# SYNTHESIS AND CHARACTERIZATION OF METALS DOPED ON FIBROUS SILICA ZEOLITES FOR BENZENE ALKYLATION WITH METHANOL

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# DEDICATION

***Specially dedicated to my husband and daughters,***
***(Mohamed Izal Bin Sardan, Aisyah Humaira and Aisyah Safiya)***
*'Thank you for always standing next to me and wait for me patiently'*

***To Ma and Aboh***
***(Che Zaleha Che Endek and Razak Bin Kadir)***
*'Thank you for always being there; your endless love, faith and encouragement never fail to strengthen me'*

***To my late father,***
***(Abdul Rahman Bin Mat Jusoh)***
*'You may be gone from my sight but you are never far from my heart'*

*&*

***To my beloved siblings, family, in laws and friends***
*'Thank you for your endless love, support and encouragement during my hard time'*

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**ABSTRACT**

Benzene alkylation with methanol (benzene methylation) offers an alternative process to produce toluene, which is an important chemical intermediate in petrochemical industries. However, the existing catalysts have low performance for toluene yield due to their intrinsic micropores and high acidity. In this research, zeolite catalysts (ZSM-5, Y and Beta) with fibrous morphology (HFZ, HFY and HFB) were prepared to study their properties and catalytic activity's relationship with benzene methylation. The fibrous ZSM-5 (HFZ) was further modified using different concentrations of silica source, tetraethylorthosilicate (TEOS). Then, different transition metals (TMs) such as cobalt (Co), titanium (Ti) and manganese (Mn), as well as various Mn loading (1-10 wt%) were loaded on HFZ catalyst using impregnation method to enhance the benzene methylation performance. The catalysts were characterized using X-ray diffraction, nitrogen physisorption, field emission scanning electron microscopy, transmission electron microscopy, Fourier transform infrared (FTIR) spectroscopy, pyridine adsorbed FTIR, 2,6-lutidine adsorbed FTIR, Raman spectroscopy and thermogravimetric analysis. The catalytic testing was conducted at 300 – 400 °C under atmospheric pressure. The toluene yield for different fibrous zeolite catalysts and concentration of TEOS was found in the order: 1.0HFZ (63.1 %) > 0.5HFZ (57.5 %) > 1.5HFZ (55.7 %) > HFBEA (50.9 %) > HFY (50.4 %) at 300 °C. This result could be attributed to the adequate mesoporosity and Brönsted acid sites of the 1.0HFZ, thus decreasing the diffusion limitation and side reactions. For different TMs loaded on HFZ, the Mn/HFZ outperformed Co/HFZ and Ti/HFZ. Among the Mn loadings (1 – 10 wt%), the 5Mn/HFZ reached the highest toluene yield of 69.6 % at 350 °C, carrier gas flowrate of 20 $cm^3s^{-1}$ and benzene: methanol ratio of 1. In addition, the 5Mn/HFZ possessed outstanding stability over 72 h time on stream, as compared to pristine HFZ with activity loss of 10.8 % for toluene yield. The in-situ FTIR study corroborated that Lewis acid sites originated from Mn are beneficial for toluene formation by enhancing the benzene ring stabilization and adsorption during the alkylation reaction and inhibit the side reaction. The optimum toluene yield predicted by response surface methodology was 68.8 % at reaction temperature of 361 °C, carrier gas flowrate of 19.0 $cm^3s^{-1}$ and benzene:methanol ratio of 1.45. Based on the above observations, this study highlights the potential role of fibrous silica ZSM-5 and Mn catalysts in the benzene methylation reaction, particularly in the production of toluene.

