

Selective Cracking of Durene to Para-Dimethyl Benzene over ZSM-5 Zeolite

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Abstract

In this work, ZSM-5, a size selective heterogeneous catalyst was employed for the synthesis of p-xylene from durene by cracking. The reaction was carried out in gas phase using a fixed bed reactor. During the reaction, benzene was used as solvent together with durene. To optimize the reaction conditions, temperature, feed ratio, feed flow rate, reaction time and catalyst load weight were investigated. The products were analyzed by gas chromatography (GC). The selectivity of p-xylene and the conversion of durene was 20.04% and 40.09% respectively when the reaction was carried out at 450 °C for 1 h using 1.0 g catalyst with feed ratio 1: 8 and flow rate 2.0 ml/h.

Keywords: *Para-xylene, durene, catalytic cracking, zeolite, ZSM-5*

1. Introduction

P-xylenes is an important organic compound that can be used as a solvent in printing, rubber, synthetic fiber, plastic, insecticide, pesticides and leather industries and as a cleaner and a paint thinner [1-2]. In the industry, p-xylene is used as a source for large scale manufacture of the chemical and pharmaceutical intermediate, terephthalic acid, which is further used in the production of polyester resin and fibers. In traditional process, p-Xylene is separated from the BTX aromatics (benzene, toluene and the xylene isomers) through the catalytic reforming of petroleum naphtha by series of distillation, adsorption or crystallization, however, these separation methods are difficult to conduct because the xylene isomers have similar boiling point [3], in addition, they need more energy for their recovery [4].

Cracking of hydrocarbons have been widely used in the manufacturing of olefins and diolefins, however, traditional steam cracking process needs high reaction temperature and cause many environmental problems [5]. In order to overcome above mentioned disadvantages, catalytic cracking has been employed in the industrial process using various kinds of catalysts such as transition metals [6, 7], silica [8], zeolite and modified zeolite [9], mesoporous mixed oxide catalysts [10], metal organic frameworks.

ZSM-5 zeolite has drawn much attention since it was first reported by Mobil Oil Company in 1972 [11] because of its unique channel structure, thermal stability, acidity, shape-selective property [12-15], recent year, many research has been devoted for the synthesis and applications of ZSM-5 zeolites [16-18]. ZSM-5 has been used as sorbents as well as catalysts, in petrochemical, fine chemical production [19, 20]. Recent years, as a heterogeneous catalyst, ZSM-5 has been employed to many organic reactions such as oxidation [21], hydroxylation

[22], dehydrogenation [23], cracking [24, 25] and so on. The structure of ZSM-5 makes it possibility to be used as a shape-selective catalyst in some isomerization reaction such as the isomerization of m-xylene to p-xylene.

In this work, we applied ZSM-5 for durene cracking process to get selective product p-xylene, in order to optimize the reaction condition, the effect of temperature, feed ratio, feed flow rate, time and catalyst weight were studied.

2. Experimental

2.1. Materials

Durene (C₁₀H₁₄, 98.0%, Tokyo chemical industry), benzene (C₆H₆, 99.5%, Daejung reagents chemicals), p-xylene (C₆H₄(CH₃)₂, 99.0%, Yakuri pure chemicals).

2.2. Preparation of catalyst

The ZSM-5 catalyst was purchased from Zeolyst International Company and used directly without any other processing.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku D/Max 2200+Ultima diffractometer with Cu-K α radiation ($\lambda=0.154$ nm). The diffraction data were recorded in the 2θ range 5-50° with a step of 0.02 °/s. Thermogravimetric analysis (TGA) was performed by Scinco TGA N-1000 thermo gravimetric (TG) analyzer, the sample was heated from room temperature to 800 °C under N₂ at a temperature ramp of 10 °C/min. The nitrogen adsorption-desorption isotherms were measured at 77 K on a Belsorp mini II volumetric adsorption analyzer. Prior to each adsorption measurement the samples were evacuated at 250 °C under vacuum ($p<10^{-5}$ mbar) for 6 h in the degassing port. The surface area (S_{BET}) was determined from the linear part of the Brunauer-Emmett-Teller (BET) equation, and the pore volume was calculated using a BET plot based on the amount of nitrogen gas adsorbed at the last adsorption point ($p/p_0 = 0.99$) and the pore size distribution using the Barrett-Joyner-Halenda (BJH) method. SEM images were captured on JEOL JSM 5600 scanning electron microscope.

