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Shape selective alkylation of benzene with methanol over different zeolite catalysts

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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 (H β) 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 (NH_3NO_4) 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 N_2 adsorption desorption at $-196\text{ }^\circ\text{C}$ by a Beckman Coulter SA 3100. Analysis were carried out after the samples was degassed at $300\text{ }^\circ\text{C}$ 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 CaF_2 windows. All catalysts were pre-treated at $400\text{ }^\circ\text{C}$ for 1 h before measurements. Next, the 4 Torr of 2,6-lutidine was adsorbed on pre-treated catalysts for 15 min at $25\text{ }^\circ\text{C}$, followed by degassing at $50\text{ }^\circ\text{C}$ change to K for 15 min.

2.3. Catalytic reaction

The benzene methylation was performed in a microcatalytic pulse reactor at atmospheric pressure and $400\text{ }^\circ\text{C}$. Before the reaction, 200 mg of catalyst was pre-treated at $450\text{ }^\circ\text{C}$ for 2 h in air stream, then cooled to $400\text{ }^\circ\text{C}$ 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 (X_B), yield (Y_i) and product selectivity (S_i) were calculated by the following equation:

$$X_B = \frac{\sum C_i - C_B}{\sum C_i} \quad (1)$$

$$S_i = \frac{C_i}{\sum C_i - C_B} \times 100\% \quad (2)$$

$$Y_i = \frac{X_B \times S_i}{100} \quad (3)$$

where C_i and C_B are mole number of products and residual benzene.

3. Results and Discussion

3.1. Structural properties of catalysts

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 $P/P_0 < 0.2$, confirming the microporous characteristic of the catalysts. A large portion of the micropore was found in HZ catalyst. Meanwhile, $H\beta$ showed a H3 hysteresis loop with type IV isotherms, signifying the existence of mesopores materials and classification of slit-like pores [18].

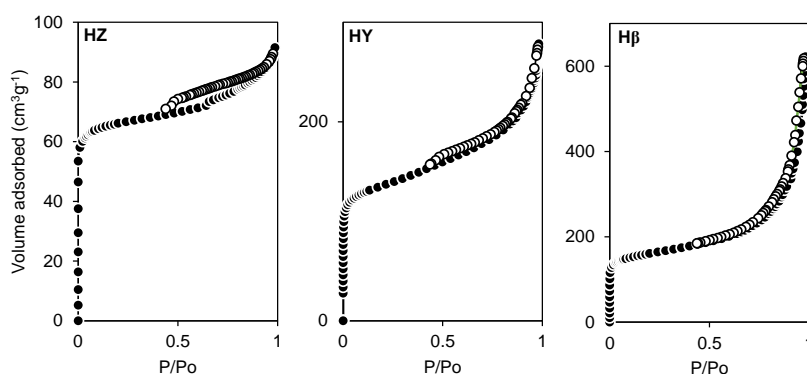


Figure 1. N_2 adsorption-desorption isotherm of catalysts.

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

Table 1. Textural properties of catalysts.

Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)	Micropore volume (cm^3/g)
HZ	225	0.139	0.089
HY	475	0.427	0.137
$H\beta$	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 $1703 + 1677 \text{ cm}^{-1}$ and $1652 + 1628 \text{ cm}^{-1}$, which corresponded to the Brönsted acid sites. Additionally, another peak was observed at $1607 + 1586 \text{ cm}^{-1}$, 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 alkylation reaction [18,20].

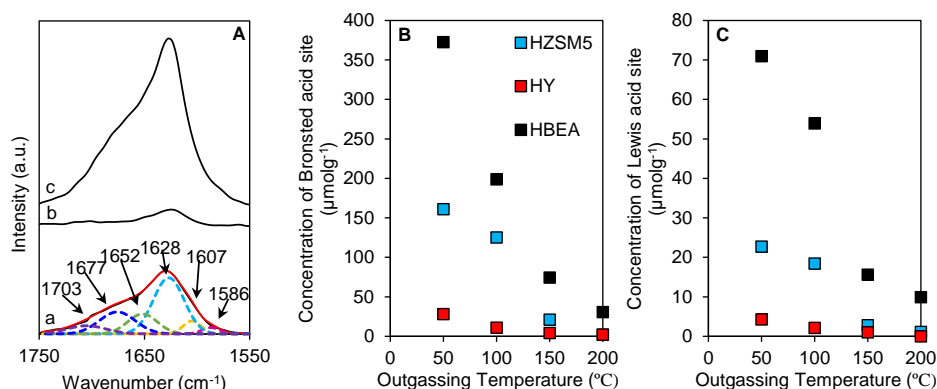


Figure 2. FTIR spectra of 2,6-lutidine for (a) HZ (b) HY (c) H β and variation of peak intensity as a function of outgassing temperature 2,6-lutidine adsorption for (B) Brønsted acid site (C) Lewis acid site.

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 H β 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 H β , 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.

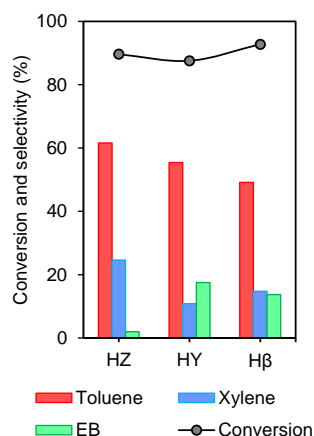


Figure 3. Conversion of benzene and Selectivity of products.

4. Conclusion

In this study, the activity of the HZ, HY and H β 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 Brønsted acid sites and low micropore volume are important in the reaction as the high and low of Brønsted acid sites in HY and H β 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.

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