# ABSTRAK

Alkilasi benzena dengan methanol (metilasi benzene) menawarkan proses alternatif untuk menghasilkan toluena, yang merupakan perantara kimia yang penting dalam industri petrokimia. Walau bagaimanapun, mangkin yang sedia ada mempunyai prestasi yang rendah untuk hasil toluena yang disebabkan oleh mikropori intrinsik dan keasidannya yang tinggi. Penyelidikan ini, mangkin zeolit (ZSM-5, Y dan Beta) dengan morfologi berserat (HFZ, HFY dan HFB) telah disediakan untuk mengkaji sifatnya dan hubungan aktiviti bermangkin dengan metilasi benzena. ZSM-5 berserat (HFZ) selanjutnya diubahsuai menggunakan kepekatan sumber silika, tetraetilortosilikat (TEOS) yang berbeza. Kemudian, logam peralihan yang berbeza (TM) seperti kobalt (Co), titanium (Ti) dan mangan (Mn), serta muatan Mn yang pelbagai (1-10 wt%) dimuatkan pada mangkin HFZ menggunakan kaedah impregnasi untuk meningkatkan prestasi metilasi benzena. Mangkin telah dicirikan dengan menggunakan pembelauan sinar-X, penjerapan fizikal nitrogen, mikroskopi elektron imbasan pancaran medan, mikroskopi elektron transmisi, spektroskopi inframerah transformasi Fourier (FTIR), FTIR terjerap piridin, FTIR terjerap 2,6-lutidina, spektroskopi Raman dan analisis termogravimetrik. Ujian bermangkin dijalankan pada suhu 300 - 400 ºC di bawah tekanan atmosfera. Hasil toluena untuk mangkin zeolit berserat dan kepekatan TEOS yang berbeza didapati mengikut urutan: 1.0HFZ (63.1%)> 0.5HFZ (57.5%)> 1.5HFZ (55.7%)> HFB (50.9%)> HFY (50.4%) pada suhu 300 ºC. Keputusan ini dapat dikaitkan dengan mesoporositi dan tapak asid Brönsted yang mencukupi pada 1.0HFZ, sehingga mengurangkan batasan penyebaran dan reaksi sampingan. Untuk TM berbeza yang dimuatkan pada HFZ, Mn / HFZ mengatasi Co / HFZ dan Ti / HFZ. Di antara muatan Mn (1-10 wt%), 5Mn / HFZ mencapai hasil toluena tertinggi 69.6% pada 350 ºC, kadar alir gas pembawa 20 $cm^3s^{-1}$ dan nisbah benzena:methanol bersamaan 1. Sebagai tambahan, 5Mn / HFZ mempunyai kestabilan yang luar biasa selama 72 jam dalam aliran, berbanding dengan HFZ dengan kehilangan aktiviti 10.8% untuk hasil toluena. Kajian FTIR in-situ membuktikan bahawa tapak asid Lewis yang berasal daripada Mn bermanfaat untuk pembentukan toluena dengan meningkatkan kestabilan dan penjerapan benzena semasa tindak balas alkilasi dan menghalang reaksi sampingan. Hasil toluena optimum yang diramalkan oleh kaedah sambutan permukaan ialah 68.8% pada suhu tindak balas 361 ºC, kadar alir gas pembawa 19.0 $cm^3s^{-1}$ dan nisbah benzena: metanol bersamaan 1.45. Berdasarkan pemerhatian di atas, kajian ini menekankan potensi peranan mangkin silika berserat ZSM-5 dan Mn dalam tindak balas metilasi benzena, terutamanya dalam penghasilan toluena.

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## LIST OF ABBREVIATIONS

| | | |
|---|---|---|
| Al | - | Aluminium |
| ANOVA | - | Analysis of Variance |
| BET | - | Branauer Emmett Teller |
| BJH | - | Barret Joyner Halenda |
| CTAB | - | Cetyltrimethylammonium bromide |
| CCD | - | Central Composite Design |
| $E_a$ | - | Activation energy |
| EB | - | Ethylbenzene |
| FESEM | - | Field Emission Scanning Electron Microscopy |
| FID | - | Flame Ionization Detector |
| FTIR | - | Fourier Transform Infra-red Spectroscopy |
| GC | - | Gas Chromatography |
| HFB | - | Protonated fibrous silica Beta |
| HFY | - | Protonated fibrous silica Y |
| HFZ | - | Protonated fibrous silica ZSM-5 |
| JCPDS | - | Joint Committee on Powder Diffraction Standards |
| KCC | - | KAUST Catalytic Centre |
| NLDFT | - | Non-local density functional theory |
| RSM | - | Response surface methodology |
| Si | - | Silicon |
| TGA | - | Thermogravimetric |
| TEM | - | Transmission Electron Microscopy |
| TEOS | - | Tetraethylorthosilicate |
| XRD | - | X-ray diffraction |

