

Isomerization and Formation of Xylenes over ZSM-22 and ZSM-23 Zeolites

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The shape selective catalytic properties of H-ZSM-22 and H-ZSM-23 in the isomerization of *meta*-xylene and methylation of toluene are compared with those of H-ZSM-5. Their activities in both these reactions decrease in the order ZSM-5 > ZSM-23 > ZSM-22. Their *para* selectivities, however, follow the reverse order. Even though all three zeolites contain pores constituted by 10 membered rings, differences in the shape of the pores as well as the presence of pore intersections (in ZSM-5) lead to significant differences in their shape selective catalytic properties. While loss of xylenes in the xylene isomerization process occurs due to transalkylation reactions over ZSM-5 zeolites, dealkylation is the main cause over ZSM-22. ZSM-23 occupies an intermediate position. ZSM-22 and ZSM-23 are shown to have superior shape selectivity vis-à-vis ZSM-5 even at high equivalent conversion levels. © 1989 Academic Press, Inc.

INTRODUCTION

Shape selective catalysis of reactions of aromatic hydrocarbons over zeolites forms the basis of many important industrial processes like xylene isomerization (1, 2), production of ethylbenzene (1, 2), and toluene disproportionation (2). The ZSM-5 zeolites are used in all these processes and their discovery and development were major achievements in catalysis during the last two decades. In the meantime, novel zeolites with different pore structures continue to be discovered. It is desirable to evaluate and document the shape selective catalytic properties of these novel zeolites in various applications of industrial interest. ZSM-22 and ZSM-23 are two such zeolites synthesized by Mobil workers (3, 4). The structure of ZSM-22 consists solely of 5-, 6-, and 10-rings of 24 T-atoms per unit cell (5). There are no 4-rings. The one-dimensional, nonintersecting channel system running parallel to the C-axis has maximum and minimum free diameters of 0.55 and 0.45 nm with 10-membered ring openings. The crystal structure of ZSM-23 closely resembles ZSM-22 (6) in being composed of 5-,

6-, and 10-rings of 24 T-atoms per unit cell and absence of 4-rings. ZSM-23, a recurrently twinned variant of ZSM-22 (6a), possesses a linear noninterpenetrating channel pore system parallel to the A-axis. The 10-membered ring openings have dimensions of 0.56×0.45 nm. However, there is a significant difference in the shape of the pores in ZSM-22 and ZSM-23. While the pores in ZSM-22 are elliptical in shape, those in ZSM-23 are tear drop shaped, leading to expectations of differences in shape selectivity in catalytic reactions. By comparison, the linear and sinusoidal channels of ZSM-5 are 0.56×0.54 and 0.55×0.53 nm, respectively. The slightly smaller width of the pores in ZSM-22 and ZSM-23 vis-à-vis those in ZSM-5, makes these zeolites interesting from the catalytic point of view with potential for improved shape selectivity in applications which are currently performed with ZSM-5 zeolites.

Kresge *et al.* (7) claimed that in a process for isomerizing xylenes in admixture with ethylbenzene, the presence of H-ZSM-23 suppressed the transalkylation reactions involving xylenes and ethylbenzene. When toluene was methylated over H-ZSM-22,

the xylene fraction was reported to be enriched in the *para* isomer (8). The same patent (8) also claimed the *para*-selective behavior of H-ZSM-22 in the disproportionation of toluene, ethylation of toluene, and cracking a mixture of *meta/para*-xylene isomers. The superior shape selectivity of H-ZSM-23 in the dewaxing of petroleum distillate fractions was reported by Bendoraitis *et al.* (9). The advantages of ZSM-22 as a catalyst for dewaxing of petroleum stocks have also been claimed in a patent by Dwyer (10). Recently, Ernst *et al.* (11) have concluded that ZSM-22 and ZSM-23 are more shape selective than ZSM-5. On the basis of long chain *n*-alkane conversion on 1% Pt/H-ZSM-22 and 1% Pt/H-ZSM-23, it was shown that the former has slightly smaller effective pore width.

Apart from the above reports, there exists very little information, especially in the open literature, on the reactions of aromatic hydrocarbons over these two novel zeolites of potential industrial importance. While the shape selective properties of ZSM-5 zeolites in xylene isomerization and methylation of toluene have been published by Kaeding *et al.* (12, 13), no such detailed reports on ZSM-22 and ZSM-23 are available either in the patent or in the open literature.

