Shape selective alkylation of benzene with methanol over different zeolite catalysts

A F A Rahman¹, A A Jalil¹,², N W C Jusoh³,⁴, M Mohamed¹, N A A Fatah¹ and H U Hambali¹

¹School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
²Centre of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.
³Department of Chemical and Environmental Engineering, Malaysia-Japan International Institute of Technology (MIJIT), Universiti Teknologi Malaysia, Kuala Lumpur, Jalan Sultan Yahya Petra, 54100 Kuala Lumpur, Malaysia.
⁴Centre of Hydrogen Energy, Universiti Teknologi Malaysia, 54100 Kuala Lumpur, Malaysia

*aishahaj@utm.my

Abstract. Benzene methylation is an important process for removing excess benzene in petrochemical industries to produce value-added products such as toluene and xylene. In this study, the performance of three types of zeolites, which is ZSM-5 (HZ), zeolite Y (HY) and zeolite β (Hβ) were investigated as catalyst in the benzene methylation reaction. The catalysts were characterized by N₂ adsorption-desorption and FTIR. The N₂ adsorption-desorption verified that the mesopores volume of the catalysts was in the following order: HB > HY > HZ. While, the FTIR-lutidine revealed that the HB possessed the highest amount of Brönsted acid sites followed by HZ and HY. The catalytic testing at 573 K showed that HZ gave good performance in benzene methylation with 55.2% and 22.1% yield of toluene and xylene, respectively. It is suggested that HZ catalyst with moderate amount of Brönsted acid sites and smallest mesopores volume appear to be effective for shape selective synthesis of toluene and xylene. In addition, pore structure of HZ also contributed to the high catalytic activity of benzene methylation.

1. Introduction
The aromatic hydrocarbons alkylation with methanol is widely used in the chemical industry for production of toluene and xylene [1,2]. Toluene and xylene are widely used as intermediates in the chemical industry to obtain textile fabric, plastics and detergents [3,4]. These chemicals are generally obtained via naphtha pyrolysis and catalytic reforming, along with the production of benzene [5]. However, these processes are greatly depended on the consumption of petroleum and have been called into question because of the lack of petroleum resources. Therefore, benzene methylation is regarded as a potential approach to produce toluene and xylene [6,7].

Previously, these alkylation reaction are performed with strong mineral acids catalysts such as H₂SO₄, HF, and AlCl₃, which are highly corrosive and toxic [8,9]. Generally, the acid need to be
separated from the alkylation products, which considered as an energy consuming process. Presently, zeolites catalysts such as BEA, H-Y, H-mordenite and H-ZSM-5 are considered as a potential catalyst for the benzene alkylation with methanol because of their advantages such as highly unique shape selectivity for acid catalyzed reaction, environmentally friendly, and less toxic [10–12]. Usually, the alkylation reaction to produce aromatic compounds was influenced by the shape selectivity. The shape selectivity are greatly depends on the acidity, the porosity, the size of channels and the dimensionality of zeolites [13,14].

Thus, the objective of this present work is to examine the effect of the different zeolite towards the catalytic activity of benzene alkylation with. The acidity and porosity properties were comprehensively characterized and their effect on the catalytic activity in the reaction was investigated thoroughly.

2. Experimental

2.1. Catalyst preparation

The ZSM-5, zeolite Y and zeolite β was obtained from Zeolyst International. All zeolites were ion exchange with ammonium nitrate (NH₃NO₃) to form protonated zeolite followed by drying overnight at 383 K and calcined for 3 h under an air atmosphere at 823 K.

2.2. Catalyst characterization

BET method was used to evaluate the textural properties of the catalysts. This was achieved from N₂ adsorption desorption at -196 ºC by a Beckman Coulter SA 3100. Analysis were carried out after the samples was degassed at 300 ºC for 1 h. The catalysts acidity was obtained by 2,6-lutidine acid probe molecule. The measurements were achieved on FTIR Agilent Cary 640 FTIR spectrometer assembled with a stainless steel cell and CaF₂ windows. All catalysts were pre-treated at 400 ºC for 1 h before measurements. Next, the 4 Torr of 2,6-lutidine was adsorbed on pre-treated catalysts for 15 min at 25 ºC, followed by degassing at 50 ºC change to K for 15 min.

