PMAA) in the single-step synthesis of phenol from benzene.

1.3 Scope of Study

The scope of this research is to synthesize iron(III)-porphyrin encapsulated Al-MCM-41 and iron(III)-porphyrin supported on polymethacrylic acid (PMAA), to characterize these catalyst by XRD, FTIR, UV-Vis DR, ESR, Luminescence, and ^{13}C CP/MAS NMR spectroscopies along with Single-point BET surface area analysis, AAS, TGA and SEM, to test the performance of these catalysts for the liquid phase single-step oxidation of benzene to phenol and finally, to analyze the reaction products using GC, GC-MS and HPLC techniques.

1.4 Outline of Research



1.5 Outline of Thesis

This thesis focuses on the development of hybrid catalyst systems with the main aim at the preparation, characterization and catalytic application of iron(III)-porphyrin (Fe-TPyP) supported on mesoporous molecular sieve Al-MCM-41 and polymethacrylic acid (PMAA). This thesis is also organized into six chapters.

Chapter 1 describes the research background and problem statement, research objectives, scope of the research, outline of research and outline of the thesis.

Chapter 2 presents some literature review on the chemistry of metallo-porphyrin, mesoporous molecular sieve MCM-41, the polymer support, and the liquid-phase oxidation of benzene to phenol.

Chapter 3 demonstrates that iron(III) tetra-(4-pyridyl)-porphyrin (Fe-TPyP) may be encapsulated into the pores and channels of the mesoporous material Al-MCM-41 by impregnation method, while Chapter 4 presents the preparation of iron-porphyrin supported into polymethacrylic acid (PMAA) by direct polymerization of iron(III) tetra-(4-pyridyl)-porphyrin (Fe-TPyP) with the monomer, methacrylic acid (MAA).

Chapter 5 discusses the catalytic activity of these materials in the single-step synthesis of phenol from benzene. Finally, Chapter 6 presents the conclusion of the results obtained and provides recommendations for future research.

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