EFFECTS OF UREA-SILICA PRECURSOR RATIO IN THE SYNTHESIS OF FIBROUS SILICA BETA ZEOLITE FOR TOLUENE METHYLATION

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Specially dedicated to

My beloved mother

My late father, grandmothers and grandfathers

&

My supportive siblings

“Thank you for positive words, encouragement and endless support “

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ABSTRACT

Recently, the need to create a versatile toluene methylation catalyst receives a major attention in the production of *p*-xylene due to its less energy intensive. The current catalyst produced low *p*-xylene yield due to its strong acidity and large pores. A novel fibrous silica beta zeolite (FSB) was successfully prepared by microemulsion assisted with zeolite-seeds crystallization using different urea-silica ratio. The properties of the catalysts were characterized using X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy, nitrogen adsorption-desorption, Fourier transform infrared spectroscopy using potassium bromide method and adsorption of 2,6-lutidine. The results indicate that different urea-silica ratio altered the density and perfection of dendrimeric silica fibres, consequently decreased the acidities, surface area and pore volume of the catalysts. Catalytic performance was conducted at 573 - 723 K under atmospheric pressure with a reactant molar ratio of 1. At 673 K, the *p*-xylene yield was in the following order: 0.5:1-FSB (23.3%) > 1:1-FSB (23.05%) > 1:0.5-FSB (7.59%) > beta (5.79%). Furthermore, the optimization using response surface methodology for 1:1-FSB catalyst demonstrated the reactant molar ratio and temperature as significant parameters with high coefficient of determination (R^2 =0.9159). The Weisz-Prater criterion is in the following order: 1:1-FSB > 1:0.5-FSB > 0.5:1-FSB > beta. The employment of the synthesized catalyst in the toluene methylation revealed a remarkable performance, suggesting its potential as a future catalyst in industrial application of toluene methylation and in other chemical processes.

ABSTRAK

Baru-baru ini, keperluan untuk mencipta mangkin serba guna bagi aplikasi metilasi toluena mendapat perhatian besar dalam pengeluaran *p*-xilena kerana kurang menggunakan tenaga. Mangkin yang digunakan pada masa ini menghasilkan produk *p*-xilena yang rendah disebabkan keasidan yang kuat dan saiz liang yang besar. Satu zeolit beta berserat silika (FSB) telah berjaya disediakan dengan menggunakan kaedah mikroemulsi dibantu dengan penghabluran benih zeolit dengan nisbah urea-silika yang berlainan. Sifat-sifat mangkin telah dicirikan menggunakan pembelauan sinar-X, miskroskop elektron imbasan pancaran medan, mikroskop elektron transmisi, penjerapan-penyahjerapan nitrogen, spektroskopi inframerah transformasi Fourier menggunakan kaedah kalium bromida dan penjerapan 2,6-lutidin. Keputusan menunjukkan bahawa nisbah urea-silika yang berbeza mengubah ketumpatan dan kesempurnaan serat silika dendrimerik yang menyebabkan pengurangan keasidan, luas permukaan dan isipadu liang mangkin. Aktiviti pemangkinan telah dijalankan pada suhu 573- 723 K di bawah tekanan atmosfera dengan nisbah molar bahan tindak balas 1. Pada 673 K, penghasilan *p*-xilena adalah seperti berikut: 0.5: 1-FSB (23.3%) > 1: 1-FSB (23.05%) > 1: 0.5-FSB (7.59%) > beta (5.79%). Pengoptimuman menggunakan kaedah gerak balas permukaan untuk mangkin 1: 1-FSB menunjukkan nisbah molar bahan tindakbalas dan suhu tindakbalas sebagai parameter yang penting dengan pekali penentu yang tinggi (R^2= 0.9159). Kriteria Weisz-Prater adalah dalam susunan berikut: 1:1-FSB > 1:0.5-FSB > 0.5:1-FSB > beta. Penggunaan mangkin dalam metilasi toluena menunjukkan prestasi yang luar biasa, mencadangkan potensi ia sebagai mangkin masa hadapan dalam aplikasi industri metilasi toluena dan juga proses-proses kimia yang lain.

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LIST OF ABBREVIATIONS

Al - Aluminium
ANOVA - Analysis of variance
B - Benzene
BET - Branauer Emmett Teller
BEA - Beta zeolite
BJH - Barret Joyner Halenda
BP - Bulkier products
CTAB - Cetyltrimethylammonium bromide
EB - Ethylbenzene
FESEM - Field Emission Scannng Electron Microscopy
FSB - Fibrous silica beta
FTIR - Fourier Transform Infra-red Spectrroscopy
mx - *m*-xylene
ox - *o*-xylene
px - *p*-xylene
RSM - Response surface methodology
Si - Silicon
TEM - Transmission Electron Microscopy
TEOS - Tetraethylorthosilicate
TriMB - Trimethylbenzene
XRD - X-ray diffraction

LIST OF SYMBOLS

K - Kelvin
H - Hour
g - Gram
cm - centimeter
µL - Microlitre
Nm - Nanometer
mL - Milliliter
s - Second
% - percentage
P - Pressure
kJ - Kilo Joule