## LIST OF SYMBOLS

| | | |
|---|---|---|
| $\lambda$ | - | wavelength |
| $2\theta$ | - | Bragg angle |
| ºC | - | Degree celcius |
| Å | - | Angstrom |
| $\theta$ | - | angle |
| µm | - | micrometer |
| % | - | percentage |
| cm | - | centimeter |
| g | - | gram |
| h | - | hour |
| kJ | - | Kilo Joule |
| min | - | minutes |
| mL | - | mililitre |
| nm | - | nanometer |
| s | - | second |
| wt% | - | Weight percentage |

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# CHAPTER 1

# INTRODUCTION

## 1.1 Background of Study

Toluene as an important chemical intermediate has been broadly used in industry for the production of fine chemicals (Hu *et al.*, 2014). It was reported that the global toluene market size was valued at $29.14 billion in 2021, and is expected to reach $35.14 billion by 2026, registering a Compound Annual Growth Rate (CAGR) of 8.4% from 2021 to 2026. Toluene is mainly used as a solvent in dilution, extraction, pharmaceutical, paint stripping, carpet adhesive solvents, machinery, insecticide and rubber manufacture. Besides, toluene is also high in demand for printing and car seat industries as a starting material for the formation of polyethane from toluene diisocyanate (CMA 1998). The conventional methods used to produce toluene and xylene are catalytic reforming and naphtha pyrolysis. These processes greatly depend on the consumption of petroleum, thus becoming a worldwide concern due to the shortage of petroleum resources. In addition, these processes are energy-intensive which is caused by repetitive adsorption, separation and isomerization (Miyake *et al.*, 2016). Thus, an alkylation reaction with simple alcohols or alkenes is an alternative method for the production of toluene from natural gas and coal. In fact, this approach is able to improve the octane number and gasoline volume (Wang *et al.*, 2013; Saxena and Viswanadham, 2016). Furthermore, according to the United States Environmental Protection Agency (EPA), gasoline from the catalytic reforming process accounts for 70–85% of the benzene in the gasoline pool. Therefore, converting surplus benzene to more valuable toluene and xylene could help to balance the demand for aromatics ( Wang *et al.*, 2017a).

Alkylation of benzene with methanol is a well-known acid-catalyzed reaction, which can produce a mixture of aromatics. In general, the production's selectivity of this process is highly dependent on the characteristics of the catalyst. In previous studies, various homogeneous catalysts like $AlCl_3$, HF, $H_2SO_4$, HCl, etc have been employed in benzene alkylation (Laribi *et al.*, 2016; Zhao *et al.*, 2019). However, several drawbacks such as high energy requirement, corrosion to equipment, difficulty in recovery and separation from reaction limits their application in alkylation (Dong *et al.*, 2019). Therefore, the use of a heterogeneous catalyst, especially zeolite has emerged as a promising candidate owing to its high surface area, thermal stability and easy to regenerate (Odedairo and Al-Khattaf, 2013; Shi *et al.*, 2016b). It is worth mentioning that the acidity, size of channels and dimensionality of zeolites could significantly influence the activity and selectivity in transformations of organic compounds (Liu *et al.*, 2019). Zeolites with 10 membered-rings typically exhibit suitable catalyst for the synthesis of para-dialkyl benzene isomers (Corma *et al.*, 2009; Odedairo and Al-Khattaf, 2013). Meanwhile, large pore zeolites such as Y and Beta type are useful in the synthesis of monoalkyl benzenes such as ethylbenzene and cumene. In this respect, an appropriate modification procedure if zeolite is required to improve its performance towards benzene methylation.

