

SYNTHESIS AND CHARACTERIZATION OF FIBROUS HZSM-5
FOR ALKYLATION OF BENZENE

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*2 years and half is not an easy journey,
Dedicated to myself,
For today is better than yesterday and
tomorrow must better than today,
My father and mother,
Zolkifli Bin Salleh and Ruziah Binti Sahadan,
Thank you for giving me a full support and understanding,
To my beloved siblings,
&
Specically dedicated to Mohamad Khaled Bin Walid,
Thank you for become my amazing gift toward the end of my master journey.*

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ABSTRACT

The global demand of toluene is expected to increase at an annual rate of 1.5% from 1995 to 2020. Thus, it is important to increase the yield of toluene by upgrading the productivity of benzene methylation process without constructing a new plant. One of the alternatives is by modifying the catalysts that are commonly used in industry to provide a better catalytic activity and performance. During the synthesis, the oil phase was varied using benzene (HFZSM-5-B), toluene (HFZSM-5-T) and xylene (HFZSM-5-X). All catalysts were characterized with X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), N₂ physisorption, Fourier transform infrared (FTIR), and electron spin resonance. The acidic property was determined by lutidine adsorbed FTIR spectroscopy, while the catalytic activity was carried out in a microcatalytic pulse reactor in the reaction temperature range of 423-673 K. The XRD, FESEM and N₂ physisorption results have confirmed the structure of all HFZSM-5 type catalysts with a spherical dendrimer silica fiber possessing high surface area of HFZSM-5-B (717 m²/g), HFZSM-5-T (691 m²/g) and HFZSM-5-X (307 m²/g). The 2,6 - lutidine adsorbed in FTIR revealed that HFZSM-5-B has abundant strong Bronsted and Lewis acid sites, followed by HFZSM-5-T and HFZSM-5-X. At a low temperature of 423 K, all HFZSM-5 type catalysts possessed excellent conversion of more than 90%. HFZSM-5-X gave the highest yield of toluene (35.27%) which attributed from its controllable micropores area in inter-dendrimer structure and reduction amount of Bronsted and Lewis acid sites. Meanwhile, it was noted that HFZSM-5-T revealed the highest yield of C₈ (71%) due to high mesopore area (647 m²/g).

ABSTRAK

Permintaan dunia terhadap toluena dijangka akan meningkat pada kadar 1.5% setahun dari 1995 hingga 2020. Oleh itu, adalah penting untuk meningkatkan penghasilan toluena dengan cara menaik taraf produktiviti metilasi benzena dengan tanpa membangunkan loji yang baharu. Salah satu cara adalah dengan melakukan modifikasi terhadap pemangkin yang biasa digunakan di industri bagi menghasilkan aktiviti pemangkinan yang lebih baik. Semasa sintesis, pelarut diubah dengan menggunakan benzena (HFZSM-5-B), toluena (HFZSM-5-T) dan xilena (HFZSM-5-X). Semua pemangkin dicirikan dengan belauan sinar-X (XRD), mikroskop elektron imbasan pancaran medan (FESEM), penyerapan fizikal nitrogen (N_2), infra-merah jelmaan Fourier (FTIR), dan resonans putaran elektron. Sifat berasid ditentukan oleh lutidina yang terserap oleh spektroskopi FTIR, manakala aktiviti pemangkin dilakukan dalam reaktor denyut mikrobermangkin dengan julat suhu tindak balas 423-673 K. Keputusan XRD, FESEM dan penyerapan fizikal N_2 telah mengesahkan bahawa semua struktur jenis mangkin HFZSM-5 dengan serat silika *dendrimer* sfera mempunyai luas permukaan yang tinggi HFZSM-5-B (717 m^2/g), HFZSM-5-T (691 m^2/g) dan HFZSM-5-X (307 m^2/g). 2,6 - lutidina yang diserap oleh FTIR mendedahkan bahawa HFZSM-5-B mempunyai banyak tapak asid Bronsted dan Lewis yang kuat, diikuti oleh HFZSM-5-T dan HFZSM-5-X. Pada suhu rendah 423 K, semua mangkin jenis HFZSM-5 mempunyai penukaran yang baik melebihi 90%. HFZSM-5-X memberikan hasil toluena tertinggi (35.27%) yang disebabkan oleh liang mikro yang terkawal di dalam struktur *inter-dendrimer* serta pengurangan jumlah tapak asid Bronsted dan Lewis. Sementara itu, telah diperhatikan bahawa HFZSM-5-T menghasilkan C_8 tertinggi (71%) kerana mempunyai kawasan liang meso yang tinggi (647 m^2/g).