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Global demand of xylenes saw continued growth from years 2010 till 2015 with the consumption of xylenes over the period increased at an average annual rate of 3.5 %. In October 2015, IHS Markit reported that the consumption is anticipated to increase up to 4.5 % in 2020 with growing capacity of 21% (IHS Markit, 2015). The growing demand is driven by the increasing demand in polyester industry where xylene finds its ultimate role as the basic chemical in producing the polyester monomers, mainly dimethyl terephthalate and terephtalic acid. Xylene is a benzene derivative with three variation of methyl group positioned on the benzene ring, basically known as xylene isomers. The three isomers are ortho-, meta- and para-xylene. Among the three isomers, para-xylene is leading the way as commercially desirable feedstock (Miyake *et al.*, 2016).

The aromatics of benzene, toluene and xylene (BTX) are generally obtained in one package via catalytic reforming and naphtha pyrolysis. However, since these processes involve petroleum resources, there has been motivation to find new alternatives to produce the aromatics, especially xylenes. This is due to the forecast of petroleum resources getting exhausted in the future. In addition, these processes are energy intensive due to the repetitive adsorption, separation and isomerization (Miyake *et al.*, 2016). Furthermore, in these processes, benzene and xylene are produced insufficiently in relative to the market demand since the fraction of BTX is determined by the thermodynamic equilibrium (Lu *et al*., 2013). Hence, transformation of toluene to xylene would therefore be of great importance to balance the deficiency of xylene production.

Alkylation, disproportionation and trans-alkylation are among several different approaches in producing the valuable xylene. Nevertheless, extensive researches have been done over toluene alkylation currently as a promising way of producing xylenes. In toluene alkylation, usually a specific alcohol or olefin is adopted as the alkylating agent. In the present work, methanol is proposed to be the alkylating agent because it can be produced from nonpetroleum resources and the catalyst for its production has been widely studied (Miyake *et al*., 2016). In toluene methylation with methanol, toluene is reacted with methanol to form xylene. Under certain reaction conditions, the reaction is reported to be accompanied by several side reactions, for instance, dealkylation, disproportionation and trans-alkylation, which lead to formation of benzene, light hydrocarbons and bulkier aromatic products such as trimethylbenzene and tetrametylbenzene (Ahn *et al*., 2014).

In general, varieties of zeolite-based catalysts have been studied in used for catalyzing toluene alkylation with methanol. The reaction has been carried out over mordenite, ZSM-5, beta (Ahn *et al*., 2013). These zeolites have caught attention as alkylation catalyst with their remarkable properties that provide the development of cleaner and more efficient processes where they allow easy separation from reaction products and elimination of problems associated with disposal of spent catalysts such as $AlCl_3$ (Guisnet and Gilson, 2002). Owing to their ordered framework and specific pore structures, these crystalline aluminosilicates possess unique properties of high thermal stability, high active sites and selectivity which enable application in various reactions (Qiao and Huo, 2017). Among the available zeolites, only a few studies had been reported utilizing beta zeolite in toluene alkylation with methanol due to its poor performance (Tangesnifard and Ghaziaskar, 2016; Smirniotis and Ruckenstein, 1995). Beta zeolites contain 12-membered rings with three-dimensional pore opening systems. Its large pore opening size (7.6 x 6.4 Å) might play a role in shape selectivity and minimizing diffusion limitation in toluene alkylation reaction (Tian et al., 2016).

The shape and size of zeolites significantly affects their performances in both fundamental research and industrial which indicate the essential of morphological control study. In 2010, Polshettiwar and his research groups initiated the first fibrous morphology using silica-based material by adopting microemulsion technique. The new class catalyst, namely fibrous nano-silica (KCC-1), is reported to exhibit excellent physical properties, including a high surface area, good thermal properties and high mechanical stability. Furthermore, it has also been successfully applied in a range of important applications such as catalysis, drug delivery, CO_2- conversion (Huang *et al*., 2014). The fibrous structure which consists of dendrimeric fibres contributes to high surface area and enhance the accessibility of active sites. The microemulsion technique involves the combination of surfactant, oil phase and water. The formation of fibrous morphology is believed to be sensitive to the synthesis conditions thus a motivation to explore the effects of synthesisparameters on the morphology of catalysts.

To the best of our knowledge, there is no report utilizing fibrous beta zeolites in toluene methylation reaction. Hence, present work would be of synthesizing fibrous beta zeolites by using microemulsion templating method. The fibrous beta zeolite is proposed for toluene alkylation with methanol to give xylene isomers. It is predicted that fibrous beta would provide suitable acidity with higher diffusion limitation which lead to better performance of catalytic activity.

1.2 Problem Statement

Previous decades have shown the increasing demand for xylene and the trend is anticipated to continue growing. This situation has caught researchers' attention in finding new alternative route for production of xylene due to the problem that might arise regarding petroleum resources. The methylation of toluene holds as the key alternative process in overcoming the current xylene deficiency. The alkylation of toluene with methanol is advantageous from the excess toluene produced, which is an efficient and economically viable in producing the required xylene (Lu e*t al*., 2013).