2.4. Catalytic cracking of durene over ZSM-5

A inhouse fixed bed reactor was used for the cracking of durene using ZSM-5 in gas phase condition. The reactant (durene and benzene mixed with a proper ratio) was added to the reactor with constant rate controlled by an automatic syringe. The reaction was carried out in N₂ atmosphere to prevent the oxidation reaction. The ZSM-5 catalyst was mixed with ceramic balls and placed in a quartz tube. Before started each experiment run the catalyst was activated at 550 °C for 5 h. In order to optimize the reaction conditions, the temperature (300, 350, 400, 450, 500 °C), feed ratio (1: 5, 1: 6, 1: 7, 1: 8, 1: 9, 1: 10), feed flow rate (1 ml/h, 1.5 ml/h, 2 ml/h, 2.5 ml/h, 3 ml/h), time (1, 2, 3, 4, 5, 6 h) and catalyst weight (0.5, 1.0, 1.5, 2.0 g) were investigated. The products were analyzed by GC (Agilent, HP-5 column 50 m x 320 μ m x 0.52 μ m and FID detector) and GC-MS (Bruker, VF-5ms column 30 m x 0.53 mm x 1.5 μ m) wherever required.

3. Results and Discussion

3.1. Characteristics of catalyst

Figure 1 shows the XRD patterns of ZSM-5 catalyst. The characteristics patterns were observed in the 2θ range of 5 to 50 °, the main peaks appeared in the 2θ angle around 8.05, 9.08, 24.47 and 45.67, which are the significant patterns of ZSM-5, which matches well with those reported in the literatures [17, 26, 27]. The XRD patterns demonstrated higher crystallinity of ZSM-5 catalyst used.

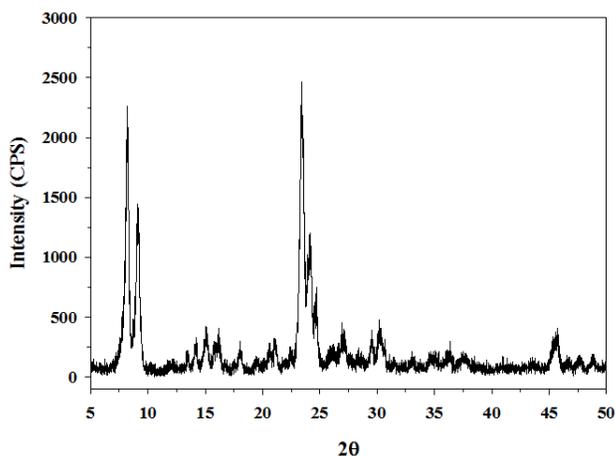


Figure 1. XRD patterns of ZSM-5

The nitrogen adsorption-desorption isotherms of ZSM-5 catalyst are shown in Figure 3. It displayed Type I isotherm, a significant characteristic of microporous materials, which was consistent to the literature [28, 29]. The surface area and pore volume ZSM-5 was found to be $565.13 \text{ m}^2\text{g}^{-1}$ and $0.3105 \text{ cm}^3\text{g}^{-1}$ respective.