Amongst the zeolites, Zeolite Socony Mobil–5 (ZSM-5) with unique properties, shape-selective and tunable acidity have gained wide-ranging researches for heterogeneous catalytic systems (Ghavipour *et al.*, 2013; Qiao *et al.*, 2019). Generally, the porosity and acidity of the catalysts are the major concerns in benzene alkylation activity (Liu *et al.*, 2011; Galadima and Muraza, 2015). Although ZSM-5 offers the abovementioned benefits in a heterogeneous catalytic system, its narrow micropores limit the diffusion of reactants and products through the pore, thus resulting in less formation of desired products (Wang *et al.*, 2017b). In addition, the high acidity of the commercial ZSM-5 would lead to the unwanted methanol-to-olefin (MTO) reaction and subsequently induced deactivation of the catalyst (Dong *et al.*, 2019). In the past years, researchers have pursued several different preparative strategies in order to synthesize zeolite materials with controlled shapes and porosities to minimize this problem (Shen *et al.*, 2019). Among these strategies, the development of mesopore in microporous zeolite has been proved could successfully solve the diffusion limitation and pore blockage that are faced by the conventional zeolite (Wang *et al.*, 2017a; Wang *et al.*, 2019).

Based on our previous studies, dendrimeric fibers mesoporous silica zeolite (FZSM-5) that is originated from fibrous silica KAUST Catalysis Center-1 (KCC-1) has been explored as an acid-base catalyst in CO methanation (Teh *et al.*, 2016), cumene hydrocracking reaction (Firmansyah *et al.*, 2016) and dry reforming of methane (Hambali *et al.*, 2021). The widely used of this catalyst is mainly due to its beneficial properties of high surface area (>500 $m^2/g$), large pore sizes, high thermal stability and unique bicontinuous concentric lamellar morphology. These behaviours allow the increased accessibility of bulky mass reactants to the active sites, consequently improving the reaction rate and products formation (N A A Fatah *et al.*, 2017). In addition, the unique fibrous morphology enhances the dispersion of metals on the catalyst.

Besides, it is well known that the variation of synthesis parameters significantly affects the physicochemical properties of catalysts and their catalytic performance. Based on previous studies, the synthesis of this emerging material typically was performed using toxic cetylpyridinium bromide (CPB) as a common structure directing agent or solvent in conjunction with the combination of cyclohexane and n-pentanol as oil face and co-solvent, respectively (Polshettiwar *et al.*, 2010). Moreover, other study has reported that the less toxic cetyltrimethylammonium bromide (CTAB) can replace the CPB together with toluene and n-butanol as affordable solvents to synthesize dendrimer fiber with high surface area (Moon and Lee, 2012). Furthermore, by changing the urea concentration as a hydrolysis agent to hydrolyse tetraethyl orthosilicate (TEOS) as a silica source, the particle size of the catalyst was also changed. Xu et al., (2011) reported that the particle size of ZSM-5 increases with the content of triethoxyphenylsilane increased in the synthesis system. However, to the best of our knowledge, the effect of TEOS concentration on the formation of different particle size and fiber density of fibrous-type nanoparticles are still under debate.

In addition, the introduction of metals onto the catalysts could markedly improve the activity and stability of the catalyst, especially in suppressing the formation of undesired products such as ethylbenzene (Hu *et al.*, 2014). In particular, metals with good hydrogenation properties, such as Pt, Pd, Co and Ni, will most likely bring good results in this context (Wang *et al.*, 2017b). Wang et al., (2013) have previously studied the performance of Zn/ZSM-5 catalysts in the alkylation of benzene with methane, and it is found that the addition of Zn onto HZSM-5 could enhance the toluene selectivity at 250 ºC by increasing the activity of methoxy species to initiate the alkylation reaction. Furthermore, Gao et al., (2015) found that the Brönsted acid sites (BAS) concentration of $Co_3O_4$-$La_2O_3$/ZSM-5 was lower than pure ZSM-5 sample, which suggesting that significant number of BAS were shielded by the metal particles after $Co_3O_4$-$La_2O_3$ loading on ZSM-5 samples. Therefore, exploring the transition metals in the (cobalt, manganese and titanium) is expected to enhance the benzene alkylation activity by decreasing the BAS and stabilize the benzene ring.