In the present paper, H-ZSM-22, H-ZSM-23, and H-ZSM-5 of similar chemical composition, acidity, and crystallite size are compared for their catalytic activity and shape selectivity in the isomerization of *meta*-xylene and methylation of toluene to xylenes. The influence of process parameters like temperature and space velocity on the catalytic performance has been evaluated. It is established that while these two zeolites are less active under comparable process conditions than ZSM-5 type zeolites in reactions of aromatic hydrocarbons, they exhibit an enhanced shape selectivity in yielding the desired products at equivalent conversion levels.

EXPERIMENTAL

Materials

The zeolites were synthesized hydrothermally in stainless-steel autoclaves. ZSM-22 was synthesized using 1-ethylpyridinium bromide (14). A solution of 1.35 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ and 8.0 g of 1-ethylpyridinium bromide in 100 g of distilled water was added to a silicate solution comprising 50 g of sodium silicate (27.8% SiO_2 , 8.2% Na_2O , and 64% H_2O , wt) and 40 g of H_2O . Finally 2.5 g H_2SO_4 (98%, wt) was added slowly under vigorous stirring. The gel was then charged in an autoclave and crystallization was carried out at 433 K for 4 days without stirring. ZSM-23 was synthesized according to the procedure reported previously (4, 15). To 13.2 g of fumed silica (Cab-O-Sil, M5) were added 140 g of distilled water, 3.6 g of NaOH, and 7.1 g of pyrrolidine, under stirring. To this mixture, a solution of 1.5 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 40 g of H_2O was added. Finally, 3.5 g H_2SO_4 (98%, wt) was added very slowly under vigorous stirring. The whole mixture was stirred for a few minutes before transferring to an autoclave. The crystallization was done at 453 K for 24 hr under agitation. The ZSM-5 zeolite was synthesized according to the procedure published earlier (16). In all the three cases, after the completion of the synthesis, the contents of the autoclave were quenched in cold water. The crystalline products were filtered, washed thoroughly with deionized water and dried overnight at 383 K in air. To convert them into the catalytically active protonic form, the as-synthesized forms of the zeolites were first calcined in flowing air at 813 K to remove the organic material from the zeolite pores. The calcined form was next converted to the ammonium form by ion-exchange with NH_4Cl solution (5 N), till the Na content in the zeolite was less than 100 ppm. The catalytically active protonic form was obtained by calcination of the ammonium form at 813 K for 16 hr in flowing air.

For determination of catalytic activity, finely powdered material (10–20 mesh) was used (1 g, dry basis). *Meta*-xylene, toluene, and methanol used were of high purity (Analar).

Procedures

The chemical composition of the zeolites was analyzed by a combination of wet chemical, atomic absorption (Hitachi, Z-8000), and ICP (Jobin Yuon-JY-38 VHR) methods. The zeolites were further characterized by X-ray diffraction, scanning electron microscopy, solid state MAS NMR spectra (Bruker MSL-300), surface area, and adsorption techniques. The procedures adopted and the apparatus used have been described earlier (16). The procedure adopted for determination of catalytic activity was identical to that published earlier in the investigation of xylene isomerization over ZSM-5 zeolites (17). Material balances were routinely calculated for all runs reported here and were found to be $100 \pm 3\%$.

RESULTS AND DISCUSSION

Physicochemical Characterization of the Zeolites

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in Na-ZSM-5, -22, and -23 were experimentally found to be 90, 114, and 110, respectively. The unit cell composition on anhydrous basis is ZSM-5, $\text{Na}_{2.18}(\text{AlO}_2)_{2.18}(\text{SiO}_2)_{93.82}$; ZSM-22, $\text{Na}_{0.42}(\text{AlO}_2)_{0.42}(\text{SiO}_2)_{23.58}$; and ZSM-23, $\text{Na}_{0.44}(\text{AlO}_2)_{0.44}(\text{SiO}_2)_{23.56}$. The X-ray diffraction patterns of ZSM-22, -23, and -5 (Fig. 1) were found to match very closely those published earlier (3–6, 16). Along with the scanning electron micrographs (Fig. 2), they established the crystalline nature and phase purity of the three zeolites. The crystals of ZSM-5 (Fig. 2a) are about $0.3 \mu\text{m}$ in dimension and consist of cuboids. ZSM-22 (Fig. 2b) consists of fine, needle-like crystals of diameter $0.3 \mu\text{m}$ and length $2 \mu\text{m}$. ZSM-23 (Fig. 2c) also has similar shape and dimensions. These photographs also estab-