Zeolites such as MOR, beta, MCM-22 and ZSM-5 have been employed as catalysts in toluene alkylation process due to tunable intrinsic acidity, surface area and uniform pores (Ahn *et al*., 2014; Tangesnifard and Ghaziaskar, 2016; Wang *et al*., 2017). Zeolite consisting of aluminosilicate framework possesses with good thermal stability, different pore size and wide varieties of Si/Al ratio which in turns provide the tunable acidity. These properties make it suitable for facilitating acid-catalyzed reactions. However, diffusion limitation and accessibility of active sites become the major constraints to the zeolite catalytic activity in certain reactions. In effort to overcome the diffusion limitation, development of hierarchically porous zeolite is one of the great invention where this material has been proved to increase the catalyst ability in isomerization, alkylation and cracking (Teh *et al*., 2015).

Although beta zeolite has been used as catalyst for alkylation of toluene and has favorable properties such as three-dimensional structure, mild acidity and thermal stability, the material possesses large pore structure that disabled the shape selectivity and diffusion limitation function hence resulting in low selectivity (Ahn *et al*., 2016; Ahn *et al.*, 2013). In the toluene alkylation with methanol, the reaction yields multi-products which is affected by undesired reactions. Cracked products and higher methylated compounds other than xylenes such as ethylbenzene and trimethylbenzenes are some of the common undesired products. The presence of cracked products and higher methylated compounds reduced the selectivity and yields of desired xylenes. The utilization of beta zeolite favors secondary reactions due to its large opening. The wide pore openings reduce the diffusion limitation and allows further methylation of desired product thus producing bulkier aromatic compounds. Despite the drawbacks, the catalytic activity can still be enhanced by increasing the diffusion limitation and lowering the acidity, simultaneously.

In order to suppress the formation of these undesired products, there is a need to design a new modified catalyst with better properties which could possibly better the selectivity in toluene alkylation. Implementation of silica-based fibrous material to zeolite is foreseen to be able to overcome these problems. The material is anticipated to mild the acidity which is compatible with the need of reaction and increase the diffusional limitation of products. The presence of dendrimeric fibres aid in increasing the diffusion limitation, where smaller size molecules will easily diffuse out from the zeolite and preventing larger molecules out, thus improving the selectivity of desired products. Utilizing microemulsion technique, the zeolite-based fibrous material is expected to be successfully synthesized.

1.3 Objectives of Study

The aims of this study are:

i. To synthesize and characterize fibrous-silica beta (FSB) zeolite with different urea-TEOS ratio.
ii. To study the catalytic activity of catalysts on toluene methylation.
iii. To optimize the reaction condition under various parameters (reaction treatment temperature, reactant molar ratio and reaction temperature) using Response Surface Methodology (RSM)
iv. To study the mass transfer of catalyst and propose mechanism for the toluene methylation.

1.4 Scope of Study

The scope of this study consists of five parts including catalyst preparation, characterization of catalysts, catalytic testing, optimization of reaction conditions and kinetic and mechanism of toluene methylation study. The following describes the limitations of study in details:

i. Fibrous-silica beta zeolite was synthesized using microemulsion method. Three different ratios of urea-TEOS were adopted for comparative study. The proposed urea-TEOS ratio were 0.5:1, 1:1 and 1:0.5. The catalysts were referred as 0.5:1-FSB, 1:1-FSB and 1:0.5-FSB.

ii. All catalysts were subjected to Field Emission Scanning Electron Microscope (FESEM) and Transmission Electron Microscope (TEM) studies for the observation of morphology and confirmation of fibrous formation. To obtain the surface area and pore size of catalysts, N_2 adsorption-desorption was performed onto the catalysts. Meanwhile, the nature and strength of acidity was studied by using IR of 2,6-lutidine.

iii. Catalytic testing was done using all catalysts in toluene methylation process. The reactions were carried out at atmospheric pressure using nitrogen as carrier gas in the micro quartz reactor. The reaction temperature was varied within range of 573-723 K.

iv. The optimization of toluene methylation condition was accomplished using RSM. Relationship between three independent variables such as treatment temperature (723-823 K), reaction temperature (573-623 K) and reactant molar ratio of methanol to toluene (0.5-1.5) were studied and with expectation to come out with an optimum condition.

v. The internal mass transfer of catalyst in the toluene methylation was determined based on Weisz-Prater criterion. Furthermore, Arrhenius expression was used in order to find the required activation energy. The mechanism of toluene methylation was proposed based on the product distribution obtained from the catalytic testing using 1:1-FSB.

1.5 Significance of Study

This study prepared the fibrous catalysts of beta using different urea-TEOS ratios, 0.5:1-FSB, 1:1-FSB and 1:0.5-FSB. A detailed investigation of the physical and chemical properties of the catalysts as well as its relationship to the catalytic activity in toluene methylation were conducted. These catalysts were expected to exhibit higher conversion and yield for p-xylene. Consequently, these findings would be beneficial for catalysis applications in chemical processes. and also contributing to petrochemical industries as well as for knowledge transfer.

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