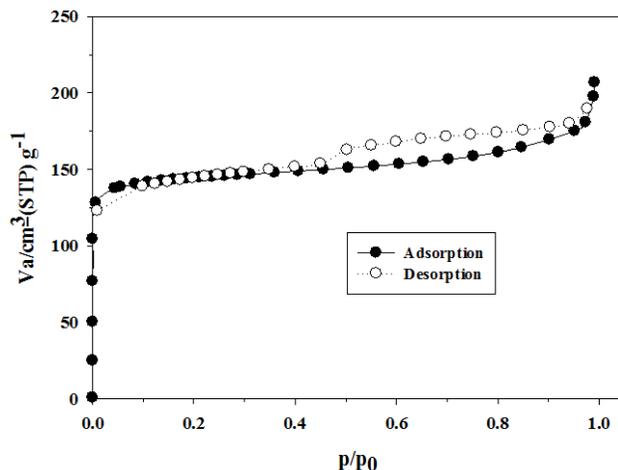


Figure 2. N₂ adsorption-desorption isotherms of ZSM-5

The thermogram of the catalyst is presented in Figure 4. A slight weight loss of about 9% at the temperature around 300 °C was observed, which was due to the loss of moisture and physical adsorbed gases. No other weight loss was exhibited until 800 °C, it indicated that ZSM-5 catalyst is stable enough to apply for the hydrocarbon cracking reaction that usually carried at higher temperature (400-600 °C).

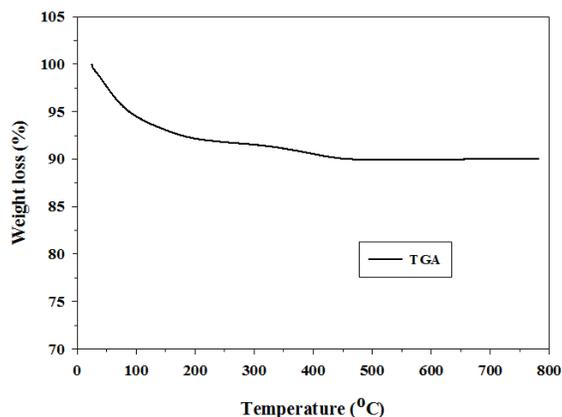


Figure 3. TGA curves of ZSM-5

3.2. Catalyst activity study

3.2.1. Effect of temperature

ZSM-5 catalyst was studied for durene cracking reaction. In order to determine the effect of temperature, reaction was carried out at 300, 350, 400, 450 and 500 °C for 1 h with 1.0 g of catalyst, and reactant feed ratio of 1: 6 (2 ml/h). The GC analysis results were shown in Figure 5. As show in Figure 5, the conversion of durene increased with increasing temperature up to 450 °C and then a decrease was observed. The same phenomenon was also happen to the selectivity of PX. From that it was found that 450 °C was the optimum temperature for durene cracking.

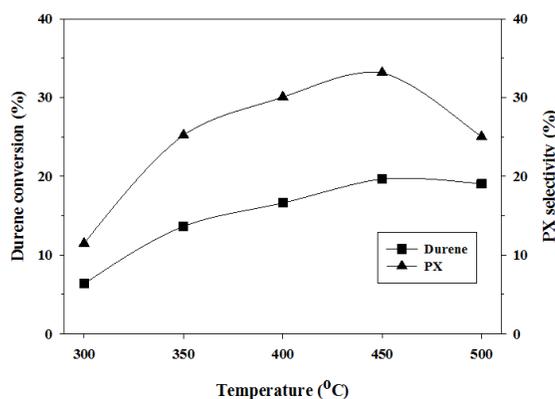


Figure 4. Durene conversion and PX selectivity over ZSM-5 at different temperatures

3.2.2. Effect of feed ratio

For study effect of feed ratio on durene conversion and PX selectivity, the reaction was carried out at 450 °C for 1 h with 1.0 g catalyst, the feed flow rate was fixed to 2.0 ml/h. Different feed ratios (durene: benzene, 1: 5, 1: 6, 1: 7, 1: 8, 1: 9, 1: 10) were studied. The results were presented in Fig. 6. Both the durene conversion and PX selectivity first shown an increase and then decreased with decreasing in the feed ratio (durene: benzene) from 1: 5 to 1: 10. The maximum conversion was found with the feed ratio of 1: 8. As in the cracking reaction of durene, benzene is not only a reactant but also a solvent carrier for durene (solid compound), so the feed ratio of durene and benzene should keep suitable to get higher durene conversion and PX selectivity.