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LIST OF ABBREVIATIONS

BET	-	Braunauer Emmett Teller
BJH	-	Barret Joyner Halenda
BTX	-	Benzene, Toluene, Xylene
CTAB	-	Cetyltrimethylammonium bromide
ESR	-	Electronic Spinning Resonance
FESEM	-	Field Emission Scanning Electron Microscope
FTIR	-	Fourier Transform Infra-red Spectroscopy
FZSM-5	-	Fibrous ZSM-5
FZSM-5-B	-	Fibrous ZSM-5 with benzene as an oil phase solvent
FZSM-5-T	-	Fibrous ZSM-5 with toluene as an oil phase solvent
FZSM-5-X	-	Fibrous ZSM-5 with xylene as an oil phase solvent
HFZSM-5	-	Protonated fibrous ZSM-5
HFZSM-5-B	-	Protonated FZSM-5-B
HFZSM-5-T	-	Protonated FZSM-5-T
HFZSM-5-X	-	Protonated FZSM-5-X
KCC-1	-	KAUST Catalyst Center
RSM	-	Response Surface Methodology
TEOS	-	Tetra-ethoxysilane
TPD	-	Temperature-Programmed Desorption
XRD	-	X-Ray Diffraction
ZSM-5	-	Zeolite Socony Mobil 5

LIST OF SYMBOLS

g	-Gram
s	-Second
α	-Alpha
β	-Beta
θ	-Theta
λ	-Wavelength
$^{\circ}\text{C}$	-Degree Celsius
cm	-Centimetre
eV	-Electron Volt
g L^{-1}	-Gram per litre

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The increase in demand for aromatics compound, such as toluene and xylene has placed alkylation process into important process in petrochemical. Toluene has been widely used in industries as an intermediate of commodity petrochemical and valueable fine chemicals. Toluene is used mainly as a solvents in dilution, extraction, pharmaceutical, paint stripping, carpet adhesive solvents, machinery, insecticide and rubber manufacture. Besides, toluene were also high in demand for printing industry and car seat industry as a initial material of toluene diisocyanate to form polyethane (CMA 1998).

Figure 1.1 shown the pai chart of the world consumption of toluene throughout year 2012. Throughout the world, the global demand for toluene is expected to grow at a steady rate in most regions. The fastest growing regions are Africa, the Indian Subcontinent and Northeast Asia. However, the Asia-Pacific region such as China, Japan, Taiwan and Republic of Korea is alone expected to dominate the market . The demand for toluene in this country regions was driven by their robust gross domestic product (GDP) growth in recent times. Since 2009, world toluene demand has been growing, and the demand level in 2012 was above the peak. This should not be too surprising, toluene is often mixed with gasoline as it improves its octane number and to reduce the vapor pressure. 85% of the toluene produced globally was used as solvents and in production of benzene and xylene.

Developed countries such as those in Asia-Pacific, Latin America, and Eastern Europe, and the Middle East are expected to show an increase in construction activity during 2012 -2018. Shell chemicals, Shanghai Dinghan Chemical co Ltd, Dongjin Semichem co ltd. etc are some of the leading global manufacturers of toluene since its usage as a solvent, paint and booming adhesives in industry (Transparency Market Research, 2016).

