

SYNTHESIS AND CHARACTERIZATION OF FIBROUS SILICA ZSM-5 FOR
METHANOL TO OLEFIN REACTION

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SYNTHESIS AND CHARACTERIZATION OF FIBROUS SILICA ZSM-5 FOR
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Specially dedicated to my amazing father and mother

Jamian and Sharah

&

My beloved ones

“Thank you for the endless support and everything “

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ABSTRACT

Olefins are one of the most important chemicals and raw materials in the petrochemical industry. However, because of the rapid increase in the price of crude oil and the oil shortage in the foreseeable future, alternative routes for production of light olefins from non-oil sources are desired. Catalytic conversion of methanol to light olefins (MTO) provides an alternative route for production of light olefins from a non-petroleum source. Protonated commercial ZSM-5 (HZSM-5) zeolite has been widely used in the MTO reaction. However, fast deactivation of HZSM-5 due to coke deposition has always been one of the key problems in MTO reaction. A novel ZSM-5 catalyst with silica fibrous morphology (HSi@ZSM-5) was successfully prepared using a microemulsion system with ZSM-5 seed assisted crystallization followed by protonation for MTO reaction. X-ray diffraction and field emission scanning electron microscopy analyses showed that the HSi@ZSM-5 possesses ZSM-5 structure and a spherical morphology with evenly distributed dendrimeric silica fibers. In addition, HSi@ZSM-5 exhibited intrinsic mesopores at 3-5 and 10-20 nm, which led to an increase in the surface area up to 22% compared with HZSM-5. Ammonia Fourier transform infrared spectroscopy result showed a remarkable reduction of Brønsted acid sites in HSi@ZSM-5. This reduction of Brønsted acid sites suppressed side reactions which led to increased olefin selectivity. These were proven in the catalytic activity as the propylene selectivity of HSi@ZSM-5 was almost two-fold higher than that of HZSM-5. Besides, the catalytic lifetime was improved significantly up to 80 hours for HSi@ZSM-5 compared to about 30 hours for HZSM-5. The high selectivity towards propylene and long catalyst lifetime of HSi@ZSM-5 could be attributed to the unique morphology of HSi@ZSM-5 which facilitates the diffusion of reactant and product into and out of the catalyst. Lowering diffusion limitation reduces the possibility of coke accumulation on the catalyst that lead to the deactivation of the catalyst. This new protonated silica fibrous ZSM-5 catalyst opens a big potential in general heterogeneous catalytic reaction.