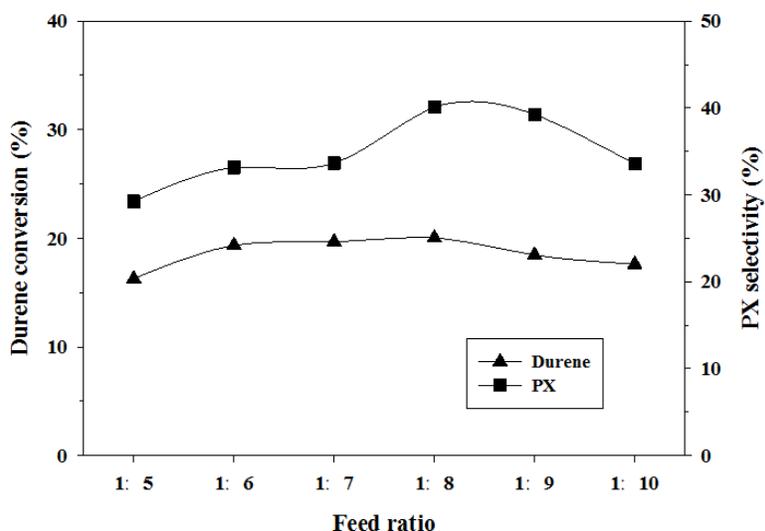


Figure 5. Feed ratio effect on durene conversion and PX selectivity over ZSM-5

3.2.3. Effect of feed flow rate

The effect of feed flow rate on durene conversion and p-xylene selectivity was studied at 450 °C for 1 h with different feed flow rate (1 ml/h, 1.5 ml/h, 2 ml/h, 2.5 ml/h, 3 ml/h), the feed ratio was fixed to 1: 8. The results were shown in Figure 7. Both the conversion of durene and PX selectivity increased with increasing feed flow rate till 2.0 ml/h, then decreased. The decrease at higher feed flow rate was due to incomplete reaction. The reactant was first adsorbed by the catalyst and reacted in the pores of the catalyst, after reaction, the product diffused from the catalyst pores. Higher feed flow gives too much reactant at same time, there was not enough catalyst site to contact with them, so that some of the durene molecular flow out without reaction.

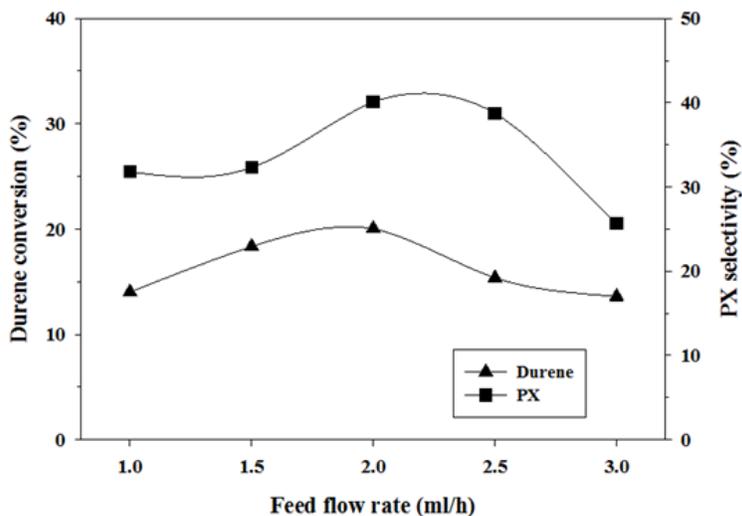


Figure 6. Feed flow rate effect on durene conversion and PX selectivity over ZSM-5

3.2.4. Effect of time

The time effect on durene conversion and PX selectivity was also studied, the reaction was carried out at 450 °C for 1 h with 1.0 g catalyst and feed ratio 1: 8, feed flow rate 2.0 ml/h. The results analyzed by GC was presented in Figure 8 which shows that increase in reaction time lead to a decrease in durene conversion and PX selectivity, the reason is during long time reaction the catalyst might be occupy by the unreacted reactant and product, therefore the catalyst activity decreased in the subsequent reactions, so after each reaction run, it was necessary to activate the catalyst.