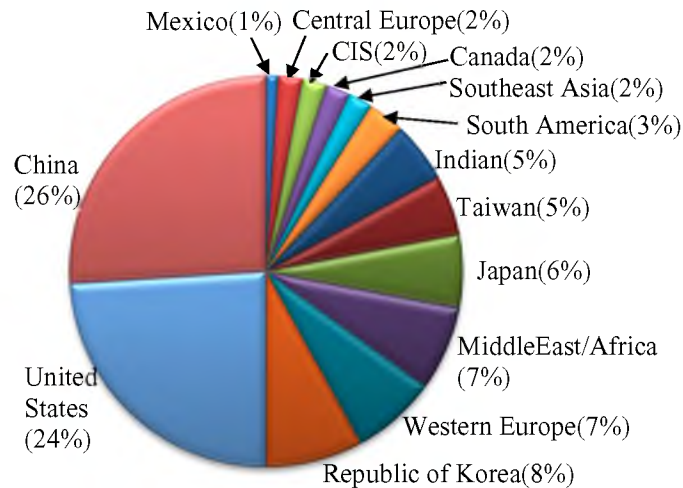


Figure 1.1 World Consumption of Toluene in 2012 (Inc. Nexant, 2009)

Toluene demand is expected to increase at average an annual rate of 1.5% from 1995 to 2020 as shown in Figure 1.2 and will be continue increase year by year (Robin *et al.*, 1998). Growth in 1995-2005 is expected to be 1.3%, while growth in 2005-2020 is estimated to be slightly higher 1.6% annually.

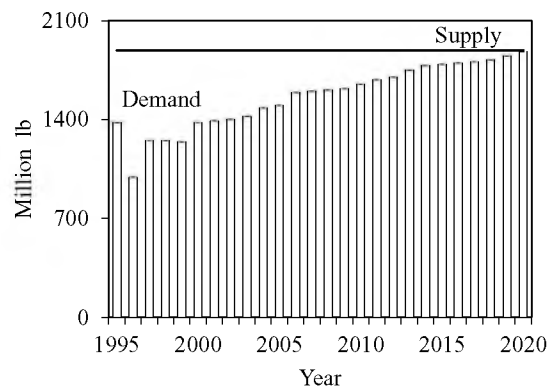


Figure 1.2 Supply/Demand Future Outlook of Toluene (Robin *et al.*, 1998)

Toluene demand consists of both domestic demand and exports demand. Domestic demand for toluene was slow after 2005 from an annual growth rate. Steady increase in demand is driven by an anticipated slower rate of fall in export volumes. This slowdown in the demand growth rate reflects the maturity of the various end-use markets for toluene. At the same time, BMAI sees no new toluene manufacture being constructed, and it is conclude by the fact that only little increased refining capacity is expected. Although overall demand rate will slow during 2005-2020, demand will still exhibit a net increase in each successive year. By keeping stocks low, demand will have to be met out of production supply.

p-Xylene is an important industrial compound, and its demand has been increasing in recent years. P-xylene is the largest volume isomer of mixed xylenes. Around 98% of p-xylene is consumed in the polyester chain, mainly in the production of fibre, film, polyethylene terephthalate (PET) bottle resin and dimethyl terephthalate (DMT). A small amount of p-xylene is used as a solvent and to produce di-paraxylene (ICIS, 2007). P-xylene strong growth driven by increasing purified terephthalic acid (PTA) consumption in polyester manufacture meanwhile DMT demand is declining slowly as polyester manufacturers prefer more economical PTA route. Due to raised issue about PX impact to environment, renewable alternatives to petroleum-based para-xylene have been offered. Figure 1.3 shown PTA capacity growth new para-xylene plants are being opened mainly in Asia Pacific and Middle East region. Global para-xylene market is expected to grow at about 5% per year (Mc Group., 2017).