lish the absence of amorphous material in the zeolite samples. The Si/Al ratio from MAS NMR matched well with those from chemical analysis indicating that all the Al atoms are in tetrahedral lattice positions. Our previous results on ZSM-5 zeolites (18) and electron probe microanalyses of the present samples suggest that in such small crystallites (less than $0.5 \mu\text{m}$), differences in concentration gradients of various zeolites of similar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios are rather negligible. It is necessary to ensure these basic structural features before any meaningful comparison of their catalytic properties is undertaken. The BET surface area (N_2) of calcined forms of ZSM-22, ZSM-23, and ZSM-5 was found to be 260, 280, and $330 \text{ m}^2/\text{g}$, respectively. The adsorption of H_2O , *n*-hexane, and cyclohexane on ZSM-22, -23, and -5 is illustrated in Table 1. The reversible sorption of cyclohexane at 298 K and $P/\text{Po} = 0.5$ was studied since its cross section is about the same as that of *m*-xylene whose isomerization was chosen as the probe reaction. The specific cyclohexane adsorption (Table 1) was lower for ZSM-22 than for ZSM-23 indicating that the internal volume accessible to cyclohexane per unit mass of zeolite is greater for ZSM-23 than for ZSM-22. ZSM-5 adsorbed even larger quantities of cyclohexane (Table 1). The ratio of adsorption of *n*- to cyclohexane was also higher (4.8) for ZSM-22 than for ZSM-23 (3.0). Since this ratio is indicative of the shape selectivity of the zeolites, it is to be anticipated that even though ZSM-23 may

TABLE I
Adsorption Characteristics of H-ZSM-22, -23, and -5

Sorbate	Adsorption (% wt)		
	H-ZSM-22	H-ZSM-23	H-ZSM-5
H_2O	4.4	4.3	7.5
<i>n</i> -Hexane	6.2	6.4	13.0
Cyclohexane	1.3	2.1	7.9

Note. Adsorption was carried out at 298 K and $P/\text{Po} = 0.5$.

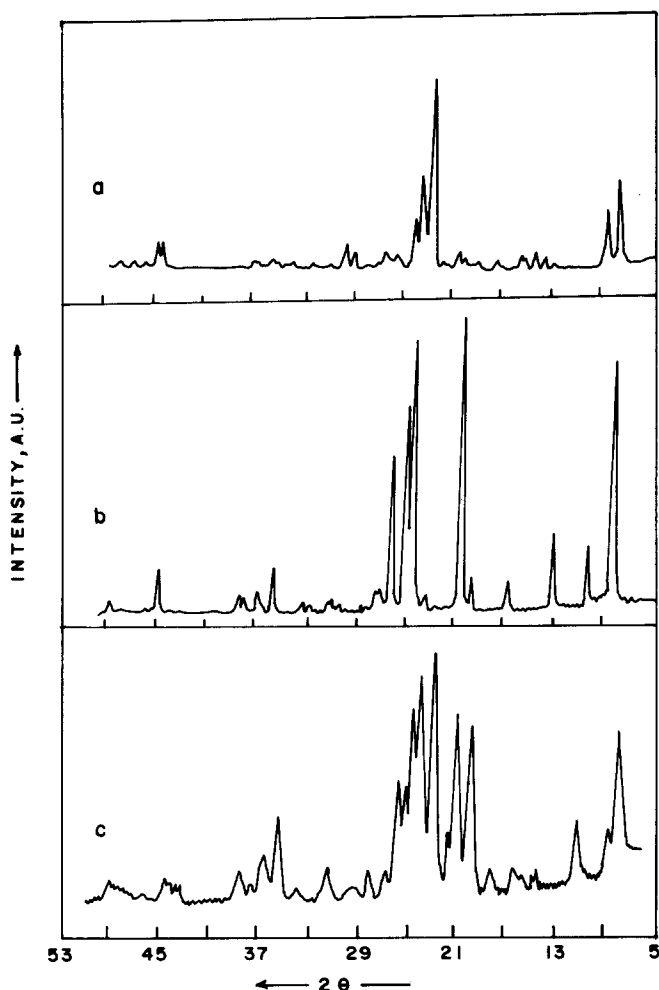


Fig. 1. X-ray powder diffractograms of (a) ZSM-5, (b) ZSM-22, and (c) ZSM-23.