ABSTRAK

Olefin adalah salah satu bahan kimia dan bahan mentah yang paling penting dalam industri petrokimia. Walau bagaimanapun, disebabkan peningkatan pesat harga minyak mentah dan kekurangan sumber minyak yang diramal pada masa depan, laluan alternatif untuk penghasilan olefin ringan daripada sumber bukan minyak adalah dikehendaki. Penukaran bermangkin metanol kepada olefin ringan (MTO) menyediakan laluan alternatif untuk pengeluaran olefin ringan daripada sumber bukan petroleum. Zeolit ZSM-5 komersial berproton (HZSM-5) telah digunakan secara meluas dalam tindak balas MTO. Walau bagaimanapun, penyahaktifan cepat HZSM-5 kerana pemendapan kok sentiasa menjadi salah satu masalah utama dalam tindak balas MTO. Mangkin ZSM-5 baharu dengan morfologi berserabut silika (HSi@ZSM-5) telah berjaya disediakan menggunakan sistem mikroemulsi dengan penghabluran berbantuan benih ZSM-5 diikuti dengan pemprotonan untuk tindak balas MTO. Analisis pembelauan sinar-X dan mikroskopi elektron pengimbas pemancaran menunjukkan bahawa HSi@ZSM-5 mempunyai struktur ZSM-5 dan morfologi sfera dengan serabut dendrimer silika yang tertabur sama rata. Tambahan lagi, HSi@ZSM-5 mempamerkan liang meso yang intrinsik pada 3-5 dan 10-20 nm, yang membawa kepada peningkatan luas permukaan sehingga 22% berbanding dengan HZSM-5. Keputusan spektroskopi inframerah transformasi Fourier ammonia menunjukkan pengurangan ketara tapak asid Brønsted pada HSi@ZSM-5. Pengurangan tapak asid Brønsted ini menindas tindak balas sampingan yang membawa kepada peningkatan kepilihan olefin. Ini telah dibuktikan dalam aktiviti bermangkin apabila kepilihan terhadap propilena bagi HSi@ZSM-5 adalah hampir dua kali ganda lebih tinggi daripada HZSM-5. Di samping itu, jangka hayat mangkin adalah bertambah baik dengan ketara sehingga 80 jam bagi HSi@ZSM-5 berbanding kira-kira 30 jam bagi HZSM-5. Kepilihan yang tinggi ke arah propilena dan jangka hayat mangkin yang panjang HSi@ZSM-5 boleh dikaitkan dengan morfologi unik HSi@ZSM-5 yang memudahkan pembauran zat tindak balas dan produk masuk dan keluar dari mangkin. Perendahan keterbatasan pembauran dapat mengurangkan kemungkinan pengumpulan kok pada mangkin yang membawa kepada penyahaktifan mangkin. Mangkin ZSM-5 serabut silika berproton baharu ini mempunyai potensi besar dalam tindak balas bermangkin heterogen umum.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	x
	LIST OF FIGURES	xi
	LIST OF SYMBOLS	xiv
	LIST OF ABBREVIATIONS	xv
	LIST OF APPENDICES	xvii
1	INTRODUCTION	1
	1.1 Background of Study	1
	1.2 Problem Statement	3
	1.3 Hypothesis	4
	1.4 Objectives of the Study	5
	1.5 Scopes of the Study	5
	1.6 Significance of Study	7
	1.7 Thesis Outline	8

2	LITERATURE REVIEW	8
2.1	Olefin Production	8
2.1.1	Steam Cracking	9
2.1.2	Catalytic Cracking	10
2.1.3	Alternative Methods	11
2.2	Methanol to Olefin	13
2.2.1	Hydrocarbon Pool Mechanism	14
2.3	Catalysts	15
2.3.1	Homogeneous Catalyst	16
2.3.2	Heterogeneous Catalyst	16
2.4	Zeolites as Methanol to Olefin Catalysts	17
2.4.1	ZSM-5	19
2.4.2	SAPO-34	20
2.4.3	Other Zeolite	21
2.4.4	Deactivation of Methanol to Olefin Catalysts	21
2.5	Zeolite Modification	22
2.5.1	Mesoporous Zeolites	23
2.5.2	Fibrous ZSM-5	24
2.5.2.1	Microemulsions	25
2.5.2.2	Zeolite Crystal-Seed Crystallization	27
3	METHODOLOGY	30
3.1	Introduction	30
3.2	Chemicals and Materials	32
3.3	Instrumentations	32
3.4	Catalyst Preparations	33
3.4.1	Preparation of Fibrous Silica ZSM-5 (Si@ZSM-5)	33
3.4.2	Preparation of Protonated Catalysts	34

3.5	Catalyst Characterizations	34
3.5.1	Field Emission Scanning Electron Microscope (FESEM) Analysis	34
3.5.2	X-Ray Diffraction (XRD) Analysis	35
3.5.3	Nitrogen Adsorption-Desorption Analysis	35
3.5.4	Fourier Transform Infrared (FTIR) Spectroscopy	35
3.5.4.1	Potassium Bromide (KBr) Pellet	36
3.5.4.2	Ammonia Molecule Adsorption	36
3.6	Catalytic Testing	37
3.6.1	Methanol to Olefin	37
3.6.2	Regeneration Study	38
4	RESULTS AND DISCUSSION	39
4.1	Structural Properties of Fibrous Silica ZSM-5 (Si@ZSM-5)	39
4.2	Proposed Formation Mechanism of Si@ZSM-5	46
4.3	Acidic Properties of Protonated Fibrous Silica ZSM-5 (HSi@ZSM-5)	48
4.4	Methanol to Olefin Reaction	54
4.5	Structural Properties of Spent Catalysts	58
5	CONCLUSION AND RECOMMENDATION	62
5.1	Conclusion	62
5.2	Recommendation for Future Work	63
	REFERENCES	64
	Appendices A - D	78