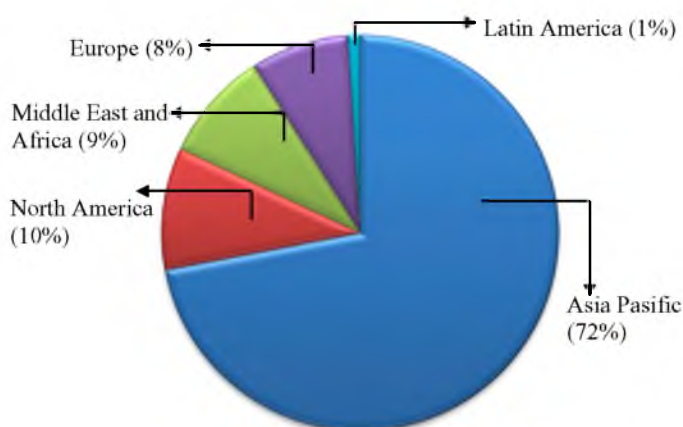


Figure 1.3 P-xylene Global Capacity by Region (Mc Group., 2017)

Global demand for para-xylene has been growing strongly and this is expected to continue. Figure 1.4 shown the supply for para-xylene is growing from 7 100 million gallons to 13 400 million gallons in between 1995 until 2015. Growth in the 1995 to 2000 timeframe will be 3.6%, while growth between 2000 and 2015 will be lower, at 2.8% annually. Domestic para-xylene demand in figure 2.5 grow in average 3.97 % annually from 6 300 million gallons in 1995 to 9 300 million gallons in 2005. Over the following 10 years, para-xylene demand rise 3.1% per year, reaching 12 700 million gallons in 2015. Although no new capacity is currently scheduled after 2000, BMAI anticipates the addition of capacity between 2000 and 2015.

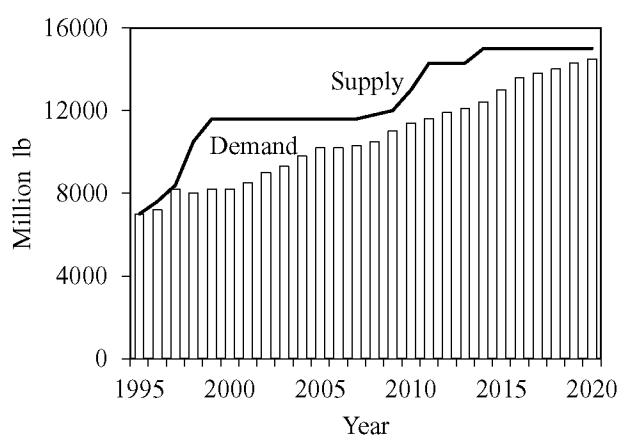


Figure 1.4 Supply/Demand Future Outlook of p-Xylene (Robin *et al.*, 1998)

Thus, it is important to increase yield by upgrading the productivity or efficiency of benzene methylation process without constructing new manufacturer and in same time could reducing cost. One of the alternative to improve this productivity of toluene and C₈ in the process is by modifying the catalysts that commonly used in industry to provide a better catalytic activity and performance.

Recently, the production of toluene and xylene by using catalytic reforming and naphtha pyrolysis is not convenient anymore due to the shortage of petroleum resources (Hu *et al.*, 2014). As an alternative route, alkylate, the cleanest gasoline-blending stream produced in a refinery is a main blend stock for reformulated gasoline (RFG) production (Pradip *et al.*, 1996). Benzene alkylation with olefins is considered

as one of the promising process that can produce toluene from natural gas and coal. Benzene alkylation technology are offer improvements in octane number and gasoline volume (Odedairo *et al.*, 2013). Benzene has been chosen because of their prices are expected to decrease in coming year since environmental regulations require to decrease the proportions of benzene in the gasoline pool. To produce high value product of aromatic toluene, any alcohol functional group has been selected as alkylating agents. Common alcohol group has been used is the smallest chain, methanol.

Most aromatics chemicals are produced by using various resources that can not be recycled such as petroleum and fuel sources. In most industrial benzene alkylations process to produce alkylbenzenes, strong lewis acids catalysts such as hydrofluoric acid, sulphuric acid and aqueous aluminium chloride were used (Carlo *et al.*, 2002). However, this type of acid catalysts were highly toxic and corrosive. Another major drawbacks in with these type of catalysts are the difficult management, especially during transportation in large scale due to corrosive to the storage or tanker, and dangerous to human health. Futhermore, the desire products and the catalysts would be difficult to separate and would consume more energy during process.