be more active than ZSM-22 in reactions of xylenes (due to its greater adsorption volume), the latter is expected to be slightly more shape selective than the former. This expectation is fully borne out by the results of catalytic activity presented below.

Catalytic Properties

Isomerization of meta-xylene. Table 2 compares the three zeolites, ZSM-5, ZSM-22, and ZSM-23, in the isomerization of *m*-xylene at similar levels of conversions. The xylene loss is computed by subtracting the concentration of total xylenes in the prod-

uct from that in the feed. The loss of xylenes over many catalysts, including ZSM-5 zeolites (17, 19), occurs mainly due to transalkylation reactions between two xylene molecules yielding toluene and trimethylbenzene (TMB). In contrast to this bimolecular reaction, isomerization of *m*-xylene to the *para* and *ortho* isomers occurs by the monomolecular 1,2 methyl shift mechanism. The isomerization reaction follows a single site reaction model involving the adsorption of xylene molecule on the protonic site and subsequent intramolecular isomerization while transalkyl-

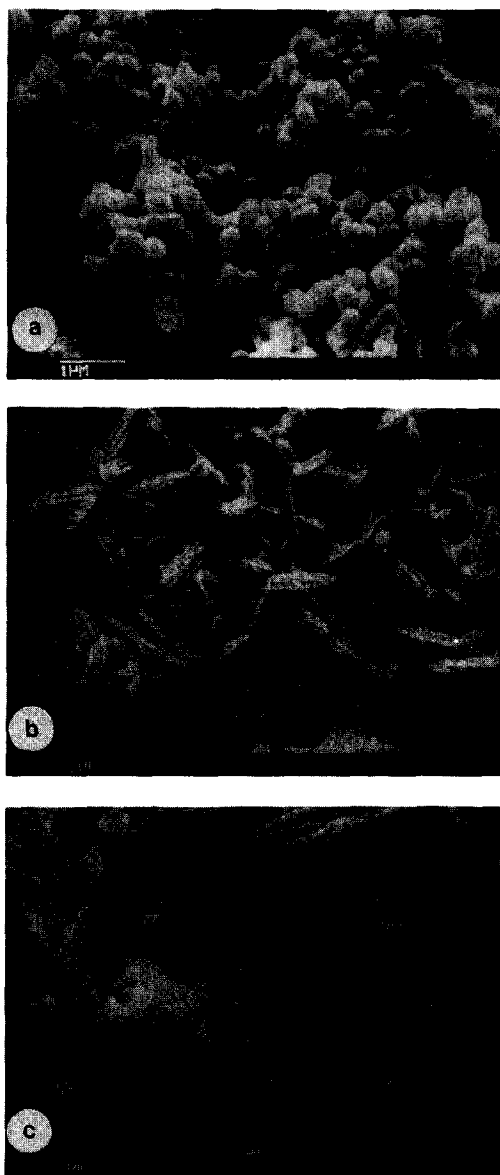


Fig. 2. Scanning electron micrographs of (a) ZSM-5, (b) ZSM-22, and (c) ZSM-23.

ation involves two molecules of xylenes adsorbed on two adjacent sites (19–23). At constant reaction conditions, the reactivity of the three zeolites decreases in the order ZSM-5 > ZSM-23 > ZSM-22. The selectivity for the isomerization of *m*-xylene (to *p*- and *o*-xylenes) vis-à-vis its conversion (to

xylenes, toluene, and TMBs) follows the order ZSM-22 \approx ZSM-23 > ZSM-5. The loss of xylenes arising as a consequence of the transalkylation reaction, hence, decreases in the order ZSM-5 > ZSM-23 \approx ZSM-22. Since the Al content, acidity, and crystal size of all the three samples are similar, the observed differences in activity and shape selectivity arise due to the differences in their pore structure and especially the shape of the pores.