LIST OF TABLES

TABLE NO.	TITLE	PAGE
3.1	List of chemicals	32
4.1	Surface area and pore analysis of HZSM-5 and HSi@ZSM-5 catalysts	44
4.2	Acid sites concentration of HZSM-5 and HSi@ZSM-5 catalysts	50
4.3	Surface area and pore analysis of spent HZSM-5 and HSi@ZSM-5 catalysts after 100 h on stream	61

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	Scheme of formation of olefin via dehydration of methanol	14
2.2	Scheme of MTO reaction pathway via hydrocarbon pool mechanism, (a) Aromatic-based cycle and, (b) Olefin based cycle	15
2.3	Zeolite framework building units	18
2.4	Channel systems in ZSM-5	19
2.5	TEM images of KCC-1	25
2.6	Winsor phase systems (I) (o/w) microemulsion, (II) (w/o) microemulsion, (III) three phase microemulsion systems, and (IV) bicontinuous microemulsions	27
2.7	Schematic illustration of zeolite crystal-seed crystallization pathways	28
3.1	Research flow chart	31
3.2	Schematic diagram of microcatalytic reactor	38
4.1	(A) and (B) FESEM images, (C) Particle size distribution, and (C) TEM images of HSi@ZSM-5 catalysts	40

4.2	X-ray diffraction patterns of HZSM-5 and HSi@ZSM-5 catalysts	41
4.3	N ₂ adsorption-desorption isotherms of (A) HZSM-5 and (B) HSi@ZSM-5 catalysts	42
4.4	Pore size distribution of (A) HZSM-5 and (B) HSi@ZSM-5 catalysts	43
4.5	IR spectra in hydroxyl stretching of (a) HSi@ZSM-5 and (b) HZSM-5 catalysts	45
4.6	Framework of hydroxyl group	45
4.7	IR spectra in lattice vibrational overtones of (a) HSi@ZSM-5 and (b) HZSM-5 catalysts	46
4.8	Schematic diagram of proposed mechanism of Si@ZSM-5 formation	47
4.9	Brønsted and Lewis acid site in zeolite	48
4.10	IR spectra of 10 torr ammonia adsorbed on (a) HZSM-5 and (b) HSi@ZSM-5 catalysts at room temperature	49
4.11	IR spectra of ammonia outgassed at different temperature for (A) HZSM-5 and (B) HSi@ZSM-5 catalysts	51
4.12	Deconvoluted spectra of NH ₄ ⁺ ions at different desorption temperature for (A) HZSM-5 and (B) HSi@ZSM-5 catalyst	52
4.13	Peak area of ammonia adsorbed on (A) HZSM-5 and (B) HSi@ZSM-5 as the function of outgassing temperature	53
4.14	Conversion of methanol as a function of reaction temperature	54

4.15	Product distribution for methanol to olefin conversion over (A) HZSM-5 and (B) HSi@ZSM-5 catalysts as a function of reaction temperature	56
4.16	Conversion of methanol as a function of time on stream	59
4.17	TGA curves of (a) Spent HSi@ZMS-5 and (b) Spent HZSM-5 catalysts after 100 h time on stream	59
4.18	Pore size distribution of (A) Spent HZSM-5 and (B) Spent HSi@ZSM-5 catalysts after 100 h time on stream	60
4.19	IR-KBr spectra of (a) Fresh HZSM-5, (b) Spent HZSM-5, (c) Fresh HSi@ZSM-5 and (d) Spent HSi@ZSM-5	62