2.3. Catalytic reaction

The benzene methylation was performed in a microcatalytic pulse reactor at atmospheric pressure and 400 ºC. Before the reaction, 200 mg of catalyst was pre-treated at 450 ºC for 2 h in air stream, then cooled to 400 ºC in a nitrogen stream. Then, a 1:1 molar ratio of benzene to methanol passed by to the pre-treated catalyst, and the products were analyzed on a gas chromatograph (7820A) equipped with FID/MS detector. The benzene conversion (Xᵢ), yield (Yᵢ) and product selectivity (Sᵢ) were calculated by the following equation:

\[ Xᵢ = \frac{\sum Cᵢ - Cᵢ}{\sum Cᵢ} \times 100\% \]  

\[ Sᵢ = \frac{Cᵢ}{\sum Cᵢ - Cᵢ} \times 100\% \]  

\[ Yᵢ = \frac{Xᵢ \times Sᵢ}{100} \]  

where Cᵢ and Cᵢ are mole number of products and residual benzene.
3. Results and Discussion

3.1. Structural properties of catalysts

\( \text{N}_2 \) adsorption-desorption isotherms of all catalysts are demonstrated in Figure 1. The HZ and HY showed a type I isotherm with H4 hysteresis loop \([6,15–17]\). In addition, HZ and HY catalysts displayed high nitrogen uptake at \( \frac{P}{P_0} < 0.2 \), confirming the microporous characteristic of the catalysts. A large portion of the micropore was found in HZ catalyst. Meanwhile, Hβ showed a H3 hysteresis loop with type IV isotherms, signifying the existence of mesopores materials and classification of slit-like pores \([18]\).

![Figure 1. \( \text{N}_2 \) adsorption-desorption isotherm of catalysts.](image)

From Table 1, Hβ shows the highest surface area (555 m\(^2\)g\(^{-1}\)) followed by HY (475 m\(^2\)g\(^{-1}\)) and HZ (225 m\(^2\)g\(^{-1}\)). The total pore volume of HZ, HY and Hβ are 0.139, 0.427 and 0.943 cm\(^3\)g\(^{-1}\), respectively. In addition, Hβ possessed higher mesopore volume as compare to HZ and HY. This result is in agreement with above isotherm result, in which the Hβ showed high nitrogen uptake at \( \frac{P}{P_0} > 0.9 \).

| Catalyst | BET surface area (m\(^2\)g\(^{-1}\)) | Pore volume (cm\(^3\)g\(^{-1}\)) | Micropore volume (cm\(^3\)g\(^{-1}\)) |
|----------|-----------------------------------|---------------------------------|--------------------------------------|
| HZ       | 225                               | 0.139                           | 0.089                                |
| HY       | 475                               | 0.427                           | 0.137                                |
| Hβ       | 555                               | 0.943                           | 0.153                                |

3.2. Acidic properties of catalysts

In this study, 2,6-lutidine was utilized as a probe molecule for the evaluation of the catalyst acidity. Figure 2 shows the FTIR spectra of adsorbed 2,6-lutidine on the zeolite catalyst activated at 350 °C. It was showed that all the catalysts showed a two doublets bands at 1703 +1677 cm\(^{-1}\) and 1652 + 1628 cm\(^{-1}\), which corresponded to the Brønsted acid sites. Additionally, another peak was observed at 1607 + 1586 cm\(^{-1}\), suggesting the existence of Lewis acid sites \([19]\). Figure 2B summarizes the variation of band intensity changes in Figure 2A as a function of degassed temperature. The results demonstrated that all catalysts exhibited a strong interaction between BAS and 2,6-lutidine at 50°C, but the intensities decreased considerably when the temperature was 150°C, representing the presence of a low amount of moderate to strong BAS. It clearly seen that HZ has a moderate amount of BAS and LAS for facilitated benzene akylation reaction \([18,20]\).
3.3 Catalytic activity
The catalytic activities of the catalysts were performed with respect to benzene methylation at 400 °C. The conversion of benzene and yield of products over all of the catalysts is shown in Figure 3. It was showed that the conversion of HZ, HY and Hβ were 89.6, 87.5 and 92.8%, respectively. In addition, the result showed that HZ gave the highest yield of toluene with 61.6 %, followed by HY and Hβ, which may be related to porosity and acidity of catalyst. The acidity in HZ provide an appropriate amount of BAS to initiate the alkylation of benzene for production of toluene[6,18]. Besides acidity, HZ also possesses a small amount of micropore that make these products easy to pass through the pore and inhibited the occurrence of undesired products.