Although considerable efforts have been undertaken for the development of an active and stable catalyst for benzene alkylation, the most suitable catalyst is still in search. Therefore, in this study, we report the effect of TEOS concentration on the formation of different particle sizes and fiber density of fibrous silica ZSM-5. The potential use of metal loaded on fibrous silica-zeolite based catalysts for benzene alkylation was also investigated. The metal loaded and development of fibrous silica-zeolite material is expected to significantly suppress the formation of undesired products and overcome the diffusion limitations, thus leading to improved catalytic activity and selectivity of the desired products.

## 1.2 Problem Statement

The increasing demand of toluene as an intermediate chemical and the shortage of petroleum resources for conventional production of toluene have caught researchers' attention in recent times. In this respect, the finding of an alternative route for the production of toluene has placed alkylation reaction as an important process in the petrochemical industry. In general, the methylation of benzene holds the key alternative process in overcoming the current toluene deficiency. Also, the alkylation of benzene with methanol is advantageous from the excess benzene produced, which is efficient and economically viable in producing the required toluene (Lu *et al.*, 2013).

Basically, in alkylation, an efficient catalyst is required to achieve the highest yield of value-added products. To date, zeolite-type catalysts including HY, HBEA, HMCM-22, and HZSM-5 have been widely employed in the alkylation process due to their unique advantages of being highly selective, less toxic, environmentally friendly and readily reproducible in catalytic reactions (Shi *et al.*, 2016b). In fact, zeolite consists of the silica-alumina framework with wide varieties of Si/Al ratio for good thermal stability and tunable acidity. As one of the high potential zeolites, ZSM-5 is usually chosen as catalyst support in benzene alkylation due to its tunable intrinsic acidity, high surface area and easy to modify. However, the limited diffusion and accessibility of active sites due to the presence of small sizes apertures and cavity channels have constrained its catalytic activity (Liu *et al.*, 2010). Moreover, as a typical zeolite catalyst, an inevitable formation of ethylbenzene that is difficult to separate or remove from the C8 aromatics because of their close boiling points could not be ruled out (Hu *et al.*, 2014). In this regard, great efforts have been conducted to overcome these problems. Among those approaches, the development of hierarchically porous zeolite is one of the most versatile pathways to increase the catalyst ability in isomerization, alkylation, and cracking (Teh *et al.*, 2015).

In the last decade, ordered mesoporous material has emerged as one of the most interesting discoveries in the field of material synthesis. Besides, many studies have been done on the use and modification of mesoporous material in the alkylation reaction. Generally, mesoporous material possesses highly ordered mesoporous structures which enabled the size-selectivity and extremely high surface area with large pore volume (Zhao et al., 2012). However, this material has lower acidity and thermal stability than amorphous Si-Al, resulting in lower catalytic activity. By considering that, numerous studies have been dedicated on the search of appropriate materials comprising both high surface area properties for eased diffusion and accessibility of the active site, as well as good thermal stability and tunable acidity. It was fortunately discovered that the new developed silica-based fibrous material has the advantage of high surface area due to the presence of dendrimeric fiber. This characteristic offers better accessibility of active sites since the dispersion of active sites is probably located in their dendrimeric fiber rather than inside the catalyst pore. Besides, silica-based fibrous material also possesses high thermal stability than other materials (Polshettiwar *et al.*, 2010).

Furthermore, previous studies demonstrated that other than tailoring the morphological properties, the metal addition could also noticeably improve the catalyst's activity and stability while suppressing the formation of an undesired products during the benzene alkylation. Remarkable benzene methylation performance was obtained over noble metals such as Pt and Pd (Hu *et al.*, 2015a; Hu *et al.*, 2015c). Nevertheless, their application is not profitable and sustainable from industrial standpoint. As an alternative to the scarce and exorbitant noble metals catalysts, transition metal has been extensively used in order to enhance benzene alkylation performance.