LIST OF SYMBOLS

Å	-	Angstrom
K	-	Kelvin
kV	-	Kilovolt
µmole	-	Micromole
mA	-	Miliampere
mL	-	Mililiter
min	-	Minutes
nm	-	Nanometer
mm	-	Millimeter
%	-	Percentage
θ	-	Theta
W	-	Watt
h	-	Hour
°C	-	Degree celcius

LIST OF ABBREVIATIONS

MTO	-	Methanol to olefin
DME	-	Dimethylether
ZSM-5	-	Zeolite Socony Mobil-5
Si@ZSM-5	-	Fibrous Silica ZSM-5
HSi@ZSM-5	-	Protonated Fibrous Silica ZSM-5
HZSM-5	-	Protonated ZSM-5
BET	-	Braunauer-Emmett-Teller
NLDFT	-	Non-Linear Density Functional Theory
FESEM	-	Field Emission Scanning Electron Microscopy
FID	-	Flame Ionization Detector
FTIR	-	Fourier Transform Infrared
KCC-1	-	KAUST Catalysis Center – 1
MFI	-	Mordenite Framework Inverted
XRD	-	X-Ray Diffraction
TGA	-	Thermogravimetry Analysis
FCC	-	Fluid Catalytic Cracking
FTS	-	Fischer-Tropsch Synthesis
OCM	-	Oxidative Coupling of Methane
SAPO	-	Silicaaluminophosphate
HCP	-	Hydrocarbon Pool

BEA	-	Beta Zeolite
MTP	-	Methanol to Propylene
SDA	-	Structure Directing Agent
OSDA	-	Organic Structure Directing Agent
CTAB	-	Cetyltrimethylammonium Bromide
TEOS	-	Tetraethyl Orthosilicate

LIST OF APPENDICES

APPENDIX NO.	TITLE	PAGE
A	Calculation of acid sites concentration	
B	Results of methanol to olefin reaction from chromatogram	
C	Calculation of conversion and selectivity of products in methanol to olefin reaction	
D	List of Publication	

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Olefins which are in the class of unsaturated hydrocarbons consist of a single double bond and a chemical formula of C_nH_{2n} are one of the most important chemicals and raw materials in petrochemical industry. Economic growth and the associated increased demand for consumer goods greatly influenced the continual increase in worldwide olefin's demand (Sadrameli, 2016). Global production of ethylene and propylene are in the range of 200 million tons per year (Pinilla-Herrero, *et al.*, 2016). Ethylene is primarily used to manufacture polyethylene, ethylene chloride and ethylene oxide. These products are very useful for the packaging, plastic processing, construction and textile industry. Propylene are mostly used in the manufacture of polypropylene, but it is also a basic product necessary to produce propylene oxide, acrylic acid and other chemical derivatives. In addition to plastic processing, packaging industry, furnishing sector, and automotive industry are also known to use propylene and its derivatives, in their manufacturing process.

Olefins are conventionally produced by thermal cracking of hydrocarbons from gaseous such as ethane, propane and butane, liquefied petroleum gas, to the liquid feedstock such as light and heavy naphtha, gasoil and vacuum gas oils. (Sadrameli, 2015). Other than that, olefins were also produced via fluid catalytic cracking of petroleum fractions (Sadrameli, 2016). However, due to the rapid increase in the price of crude oil and the depletion of the non-renewable resources, alternative routes for production of light olefins from non-oil sources are desired (Dai, *et al.*, 2011).

Catalytic conversion of methanol to olefins (MTO) provides an alternative route for production of light olefins from a non-petroleum source (Yaripour, *et al.*, 2015). The MTO reaction was first proposed by Mobil Corporation in 1977 and many researchers have put great effort for the research of MTO reaction (Tian, *et al.*, 2015). The MTO technology was developed as a two-step process. The first step involves the conversion of natural gas into methanol using synthesis gas. The next step involves dehydration of methanol to dimethyl ether (DME) and the obtained equilibrium mixture consisting of methanol, DME, and water is catalytically converted to light olefins (Dai, *et al.*, 2011).