In the last five decades, vast amount of research on material development has been done to find more environmental friendly catalyst with high catalytic capability. (Xie *et al.*, 2015). Recently, a solid acid catalysts are gaining more interest from many researcher due to its advantages, such as high stability,-strong acid sites, large pores, and economically viable (Yogesh *et al.*, 2011). In addition, various solid acid catalysts such as resins, tungstated and sulfated zirconia, polyaniline sulfate, heteropolyacid, metal complexes, sulfated tin oxide, zeolite, amorphous silica-alumina, acidic ionic liquid, and others have been explored as potential solid acid catalysts. Alkylation with solid acid catalysts has more sustainability and safety advantages over conventional alkylation reaction. Some solid acid catalyst such as sulfated zirconia and SbF_5 /sulfonic acid resins has were tried in benzene alkylation. Although they were active, nevertheless they lack stability (Cheung *et al.*, 1997).

Thus, among various type solid catalysts, zeolites is widely used in various petrochemical industries (Christina *et al.*, 2003). Zeolite is composed of tetrahedral TO_4 units ($T = Si$ or Al) which linked together by sharing oxygen atoms to form channels of atomic dimensions. Zeolite has crystalline structure with coordinated Si, Al, P or certain transition metals. The zeolites are synthesized with different SiO_2/Al_2O_3 ratios are give large influenced in determining zeolite type catalysts. (Kumar *et al.*, 2013). Several zeolite type, such as ZSM-11, ZSM-5, MCM-22, ITQ-2, mordenite, β -(BEA), Y-zeolite, SAPO-34, SAPO-11/MnAPO-11, and SAPO-5/MnAPO-5 have been extensively reported used in catalyzing benzene alkylation due to its selective shape product correspond to the high surface area, good thermal stability and more environmental material compare to homogenous catalysts. (Deng *et al.*, 2014).

From all various type of zeolites, ZSM-5 is widely used in benzene alkylation industry compare to others type zeolites. This due to its unique structure that contains two intersecting channel systems composed of sinusoidal (zigzag) and straight channels with 10-membered ring openings of diameter $\sim 5.5\text{\AA}$ framework that has gives good catalytic activity and shape selectivity (Naskar *et al.*, 2012). Moreover, the synthesis of ZSM-5 has a speciality with tunable acidity structure and high thermal stability compare to other type zeolites such as zeolite Y and β . However, ZSM-5 major drawback as a catalyst in benzene alkylation it is high diffusion limitation due to micropores, and gives affect to low conversion and selectivity of benzene (Hu *et al.*, 2014). In order to enhance product diffusion, Combination of the structural features between microporosity and mesoporosity in zeolite is could help to address this drawback (Teh *et al.*, 2015). An efforts have been focused on modifying pore sizes and acidity of zeolites, so as to be used these materials in the fine chemicals, pharmaceutical and petrochemical industries. Since the kinetic diameter of possible product in benzene alkylation is almost similar dimension as the pore openings ZSM-5, thus ZSM-5 has been chosen to be used in benzene alkylation compared to other type of zeolites. Nevertheless, due to rapid deactivation, unstable structure, high temperature reaction, low selectivity of desired product and low conversion of reactant, an effort on modifying structure ZSM-5 during synthesis are still under studied and debate.

Modification of ZSM-5 material is play crucial role in order to perform better catalytic activity. Fibrous material was initially developed by Polshettiwar *et al.* in 2010. The first fibrous material is a silica-based, which has high surface area and better accessibility of active site. Several studies showed the potential of silica-based fibrous material in adsorption of nitro- and chloro- compounds. Silica-based fibrous material was developed by using microemulsion from a surfactant. Even though utilization of zeolite synthesis has been explored in many years, up to this time of study, the development of zeolite-based fibrous material has never been done. Development of zeolite-based fibrous material will significantly improves their catalytic activity, due to their tunable acidity, high surface area, and better accessible active site. Zeolite-based fibrous material will have a great potential to be applied in petroleum and petrochemical industry. Altering the morphology of zeolite material into fibrous could help to improve diffusivity active sites into pores and acidity strength.