The ratio of *para/ortho* isomers in the product of *m*-xylene isomerization is usually taken as a measure of the *para* selectivity of zeolite catalysts. These values are (Table 2) 1.6, 4.0, and 1.2 for ZSM-22, -23, and -5, respectively. While the higher shape selectivity of ZSM-23 compared to ZSM-5 is in accord with expectations, the low value of 1.6 for ZSM-22 is rather surprising, especially in view of the similar *para*-selective behavior of ZSM-22 and -23, in the methylation of toluene reported later in this paper. Since ZSM-22 absorbs less cyclohexane than ZSM-23 (1.3 vs 2.1%, Table 1) and requires a higher temperature (723 vs 623 K, Table 2) to achieve the same conversion level, it is likely that the diffusion of *m*-xylene into the pores is more hindered in

TABLE 2

Isomerization of *m*-Xylene: Comparison of Zeolites

Feed: <i>m</i> -xylene + H ₂ (1 : 4, mole)			
Pressure: atmospheric			
Zeolites:	H-ZSM-22	H-ZSM-23	H-ZSM-5
Temp (K):	723	623	553
WHSV (hr ⁻¹):	3.5	3.5	17.5
Conversion (% wt):	9.8	10.2	9.2
Products (% wt)			
Toluene	0.2	0.2	0.2
<i>p</i> -Xylene	5.9	7.9	5.1
<i>m</i> -Xylene	90.2	89.8	90.8
<i>o</i> -Xylene	3.7	2.0	3.7
1,2,4-TMB ^a	—	0.1	0.2
Xylene loss	0.2	0.3	0.4
Sel. isom. ^b	0.98	0.97	0.95

^a TMB, Trimethylbenzene.

^b Selectivity for isomerization = (*Para*-xylene + *ortho*-xylene)/*meta*-xylene converted.

TABLE 3
Isomerization of *m*-Xylene on H-ZSM-22:
Influence of Temperature

Feed: <i>m</i> -xylene + H ₂ (1 : 4, mole)				
WHSV (hr ⁻¹):	3.5			
Temp (K):	663	683	703	723
Conversion (%):	4.1	5.9	7.0	9.8
Products (% wt)				
Benzene	—	—	—	—
Toluene	0.1	0.1	0.1	0.2
<i>p</i> -Xylene	2.6	3.6	4.4	5.9
<i>m</i> -Xylene	95.9	94.1	93.0	90.2
<i>o</i> -Xylene	1.4	2.2	2.5	3.7
1,3,5-TMB ^a	—	—	—	—
1,2,4-TMB	—	—	—	—
1,2,3-TMB	—	—	—	—
Xylene loss	0.1	0.1	0.1	0.2
Sel. isom. ^b	0.98	0.98	0.98	0.98

^{a,b} See footnotes to Table 2.

ZSM-22. In such a case, the contribution of the external surface to the observed conversion values will be relatively more in the case of ZSM-22. This may account for the lower values of the *para/ortho* ratio observed over it.

TABLE 4
Isomerization of *m*-Xylene on H-ZSM-22:
Influence of WHSV

Feed: <i>m</i> -xylene + H ₂ (1 : 4, mole)				
Temp (K):	683			
WHSV (hr ⁻¹):	1.74	3.48	13.05	17.4
Conversion (%):	6.8	5.9	3.5	2.9
Products (% wt)				
Benzene	—	—	—	—
Toluene	0.1	0.1	0.1	0.1
<i>p</i> -Xylene	4.2	3.6	2.0	1.6
<i>m</i> -Xylene	93.2	94.1	96.5	97.1
<i>o</i> -Xylene	2.5	2.2	1.4	1.2
1,3,5-TMB ^a	—	—	—	—
1,2,4-TMB	—	—	—	—
1,2,3-TMB	—	—	—	—
Xylene loss	0.1	0.1	0.1	0.1
Sel. isom. ^b	0.98	0.98	0.97	0.97

^{a,b} See footnotes to Table 2.