In addition, the methanol industry has been booming for the last several years due to the shale gas revolution and the abundance of its cheap feedstock, natural gas. It is reported that natural gas prices have fallen 30 percent over the decade while crude oil prices have been increasing more than doubled (Olah, 2005). Thus, it is expected that methanol will become one of the abundant and cheap chemical. MTO is one of the ways to utilize methanol to produce more useful chemical in industry.

Zeolite is suitable to be used as catalyst in the methanol to olefin reaction due to the characteristic of zeolite that possesses catalytically active site and uniformity in micropore size and shape. ZSM-5 zeolite has been widely used in the MTO reaction and its efficiency in selectively converting light olefin from methanol has been proven (Pinilla-Herrero, *et al.*, 2016; Dai, *et al.*, 2011). However, ZSM-5 zeolite possesses significant diffusion limitation which restrict the movement of reactant and product in and out of the pores. The restriction of the diffusion will eventually lead to the deactivation of the catalyst as large size product was being trapped in the micropore (Zhang, *et al.*, 2016). To overcome such limitation, mesoporous zeolites was designed to facilitate the diffusion of reactant and products in which will help in improving the catalytic lifetime of the catalyst.

Fibrous material was initially developed by Polshettiwar, *et al.* in 2010. The first fibrous material is a silica-based equipped with high surface area and better accessibility of active site due to the dendrimeric fibres morphology. Several studies showed the potential of silica-based fibrous material in the adsorption of nitro- and

chloro- compounds and hydrogenolysis of alkene (Fihri, *et al.*, 2012). Silica-based fibrous material was developed by using microemulsion technique which originally comes from surfactant. Development of zeolite-based fibrous material will significantly improve their catalytic activity especially in acid catalyzed reaction, along with tunable acidity and high surface area. Zeolite-based fibrous material will have a great potential to be applied in petrochemical industry.

1.2 Problem Statement

Methanol to olefin conversion, has attracted much attention as one of the new route for the production of light olefins. It is mainly due to the fact that methanol can be conveniently manufactured from any carbon-containing resources such as coal, biomass and natural gas (Dai, *et al.*, 2011; Deimund, *et al.*, 2015). Research on catalysts to be used in MTO reaction have been conducted intensively and continuously as the catalyst will greatly influenced the product formed during the process.

Utilization of ZSM-5 as a catalyst in MTO reaction have been proven to yield high olefin selectivity during the process. High activity and selectivity of ZSM-5 in MTO reaction was mainly due to its well-defined microporous structure, high surface area and its high density of acid site that was responsible for the conversion (Sano, *et al.*, 1992). Despite being one of the catalysts that is suitable for MTO, the presence of micropores in ZSM-5 often associated with significant diffusion limitation. The well-defined pores restrict the diffusion of molecules into and out of the zeolite pores. Thereupon, large products could be trapped inside the micropores due to not being able to diffuse into the external surface. The trapped products will turn into coke that will deactivate the catalysts (Zhang, *et al.*, 2016). In addition, high amount of acid site possesses by ZSM-5 promote the formation of aromatic products that are undesirable in MTO reaction as it will be converted into coke if being trapped in the pores (Wei, *et al.*, 2011). Fast deactivation of ZSM-5 due to coke deposition has always been one of the key problem to be solved in order to prepare a highly efficient catalyst for MTO reaction (Qi, *et al.*, 2017).

Silica-based fibrous material has been extensively studied by researchers after the discovery of fibrous silica nanosphere (KCC-1) by Polshettiwar et al., 2010. The KCC-1 was first prepared using the microwave-assisted hydrothermal technique which exhibited excellent properties, including a high surface area, a fibrous surface morphology, good thermal and hydrothermal stabilities and mechanical stability. The unique fibrous morphology is expected to facilitate the diffusion of reactant and products, therefore enhancing the catalysts lifetime. Previous studies in MTO reaction revealed that acid site density and its strength is important in tailoring the product distribution in MTO reaction (Wei, *et al.*, 2011). However, the KCC-1 which is fully composed with silica does not provide an adequate acid sites to initiate MTO reaction (Moon and Lee, 2012).

