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Xylene Isomerization Over Zeolite Catalysts

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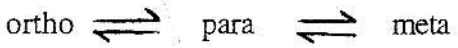
Abstract

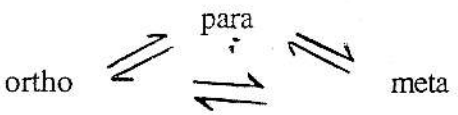
Paraxylene is used as a raw material for the production of the synthetic fibers, The production of paraxylene can be obtained by isomerization of xylene using zeolites as catalyst. At equilibrium, the mixture of xylene contains 24% para, 24% ortho and 52% of metaxylene. The objective of this experiment is to assess the effectiveness of several zeolite catalysts for the isomerization of xylene. The study was carried out using micro reactor packed with zeolite(0.5 g). In this work, the activity and selectivity of the catalyst in the isomerization of xylene depend on the type of zeolite used. HZSM-5 catalyst gives higher activity and selectivity over other type of zeolite.

Introduction

P-xylene is an aromatic molecule of high industrial value utilized as a raw material for the production of the synthetic fibers. The equilibrium amount of xylene mixture produced in the catalytic reformers is about 24% para, 24% ortho and 52% of metaxylene(1). Due to the great demand of para-xylene, a new catalyst for the isomerization of xylene has been developed to maximize the production of para-xylene. The catalyst must be able to produce high concentration of p-xylene and low levels of disproportional products. The kinetic of isomerization of xylene over zeolite was very complicated(2) and remain a controversy as to whether the reaction takes place consecutively



or through the mutual inter conversion of the three isomers



Chemical reaction catalyzed by zeolites mostly occur within the catalyst's internal pore structure. Different pore and channel size are available by selection of different zeolite species(5). Zeolites which have the shape-selective properties have been exploited in many processes such as methanol to gasoline conversion, ethyl benzene production, lube production, dewaxing, M-forming and xylene isomerization(3). Shape selectivity operates in the xylene isomerization by either reactant shape selectivity, product shape selectivity or transition state selectivity. Of the three isomers, para xylene has the smallest molecular diameter compared to meta and ortho xylene(4), thus it diffuses 1000 times faster than the other isomers(2).

The purpose of this work is to assess the effectiveness of several zeolite catalysts for the isomerization of xylene and to study the effect of shape selectivity and acidity on the distribution of product.

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Experimental

Material: High purity of o-xylene(99+%) was used without further purification.

Apparatus and Procedure:

The o-xylene isomerization were carried out using quartz tubular reactor house in a variable temperature oven. The zeolite used in this experiment were H-ZSM-5, H-Y, H-Mordenite and H-rho. The experiment were carried out at atmosphere pressure and used 0.5g of catalyst. The reactant was fed to the catalyst bed via vaporization using controlled supply of nitrogen which bubbles through a reservoir of o-xylene. The o-xylene passed over the catalyst bed which was maintained at two different temperature, i.e. 220°C and 400°C. The reactor effluent gases were then analyzed by the gas chromatography. Using packed column of 5% diisodecyl phthalate and 5% Bentone 34 on a support of acid washed chromasorb WAW (80-100 mesh). The GC was run at the temperature of 90°C and a flame ionization detector was used.

Results and Discussion

Result for the isomerization of o-xylene on various zeolite catalysts are presented in Table 1. As shown in Table 1, it is obvious that the o-xylene isomerization gives product with para xylene level below the position of the thermodynamic equilibrium(20% para xylene versus an equilibrium value of 24%). For HZSM-5, the product distribution obtained is found to be similar to the result obtained by Young et al. (2) for almost the same condition.(whsv=19, p-xylene=10.2%, meta=25.6%, o-xylene=64.3%).

The results also showed that from all the catalysts use, HZSM-5 produces the highest percentage of p-xylene, followed by H-mordenite, whereas rho and Y type do not give any isomerisation. The reactivity and product distributions observed an zeolite catalysts are attributed to their pore size. The pore size of rho type is the smallest(Dp=3.6x3.6A), and Y type is the largest(Dp=7.4x7.4A), where mordenite and ZSM-5 lie in between those two(Dpmord=2.7-7.0A, DpZSM5=5.1-5.6A). Thus only certain molecule can pass through their pore opening. The speed of molecular diffusion inside the pore will determine the distribution of the product.

Y type zeolite does not give isomer but produces toluene instead. This is due to the high rate of disproponation of xylene. Disproponation has been shown to occur on strong, isolated Bronsted acid site(6).

Table 1 also indicate the influence of temperature on xylene isomerization. Conversion and xylene loss(forming benzene and toluene) increase with increasing temperature while selectivity is not effected. The catalysts also do not show any significant deactivation effect. As can be seen in Table 1, for modernite catalyst, variation in the SiO_2 to Al_2O_3 ratio will affect the activity and the selectivity of the reaction. Higher the SiO_2 to Al_2O_3 ratio result in lower activity and selectivity. It has been found that acid catalyzed reaction is responsible for the isomerization of xylene on zeolite where the active site is provided by the acidic protons of the zeolite(7). The acid strength of the zeolite is directly proportional to the SiO_2 to Al_2O_3 ratio, and the number of the active site is inversely proportional to the ratio of the SiO_2 to $Al_2O_{3(1)}$. It has been observed that the catalyst with higher aluminium content has a greater para selectivity. This is because higher aluminium content will give more acidity and thus more reaction occurred.

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Table 1: Isomerization of o-xylene on zeolites catalysts with WHSV=0.4 g of xylene/g of cat. h

zeolite	product distribution(wt %)					activity(g xylene/ g of cat. hr)	selectivity (%)
	p-xylene	m-xylene	o-xylene	toluene	benzene		
T=220C *b							
HZSM5	17		46	0	0	0.22	31
H-Y	0	37	100	0	0	0	0
H-MOR		0					
SiO_2/Al_2O_3	0		62	8	0	0.15	0
=12	11	30	38	20	0	0.25	17
SiO_2/Al_2O_3	0	31	100	0	0	0	0
=20		0					
H-Rho	20		24	8	0	0.29	26
	0	48	64	36	0	0.14	0
T=400C		0					
HZSM5	18		15	28	4	0.34	21
H-Y	11	35	41	18	0	0.24	18
H-MOR	0	30	100	0	0	0	0
SiO_2/Al_2O_3		0					
=12							
SiO_2/Al_2O_3	20		28	0	0	0.29	28
=20	0	52	100	0	0	0	0
H-Rho		0					
	21		20	26	0	0.32	26
T=220C *a	11	33	40	18	0	0.24	18
HZSM5	0	31	100	0	0	0	0
H-Y		0					
H-MOR							
SiO_2/Al_2O_3							
=12							
SiO_2/Al_2O_3							
=20							
H-Rho							

*b = temperature before being increase to 400c
*a = temperature after being increase to 400c

Conclusions

The activity and selectivity of the catalyst in the isomerization of xylene depend on the type of zeolite used. In this study, HZSM5-5 catalyst give higher activity and selectivity over other type of zeolite. It is also found that the SiO_2 to Al_2O_3 ratio influences the product distribution of the isomerization.

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