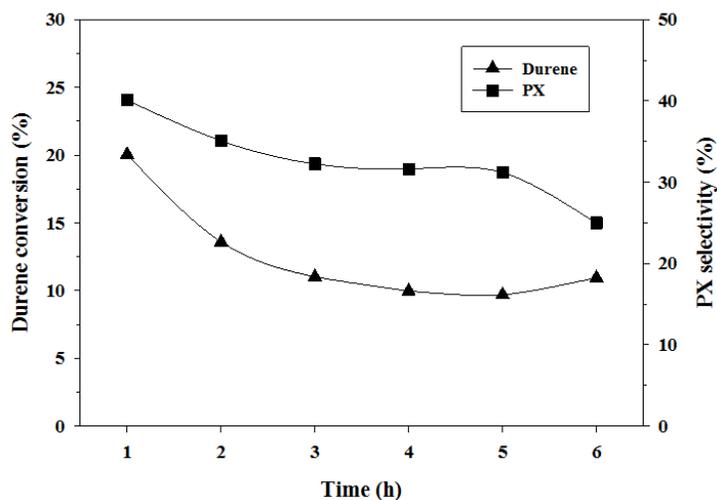


Figure 7. Time effect on durene conversion and PX selectivity over ZSM-5

3.2.5. Effect of catalyst weight

In order to study the catalyst weight effect on durene conversion and p-xylene selectivity, the reaction was carried out at 450 °C for 1 h with a feed ratio 1: 8 and the feed flow rate 2.0 ml/h, the catalyst weight was from 0.5 to 2.0 g. The results were displayed in Figure 9. The conversion of durene increased with increasing catalyst weight, when 2.0 g catalyst was used, maximum (37.16%) value of durene conversion was exhibited. As shown in Figure 9, the selectivity of PX increased with increasing catalyst weight and then decreased, at the point of 1.0 g catalyst, the highest selectivity value of 40.09 % was obtained.

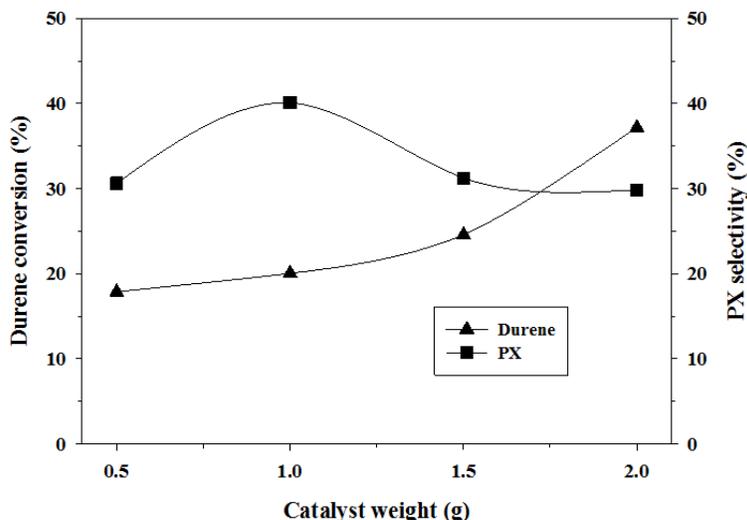


Figure 8. Catalyst weight effect on durene conversion and PX selectivity over ZSM-5

4. Conclusions

Heterogeneous catalyst ZSM-5 zeolite was used to durene cracking reaction in a fix bed reactor at N₂ gas atmosphere. Benzene was used as the solvent. In order to optimize reaction conditions, in the reaction process, temperature, feed ratio, feed flow rate, time and catalyst weight effect were studied. The reaction products were analyzed by GC and the results shown that following are the optimum conditions for conversion of durene, 0.1 g catalyst at 450 °C for 1 h using feed ratio of 1: 8 and with feed flow rate of 2.0 ml/h is required for 40.09% PX selectivity.

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