4. Conclusion
In this study, the activity of the HZ, HY and Hβ was studied for the catalytic benzene methylation at 400 °C. It was observed that the different zeolites that have different pore structure, acidity and porosity can influenced the types of products obtained by the catalytic alkylation. Besides, this study also proven that the appropriate amount of Brönsted acid sites and low micropore volume are important in the reaction as the high and low of Brönsted acid sites in HY and Hβ has lowered the toluene yield. While, HZ with low micropore volume and mild acidity exhibited the best catalytic performance with 61.6% yield of toluene.

Figure 2. FTIR spectra of 2,6-lutidine for (a) HZ (b) HY (c) Hβ and variation of peak intensity as a function of outgassing temperature 2,6-lutidine adsorption for (B) Brönsted acid site (C) Lewis acid site.

Figure 3. Conversion of benzene and Selectivity of products.
Acknowledgments
This work was financially supported by the Universiti Teknologi Malaysia through UTM Transdisciplinary Research Grant (Grant No. 06G53), Collaborative Research Grant (07G66) and the awards of UTM Zamalah Scholarship (Anis Farhana Abdul Rahman).

References
[1] Dong P, Li Z, Wang X, Yun H and Li G 2018 *Green Chem. Lett. Rev.* **11** 158–64
[2] Rui J, Lyu J, Hu H, Zhang Q, Wang Q and Li X 2019 *Chinese Chem. Lett.* **30** 757–61
[3] Lyu J, Hu H, Tait C, Rui J, Lou C, Wang Q, Han W, Zhang Q, Pan Z and Li X 2017 *Chinese J. Chem. Eng.* **25** 1187–94
[4] Wang X, Xu J, Qi G, Li B, Wang C and Deng F 2013 *J. Phys. Chem. C* **117** 4018–23
[5] Alabi W, Atanda L, Jermy R and Al-Khattaf S 2012 *Chem. Eng. J.* **195–196** 276–88
[6] Abdul Jalil A, Zolkifli A S, Triwahyono S, Abdul Rahman A F, Mohd Ghani N N, Shahul Hamid M Y, Mustapha F H, Izan S M, Nabgan B and Ripin A 2019 *Ind. Eng. Chem. Res.* **58** 553–62
[7] Lyu J H, Hu H L, Rui J Y, Zhang Q F, Cen J, Han W W, Wang Q T, Chen X K, Pan Z Y and Li X N 2017 *Chinese Chem. Lett.* **28** 482–6
[8] Vernaya O I, Krotova I N, Maksimov Y V and Rostovshchikova T N 2017 *Pet. Chem.* **57** 93–9
[9] Shen Z, Ma C, He J, Wang D, Sun H, Zhu Z and Yang W 2019 *Appl. Catal. A Gen.* **577** 20–7
[10] Ahn J H, Kolvenbach R, Neudeck C, Al-Khattaf S S, Jentys A and Lercher J A 2014 *J. Catal.* **311** 271–80
[11] Wichterlová B, Čejka J and Žilková N 1996 *Microporous Mater.* **6** 405–14
[12] H. U. H, A. A. J, T. J. S, A. A. A, N. A. A. F, I. H and M. S. A 2019 *J. Energy Saf. Technol.* **2** 9–13
[13] Liu K, Xie S, Liu S, Xu G, Gao N and Xu L 2011 *J. Catal.* **283** 68–74
[14] Li Y, Xue B and Yang Y 2009 *Fuel Process. Technol.* **90** 1220–5
[15] Teh L P, Triwahyono S, Jalil A A, Mamat C R, Sidik S M, Fatah N A A, Mukti R R and Shishido T 2015 *RSC Adv.* **5** 64651–60
[16] Jalil A A, Gambo Y, Ibrahim M, Abdulrasheed A A, Hassan N S, Nawawi M G M, Asli U A, Hassim M H and Ahmad A 2019 *Int. J. Energy Res.* **0**
[17] Triwahyono S, Jalil A A, Izan S M, Jamari N S and Fatah N A A 2019 *J. Energy Chem.* **37** 163–71
[18] Ghani N N M, Jalil A A, Triwahyono S, Aziz M A A, Rahman A F A, Hamid M Y S, Izan S M and Nawawi M G M 2019 *Chem. Eng. Sci.* **193** 217–29
[19] Izan S M, Triwahyono S, Jalil A A, Majid Z A, Fatah N A A, Hamid M Y S and Ibrahim M 2019 *Appl. Catal. A Gen.* **570** 228–37
[20] Firmansyah M L, Jalil A A, Triwahyono S, Hamdan H, Salleh M M, Ahmad W F W and Kadja G T M 2016 *Catal. Sci. Technol.* **6** 5178–82