1.3 Hypothesis

Implementation of the concept in developing silica-based fibrous material to zeolite will be the key to overcome these problems. In general, the high propylene yield and long catalytic lifetime improve economy of the MTO process and make it more comparable with the conventional processes for the olefins production (Rostamizadeh and Yaripour, 2017).

Decrease in acid site density in fibrous silica zeolite material are expected to enhance the propylene formation in the MTO reaction based on hydrocarbon pool mechanism. Presence of the dendrimeric will facilitate the movement of reactant and product into and out of the pore. These will reduce the possibility of large molecules being trapped in the pore, thus increase the lifetime of the catalyst as the catalyst become more resistant towards deactivation. Utilizing microemulsions method, the development of zeolite-based fibrous material will be successfully achieved. Zeolite-based fibrous material is the next step towards an efficient heterogeneous catalyst for methanol to olefin reaction.

1.4 Objectives

The objectives of this study are:

1. To prepare and characterize the physical and chemical properties of protonated fibrous silica ZSM-5 (HSi@ZSM-5) and protonated ZSM-5 (HZSM-5) catalysts.
2. To study the performance and stability of the catalysts in methanol to olefin reaction.
3. To study the deactivation and coke deposition of the catalysts in methanol to olefin reaction.

1.5 Scope of Study

There are three scopes in this study. The first scope discussed is the preparation of the catalysts. The crucial preparation is on the synthesis of fibrous silica ZSM-5 catalyst (Si@ZSM-5). The synthesis involved microemulsion system from cetyltrimethyl ammonium bromide (CTAB), toluene, and *n*-butanol. Cationic surfactant, CTAB, was selected due to its ability to form coulombic interaction with silicate gels and zeolite framework (Monnier, *et al.*, 1993). It was also selected because of its structure. Manipulating the packing parameter of single chain surfactant, such as CTAB, was easier due to the absence of steric hindrance. This was proved by Polshettiwar, *et al.* (2010) who discovered the loss of fibrous morphology after using benzalkonium chloride, which is a double chain surfactant. According to Moon and Lee (2012), the co-solvent, which was short-chain alcohol, had important role in controlling the thickness of dendrimeric silica fiber. Their study showed that *iso*-propanol produce thick dendrimer with narrow inter-dendrimer distance and *n*-pentanol produced thin and very wide inter-dendrimer distances. *n*-butanol was chosen as a suitable co-solvent because it produces dendrimer with adequate distance to promote high accessibility. Urea was selected as the hydrolyzing agent for the silica precursor due to its mild basicity. The addition of strong base as hydrolyzing agent, such as NaOH could compromise the microemulsion system. According to the study

by Polshettiwar, *et al.* (2010), the addition amount of urea affects the morphology of dendrimeric silica fiber. However, excess addition of urea could increase the particle size of the catalyst due to the rapid hydrolysis of silica precursor. Zeolite crystal-seed crystallization was used instead of direct zeolite crystallization. This was to avoid interaction competition between microemulsion and zeolite structure directing agent and the aluminosilicate species (Li, *et al.*, 2011). The presence of other electrolyte from zeolite precursor, such as Na^+ , could change the critical micelle concentration of CTAB, which will result in different formation of supramolecular structure. Thus, zeolite crystal-seed crystallization was best suited to be used in synthesis method to avoid the competition and minimizing the changes in CTAB critical micelle concentration. The preparation also involved protonation, in which both Si@ZSM-5 as well as commercial ZSM-5 catalysts were converted into ammonium form by ion-exchange and followed by calcination to convert the NH_4^+ species into H^+ . The first scope includes the characterization of the catalyst. The morphological features of HSi@ZSM-5 was examined with Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM). The structure of HSi@ZSM-5 was characterized with X-ray Diffraction (XRD) to confirm the presence of ZSM-5 structure. The surface and pore analysis were obtained by N_2 adsorption-desorption. The surface area was obtained by Brunauer-Emmett-Teller (BET) method, pore distribution was obtained by Non-Localized Density Functional Theory (NLDFT), and micropore analysis was obtained by *t*-plot method. Molecular vibration of HSi@ZSM-5 was assessed with Fourier transform infrared (FTIR) spectroscopy. Ammonia was chosen as the probe to investigate the acidic properties of HSi@ZSM-5 due to its size and ability to access all acid sites both on the surface and inside the pore of catalyst (Gianotti, *et al.*, 2002). For comparison purpose, commercial ZSM-5 was subjected to similar characterization.

