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# Selectivity for Xylene Isomers in the Reaction of Alkylation of Toluene with Methanol on Zeolite Catalysts[1]

## INTRODUCTION

Alkylation of toluene to xylenes with methanol has been studied in detail over a number of zeolite catalysts (*1–6*). While the acidic protons of the zeolites have been recognized as the active sites for alkylation reactions (*7*), divergent views have been reported on the factors controlling selectivity to xylene isomers (*8*). Yashima *et al.* (*2*) believe that Bronsted acid sites are responsible for *para*-xylene formation particularly in faujasites, although no mechanism was suggested for such a hypothesis. We have shown (*9*) on the basis of pulse microreactor studies on ion exchanged L zeolites that Bronsted acidity by itself is not responsible for *para* selectivity. Kaeding *et al.* (*4*) have found that even on shape selective ZSM-5 catalyst, an equilibrium mixture of xylenes is formed unless the zeolite is specially treated with phosphorous or boron. This shows that narrow pore structure alone does not give rise to *para* selectivity. We have observed, as will be described in this paper, that the selectivity to *ortho* or *para* isomer depends drastically on whether one employs continuous flow or pulse technique for studying the catalyst. This phenomenon can be caused by adsorption of reactant molecules on the cations and acid sites in the zeolite cavities giving rise to steric modification of reaction rates which is one of the mechanisms suggested by Weisz (*10*).

## METHOD

Decationated forms of zeolite L (HL with H = 43%, K = 57%, Si/Al = 3), zeolite Y (HY with H = 49%, Na = 51%, Si/Al = 2.5), and the hydrogen form of a high silica ZSM-5 type zeolite (HZSM-5; Si/Al = 32) were used. HL and HY were strongly acid catalysts while HZSM-5 was of moderate acidity. The acid characteristics of the three catalysts as measured by pyridine adsorption–desorption technique (*6*) were as follows: Strong acid sites, 0.52, 0.25, 0.1 meq/g; total acidity (medium + strong), 0.95, 0.85, and 0.8 meq/g, respectively.

Two kinds of experimental set up were used for the alkylation studies of toluene with methanol: (i) a pulse microreactor and (ii) a continuous flow reactor. In the pulse system a small U-shaped S. S. reactor was connected in series to a gas chromatograph fitted with a thermal conductivity detector and a 4 m × 3 mm column containing 5% diisodecyl phthalate + 5% Bentone-34 on Chromosorb AW. Hydrogen (40 ml/min) flowing through the reactor also served as the carrier gas. Approximately 20 mg of catalyst was taken in the reactor. After activation at 450°C the reactor was maintained at desired temperature and a pulse of 2 $\mu$l of toluene + methanol mixture (2:1 molar) was injected into the reactor. The products formed were carried into the GC where they were analyzed.

The continuous flow reactor was a conventional fixed bed system in which 4 g of catalyst was taken. $H_2$ (80 ml/min) was used as the carrier gas. The alkylation mixture was fed by means of a metering pump at a rate of 2 ml/hr. The products were condensed and the samples were analyzed periodically.

## RESULTS AND DISCUSSIONS

Table 1 shows the activity and isomer distribution of xylene for the three catalysts obtained in pulse reactor experiments at 300 and 400°C. The catalyst activity is defined as the moles of xylene formed per 100 mol of methanol fed. This table shows that the alkylation activity is in the order

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TABLE 1

Toluene Alkylation in a Pulse Reactor

| Catalyst | Activity for toluene alkylation | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 300°C | | | | 400°C | | | |
| | Total xylene yield (%) | Isomer distribution (%) | | | Total xylene yield (%) | Isomer distribution (%) | | |
| | | *para* | *meta* | *ortho* | | *para* | *meta* | *ortho* |
| HL | 22.0 | 5.2 | 8.0 | 8.8 | 38.0 | 9.5 | 18.2 | 10.5 |
| HY | 13.0 | 3.2 | 3.6 | 6.2 | 18.0 | 3.6 | 7.8 | 6.6 |
| HZSM-5 | 20.0 | 9.3 | 6.5 | 4.2 | 32.0 | 13.0 | 13.9 | 5.1 |

HL > HZSM-5 > HY. HL and HY produce *ortho*-xylene with greater selectivity than the *para* or *meta* isomer. Similar *ortho* selectivity have been observed by us earlier on various cationic forms of L zeolites, having a wide range of catalyst acidity (*9*). At higher temperatures *meta*-xylene is formed to a greater extent in the case of HL and HY presumably due to isomerization of the xylenes formed. In contrast, the HZSM-5 catalyst produces more *para*-xylene at both temperatures, clearly showing a shape selective behavior.

Table 2 shows results obtained from continuous flow experiments at 210 and 260°C in the case of HL and HY and at 275 and 350°C in the case of the HZSM-5 catalyst. These results show a trend opposite to that of pulse studies. HL shows greater selectivity to *para*-xylene at both temperatures. But, HY shows marginally higher *ortho* selectivity at 210°C while at 260°C the catalyst is more selective to the *para* isomer. HZSM-5 catalyst is more selective to *ortho*-xylene at 275°C and to *meta*-xylene at 350°C. These are similar to the results of Yashima *et al.* (*1*, *2*) on Y zeolites, who observed that strongly acid catalysts were more selective to *para*-xylene.