1.2 Problem Statement and Hypothesis

Zeolites, such as HY, HBEA, HMCM-22, and HZSM-5 have been employed as catalyst in alkylation process due to their tunable intrinsic acidity, porosity, and crystallinity. Zeolite consists of silica-alumina framework and wide varieties of Si/Al ratio, which provides good thermal stability and tunable acidity. Zeolite is a suitable catalyst for acid-catalyzed reactions. However, their catalytic activity has been limited by their drawbacks, such as diffusion limitation and accessibility of active. Great efforts have been conducted to overcome the diffusion limitation, where development of hierarchically porous zeolite is one of the most versatile pathways and has been proved to increase the catalyst ability in alkylation, isomerization, and cracking.

Silica-based fibrous material has the advantage of high surface area due to the presence of the dendrimeric fiber. Silica-based fibrous material also has better accessibility of active site because the dispersion of active sites probably located in their dendrimeric fiber rather than inside the catalyst pore. Silica-based fibrous material also possesses high thermal stability (Polshettiwar *et al.*, 2010). Because the

fibrous material is fully composed with silica, it does not have adequate acid sites to promote acid-catalyzed reaction.

Implementation of the concept in developing silica-based fibrous material to microporous zeolite will be the key to overcome these problems. The small size in the nanometer range and large surface area zeolite allows dispersion in various solvents, and their dendrimer fiber structure is expected to enhance the accessibility of bulky compounds passing fibrous zeolite catalyst. Utilizing microemulsions method into the development of zeolite-based fibrous material will be successfully achieved. The dendrimer structure is formed from the water-in-oil micelle basis.

Based on previous studies, several precursors were chosen to solve the drawbacks with choosing a suitable chemical in the synthesis of fibrous zeolite with high surface area via microemulsion system. The synthesis of this emerging material normally is realized by using toxic cetylpyridinium bromide (CPB) as common structure directing agent or solvent in conjunction with combined cyclohexane and n-pentanol as oil phase and co-solvent, respectively (Doo *et al.*, 2012). Moreover, there another has report that less toxic cetyltrimethylammonium bromide (CTAB) can be the replacement for CPB with combined toluene and n-butanol as affordable solvents to synthesize dendrimer fiber with high surface area (Erna *et al.*, 2015). There is a lot of studies on surfactant and or co-surfactant, however the effect of substitute oil phase during synthesis fibrous-type catalyst toward the catalyst morphology, physical and chemical structure properties has not been explored yet.

The synthesis of catalysts involves the use of oil phase that may strongly influence the catalyst performance. Thus, the choice of suitable oil phase is frequently critical to obtain high catalytic activity and selectivity. The main role of oil phase in synthesizing this catalyst is to form an optimal micellar condition during microemulsion process before the fibrous formation. Noted that, study has been done earlier by Gorel and he mention that in micro-emulsions process it would contain a continuous phase (water) and a dispersed phase (aliphatic hydrocarbon) presents within the core of micelle aggregates of surfactant (Gorel *et al.*, 2010). However, the optimal oil phase

selection are still requires a detailed knowledge on the relationship between the chemical nature of the oil phase, fibrous formation and benzene alkylation performance.

Therefore, in this research, bottom-up approaches was provided to control fibrous structured zeolites synthesis during micro-emulsion process in fibrous formation. Figure 1.5 shown illustration of micelles, CTAB as the surfactant, butanol as co-surfactant and in this cases, aliphatic hydrocarbon which is benzene, toluene or xylene are selected to be use as an oil phase. The same chemical properties were selected as an oil phase in synthesis fibrous zeolite. However, because of different on their size of molecules, it was expected to give a different size of micellar during micro-emulsion and which later on effected the particle size and pore size on formation of fibrous catalyst. Futhermore, in this study an understanding of the formation fibrous mechanism and the precise control of particle sizes in catalyst are still less studied, hence it found to be interested. Microporous-mesoporous zeolite-based fibrous material is the next step towards efficient catalyst for alkylation.