## 1.3 Hypothesis

It is hypothesized that by varying the TEOS concentration during synthesis of HFZ followed by further addition of various metals, could significantly enhance the activity and selectivity of benzene alkylation reaction. The fibrous morphology of the catalyst was expected to give better accessibility of reactants and/or products to the active sites for reduced diffusion limitation. Meanwhile, the metals added were anticipated dispersed homogeneously on the dendritic fibres of the silica ZSM-5, which is different from conventional zeolites. Moreover, addition of metal onto the HFZ leading to the formation of metal support interaction subsequently altered the porosity and acidity of the composite catalysts thus, improve the selectivity towards desired toluene product for the hindered formation of unwanted by-products.

## 1.4 Objective of Study

The objective of this study is to synthesize metals supported on fibrous silica zeolites for enhanced benzene methylation. The objective of this study could be specified as follows:

1. To study the effect of different fibrous silica zeolites for benzene methylation performance

2. To examine the effect of tetraethyl orthosilicate (TEOS) concentration on fibrous silica ZSM-5 (HFZ) for benzene methylation performance

3. To investigate the effect of different type of transition metals and manganese (Mn) loading over HFZ towards benzene methylation performance

4. To study the propose mechanism and optimize the benzene methylation over outperforming Mn loaded HFZ by response surface methodology (RSM)

## 1.5 Scope of Study

This study is focused on designing benzene methylation catalysts to solve the current problems pertaining to low process efficiency such as high diffusion limitation, insufficient active sites and rapid catalyst deactivation. In this perspective, the effect of different silica zeolites, various TEOS concentrations, diverse transition metals, and varied manganese loading, as well as optimization of benzene methylation have been deliberated upon. The detail of the specific research scopes are as follows:

1. The effect of different fibrous silica zeolites on benzene methylation was studied by using three different zeolite seeds (ZSM-5, Y and Beta). Fibrous silica zeolite was prepared by microemulsion method assisted with zeolite seed crystallization as reported in previous literature (Firmansyah *et al.*, 2016). The dendrimer structure was controlled by the mixture of cetyltrimethylammonium bromide (as surfactant), butanol (as co-surfactant), toluene (as oil phase), tetraethyl orthosilicate (as silica source), urea, zeolite seed and deionized water. The prepared catalysts were characterized by XRD, $N_2$ physisorption, FESEM, FTIR KBr, FTIR-lutidine. Catalytic testing on benzene methylation was done at the temperature range of 300 – 400 °C and atmospheric pressure.

2. The effect of TEOS concentration was studied by synthesizing HFZ with three different concentrations of TEOS (0.5, 1.0 and 1.5 mol). The catalysts were denoted as 0.5HFZ, 1.0HFZ and 1.5HFZ. All synthesized catalysts were

subjected to XRD, $N_2$ physisorption, FESEM, FTIR KBr, FTIR-pyridine. Performance evaluation of catalysts for benzene methylation was conducted at atmospheric pressure and a temperature range of 300 – 400 °C with a 1:1 ratio of benzene and methanol.

3. The effect of metals on benzene methylation was studied by preparing a series of transition metal loaded HFZ with various metals (Co, Mn and Ti). These metals loaded on HFZ catalysts were synthesized by impregnating 5 wt.% each metal onto HFZ, respectively. The prepared catalysts were further characterized by XRD, $N_2$ physisorption, FESEM, FTIR KBr, FTIR-pyridine. Catalytic testing on benzene methylation was performed at temperature range 300 – 400 °C and atmospheric pressure.

4. The effect of Mn loading on HFZ in benzene methylation was investigated. A series of Mn loaded on HFZ (3, 5, 10 wt.%) were prepared by the impregnation method. The prepared catalysts were characterized by XRD, $N_2$ physisorption, FESEM, FTIR KBr, FTIR-pyridine. Catalytic testing on benzene methylation was carried out at temperature range 300 – 400 °C and atmospheric pressure. The general mechanism of benzene methylation was studied using in-situ FTIR adsorbed benzene and methanol. The optimum condition of the benzene methylation process was determined by RSM using central composite design (CCD) developed by Statistica 7.0 StatSoft. The independent variables selected in this study are reaction temperature (300-400 °C), gas flowrate (15 – 25 mL/min) and benzene to methanol ratio (0.5 – 1.5). These variables were chosen based on results from literature and preliminary studies that have been conducted.