The catalytic activity of HSi@ZSM-5 was assessed with methanol to olefin reaction. The catalytic reaction was carried out in the temperature range of 473-673 K. Several reports demonstrated that the reaction was optimally performed in the reaction temperature of 573-673 K (Khaledi, *et al.*, 2017; Khare, *et al.*, 2017). The reaction was performed at lower temperature to observe the formation of product at respective temperature. The stability of HSi@ZSM-5 catalyst was studied at the optimum

reaction temperature. According to the experimental result, both catalysts showed highest activity and selectivity towards light olefin at 673 K. Therefore, the stability testing for both catalysts was performed at 673 K. The catalytic stability was conducted for 100 h. After both catalysts experienced deactivation at 100 h, the deactivated catalysts were subjected to oxidation treatment at 823 K in attempt to remove coke deposited on the catalyst (Sidik, *et al.*, 2015). After regeneration step, the reaction was continued for another 20 h to observe the ability of each catalyst to recover from coke deposition.

The final scope covered the characterization of spent catalysts in which the catalysts were subjected to 100 h methanol to olefin reaction. Coke deposition on the spent catalysts was clarified by thermogravimetry analysis (TGA). Weight loss that occurred at temperature range of 823-1073 K were often associated with combustion of coke in spent catalysts (Sidik, *et al.*, 2015). Blocking of the pore due to coke was investigated by N₂ adsorption-desorption analysis. In addition, the presence of coke in the spent catalysts was obtained by KBr-FTIR analysis. Presence of absorption band in the range of 2800-3100 cm⁻¹ confirmed coke content in the catalyst (Chen, *et al.*, 1996). For comparison purpose, spent HZSM-5 was obtained and subjected to similar characterization as spent HSi@ZSM-5 catalyst.

1.6 Significance of Study

Protonated fibrous silica HZSM-5 (HSi@ZSM-5) was prepared in this study as an efficient catalyst in methanol to olefin reaction. The investigation regarding to physical and chemical properties of the catalysts had been studied. The fibrous morphology is a novel morphology for ZSM-5. The fibrous morphology would enhance the surface area and micropore volume of ZSM-5. The unique morphology of HSi@ZSM-5 was able to enhance the catalytic activity and stability in methanol to olefin reaction compared to ZSM-5.

1.7 Thesis Outline

The study was divided into five chapters. The first chapter consists of the introduction of methanol to olefin reaction and their progress on their catalyst. The problem statement and hypothesis of the current research is stated to give a clear objective of current research. There is also scopes of study that will be conducted to meet the objectives.

Chapter 2 covers the literature review and knowledge regarding previous research in methanol to olefin reaction and catalyst, advances in zeolite development, and previous effort and research in silica-based fibrous material development. The background and the concept for developing zeolite-based fibrous material are also covered in this chapter.

Chapter 3 comprises of the details regarding materials and chemicals that are used in this research. The complete procedure with experimental setup and analysis for catalyst preparation, characterization, and catalytic testing in methanol to olefin reaction are also included in this chapter.

Chapter 4 contains the results and discussion of the present research. The data are presented and analyzed comprehensively. Finally, Chapter 5 covers the conclusion and recommendation for future work and development.

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