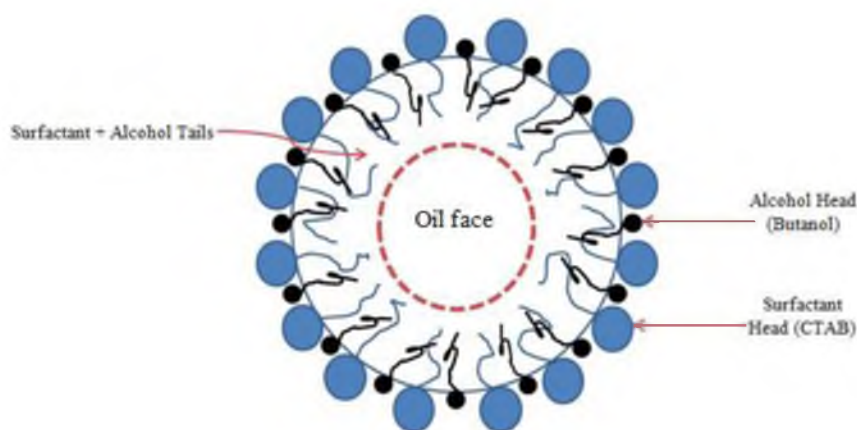


Figure 1.5 Schematic of the micellar configuration into oil-in-water micro-emulsion (Holmberg, 1999)

1.3 Objective of Study

The objective of this study are :

1. To synthesize a fibrous protonated HFZSM-5 zeolites with different oil phase.
2. To determine the physicochemical properties of the catalysts.
3. To test the activity of catalysts on benzene alkylation

1.4 Scope of Study

The scope of this study are :

1. Synthesis of fibrous fibrous protonated HFZSM-5 zeolites with different oil phase.
HFZSM-5 were prepared by microemulsion technique coupled with zeolite seed assisted crystallization and ion-exchanged method with NH_4NO_3 solution (Firmanshah *et al.*, 2016). The oil phases used in the synthesis were varied by using benzene, toluene and xylene.
2. Characterization of the catalysts
Characterization of all catalysts was conducted using X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR), N_2 adsorption-desorption, Electron Spin Resonance (ESR) and Field Emission Scanning Electron Microscopy (FESEM).
3. Catalytic activity testing.
The activity of the catalysts were tested on benzene alkylation by a microcatalytic pulse reactor connected to online 7820-A-Agilent gas chromatograph with treatment temperature at 673K, reaction temperature in range (423K-673K) and flow of hydrogen (25 ml/min) over 0.2 g weight of catalyst (Hu *et al.*, 2015).

1.5 Significance of Study

This study was prepared HFZSM-5 as an efficient catalyst in benzene alkylation. The investigation regarding physical and chemical properties of the catalysts was studied. Until this period, the fibrous morphology has only been applied to silica material. The fibrous morphology is a new way to improve the surface area and accessibility to active sites in ZSM-5. This catalyst is expected to give high conversion of benzene and high selectivity for value added product and consequently will be beneficial for knowledge transfer and also in petrochemical industries. In addition, the understanding of the properties-activity relationship of fibrous HFZSM-5 becomes an archetype in the development of new type of catalyst for benzene alkylation.

1.6 Thesis Outline

The study divides into five chapters. The first chapter consists of the introduction of aromatic compound demand and uses and cleared vision of catalytic benzene alkylation process for their progress on their catalysts. The problem statement and hypothesis of the current research is stated to give a clear objective of current research. Scopes of study are stated to give clear limitation in this study.

Chapter 2 covers the literature review and previous research regarding benzene alkylation and catalyst, advances in zeolite modification development, and principal that influence of acidity and structure of catalysts.

Chapter 3 comprise 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 benzene alkylation 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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