## 1.6 Significant of Study

In this study, the fibrous silica zeolite catalyst has recently appeared as a new emerging morphology of modified structure for zeolite materials compared to other material catalysts. Due to the revolution in microemulsion technique, the formation of fibrous morphology on advanced material is now possible for the heterogeneous catalytic system. The uniqueness of fibrous morphology remarkably improves the catalyst properties, including mesoporosity, acidity and thermal stability. In benzene methylation, the other side products reaction might also occur, which inevitably causes the competitive reaction on the catalyst. Given the specific feature of fibrous morphology, the selective benzene methylation is guaranteed under suitable BAS and as a result, the high activity of benzene methylation is achieved.

Additionally, silica fibers of zeolite offer not only fibrous morphology but also provide high surface area for well-dispersion of metals, thus enhancing the metals support interaction. The interaction between metal and high surface area fibrous silica-zeolite could enhance its Lewis acid sites and, stabilize the benzene ring as well as achieve a higher benzene methylation activity. In addition, suitable mesoporosity and acidity also can inhibit the coke formation and prolong the catalyst lifespan during the reaction. Thus, the synergistic effect of physicochemical properties with fibrous silica zeolite-based catalysts can provide applicable guidance to the design and development of catalysts in the benzene methylation process.

## 1.7 Thesis Outline

This thesis begins with Chapter 1 describing the research background, problem statement, hypothesis, objectives, scope and significance of this study. Chapter 2 reviewed the literatures related to the catalysts and current works on benzene methylation. Chapter 3 described the experimental and characterization of synthesized catalysts. Chapter 4 concerned with data processing and discussing of physicochemical properties and performance of the catalysts. The conclusions and recommendations for future studies were stated in Chapter 5.

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## LIST OF PUBLICATIONS

**Journal with Impact Factor**

1. **Rahman, A.F.A**., Jalil, A.A., Siang, T.J., Aziz, M.A.H., Abdullah, T.A.T., Mohamed, M. Mechanistic insight into low temperature toluene production via benzene methylation over mesopore-rich fibrous silica HZSM-5 zeolite. J Porous Mater (2021). (**Q2, IF: 2.496**)
2. **Rahman, A.F.A**., Jalil, A.A., Hamid., M.Y.S., Ijaz Hussain, Hassan, N.S., Asif Hussain Khoja. Improved ethylbenzene suppression and coke-resistance on benzene methylation over metals doped fibrous silica-HZSM-5 zeolite. Molecular Catalysis (Under Revision).

**Indexed Journal**

1. **Rahman, A.F.A**., Jalil, A.A., Hitam, C.N.C., Hassan, N.S., Mohamed, M., Hambali, H.U. (2021) Influence of dendrimeric silica BEA zeolite towards acidity and mesoporosity for enhanced benzene methylation. Materials Today: Proceedings. 42, 211-216. (**Indexed by Web of Science**)

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1. **Rahman, A.F.A**., Jalil, A.A., Jusoh, N.W.C., Mohamed, M., Fatah, N.A.A., Hambali, H.U. (2020) Shape selective alkylation of benzene with methanol over different zeolite catalysts. Materials Science and Engineering. 808, 012003.

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1. **Rahman, A.F.A**., Jalil, A.A., Triwahyono, S., Mohamed, M., Fatah, N.A.A., Hassan, N.S., Khusnun, N.F. "A review on ZSM-5 acidity modification for enhancement of benzene alkylation". 7$^{th}$ International Graduate Conference on Engineering, Science and Humanities, IGCESH 2018, UTM Johor, Malaysia, 13-15 August 2018.
2. **Rahman, A.F.A**., Jalil, A.A., Fatah, N.A.A., Hitam, C.N.C. "Synthesis of fibrous-silica HZSM-5 for enhanced benzene methylation". *5$^{th}$ International*

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