The inversion of selectivity on switching over from pulse conditions to flow conditions shows that the Bronsted acidity by itself is not responsible for the selectivity in the case of alkylation. To explain the phenomena one might examine the state of catalyst surface under the two sets of conditions. In pulse experiments the reactants always see a fresh surface devoid of adsorbed molecules. Hence, with large port zeolites like X, Y, or L an *ortho*-rich product distribution is obtained as required by the principles of aromatic electrophilic substitution (*11*). However, if the pores are narrower as in the case of HZSM-5, *para*-xylene is formed selectively because it would diffuse faster being the smallest of xylene isomers. Under the continuous flow conditions it can be shown that the catalyst surface is exposed to a significantly large partial pressure of reactants (approx. 0.2 atm in the present case) and hence mole-

TABLE 2

Toluene Alkylation in a Continuous Flow Reactor[a]

| Catalyst | Activity for toluene alkylation | | | | |
|---|---|---|---|---|---|
| | Temperature (°C) | Total xylene yield (%) | Isomer distribution (%) | | |
| | | | *para* | *meta* | *ortho* |
| HL | 210 | 16.2 | 6.5 | 6.1 | 3.5 |
| | 260 | 21.6 | 9.4 | 7.3 | 4.9 |
| HY | 210 | 13.6 | 4.9 | 2.7 | 6.0 |
| | 260 | 22.6 | 9.5 | 6.5 | 6.3 |
| HZSM-5 | 275 | 16.0 | 4.8 | 4.8 | 6.4 |
| | 350 | 25.0 | 6.8 | 12.6 | 5.6 |

[a] L.H.S.V. = 0.4; $H_2$ carrier flow, 80 ml/min.

cules entering the zeolite cavity would approach a surface already having an adsorbed layer of molecules. The adsorption sites in zeolites have been recognized in several studies (*12–14*) to be the metal cations and hydroxyl groups which may be acidic or neutral. One may visualize the following distribution of molecules in the adsorbed layer. (i) On strongly acid catalysts, i.e., at a high degree of decationation, the adsorption centers in the super cages are the acid sites. Adsorbed methanol and aromatic molecules would be located predominantly around these sites. The extent of interaction would depend on the acid strength of the site and the basicity of the individual molecule (*13*). (ii) On weakly acid catalyst, i.e., at a low degree of decationation, the bulky aromatic molecules by virtue of a higher interaction with metal ions would be located further away from the acid sites on which the more basic methanol molecule would be adsorbed. The first step in the alkylation reaction is presumed to be the adsorption of the alcohol molecule on the acid site forming the corresponding carbonium ion with which the toluene molecule through the Rideal mechanism (*7*) ultimately forms xylene isomers. On a strongly acid catalyst with high acid site density one may expect the carbonium ion to be greatly hindered. During the reaction, the *para* position of toluene being hindered least would easily interact with the carbonium ion. When the catalyst has fewer strong acid sites, the carbonium ion would be hindered less, and more *ortho*-xylene would be produced during the reaction.

The factor controlling selectivity according to the above hypothesis is the relative adsorption affinities between the acid sites and other adsorption centers such as cations for reactant molecules inside the cavities. Any variation in temperature would change the relative affinities; for example, by increasing the temperature the physical adsorption on cations would be weakened. Consequently raising the temperature can increase *para* selectivity as observed on the HY catalyst (Table 2). This effect has also been observed by other workers (*1–3*).

The selectivity pattern in the case of ZSM-5 type catalysts is exactly opposite to that of the large pore zeolites. The higher *para* selectivity observed in pulse studies is clearly due to shape selective inhibition in product formation. When the contact time is high as in flow experiments the *para* selectivity decreases. It is possible that due to low acid site density (*15, 16*), the adsorbed molecules are located far apart leading to low *para* selectivity. On treatment with phosphorous or similar compounds probably the number of adsorption sites on the internal surface increases yielding better selectivity to *para*-xylene. The observation of Kaeding *et al.* (*4*) that in P-treated HZSM the *para* selectivity drastically decreased when the methanol/toluene mole ratio was lowered from 1/1 to 1/8, suggests that in ZSM-5 catalysts the adsorption of methanol controls the selectivity.

Thus the "inversion" in the selectivity pattern noticed during the alkylation of toluene to xylene isomers over L, Y, and ZSM-5 type zeolite catalysts when the experimental conditions were changed from pulse to flow technique strongly suggests that the selectivity to xylene isomers is controlled by adsorption of reactant and product molecules in the zeolite cavities. Weisz (*10*) has stated that it was not clear under what situations diffusion inhibition and steric inhibitions were operating to control product selectivity. It appears from the present work that in large port zeolites probably the steric inhibition is operative whereas in ZSM-5 type zeolites both mechanisms contribute to the selectivity pattern. To verify this hypothesis it would be necessary to study adsorption on the catalyst surface under reaction conditions. Such studies are presently being attempted in our laboratory.

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