The influence of temperature and space velocity on the isomerization of *m*-xylene over ZSM-22 is shown in Tables 3 and 4, respectively. While conversion and xylene loss increase with temperature, the selectivity for isomerization decreases. In contrast to the behavior of ZSM-5 zeolites (12, 13, 17–19, 23), the xylene loss in the case of ZSM-22 arises due to the dealkylation of xylene to toluene rather than its transalkylation to toluene and TMBs. This may be seen (from the absence of TMBs) in Tables 3 and 4 and is a consequence of the smaller dimension of the pores in ZSM-22. TMBs are observed in larger amounts over H-ZSM-23 (Table 5). However, the values are still lower than those observed for H-ZSM-5 (Table 2). Thus, while xylene loss in the xylene isomerization occurs mainly due to transalkylation reaction over ZSM-5 zeolites, it is due to dealkylation (to toluene) over ZSM-22, with ZSM-23 occupying an intermediate position. Figure 3 illustrates the routes followed in the approach to the equilibrium composition in the isomerization of *m*-xylene over H-ZSM-5, -22, and -23. While ZSM-5 follows a path close to the nonshape selective route, ZSM-22 and -23 follow a more shape selective route yielding more *p*-xylene (and less *o*-xylene).

TABLE 5
Isomerization of *m*-Xylene over H-ZSM-23:
Influence of Temperature

Feed: <i>m</i> -xylene + H ₂ (1 : 4, mole)					
WHSV (hr ⁻¹):	3.5				
Temp (K):	623	663	683	703	723
Conversion (%):	10.2	18.2	22.7	28.2	30.6
Products (% wt)					
Benzene	—	—	—	—	—
Toluene	0.2	0.2	0.3	0.5	0.6
<i>p</i> -Xylene	7.9	14.3	17.9	21.0	22.9
<i>m</i> -Xylene	89.8	81.8	77.3	71.8	69.4
<i>o</i> -Xylene	2.0	3.4	4.2	6.4	6.8
1,3,5-TMB ^a	—	0.1	0.1	0.1	0.1
1,2,4-TMB	0.1	0.1	0.2	0.2	0.2
1,2,3-TMB	—	—	—	—	—
Xylene loss	0.3	0.4	0.5	0.8	0.9
Sel. isom. ^b	0.97	0.97	0.97	0.97	0.97

^{a,b} See footnotes to Table 2.

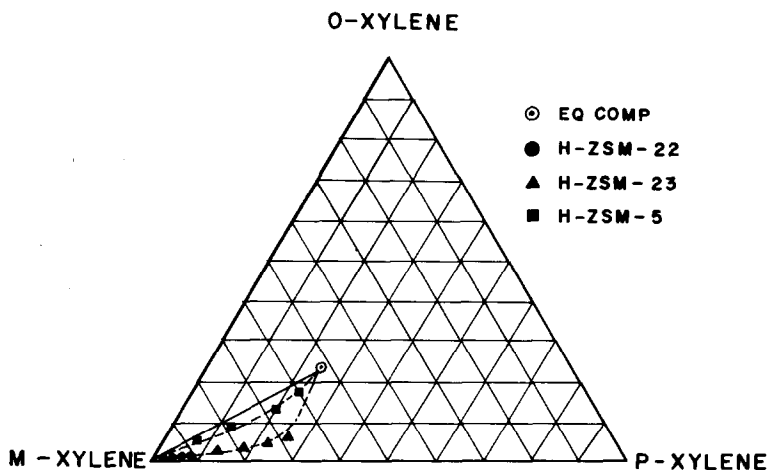


Fig. 3. Reaction paths for the isomerization of *meta*-xylene on H-ZSM-5, H-ZSM-22, and H-ZSM-23 (H_2 /oil, mole = 4 and pressure = atmospheric).

Methylation of toluene. Table 6 compares the activity and selectivity, under identical reaction conditions, of the three

TABLE 6
Alkylation of Toluene with Methanol:
Comparison of Zeolites

Zeolites:	H-ZSM-22	H-ZSM-23	H-ZSM-5 ^a
Feed: toluene + CH ₃ OH (4:1, mole)			
Temp: 683 K; WHSV: 3.5 hr ⁻¹ ; pressure: atmospheric			
Conversion (% wt):			
Toluene	12.2	15.5	31.4
Methanol	94.0	100	100
Products (% wt)			
Aliphatics	5.5	3.0	0.3
Methanol	1.5	—	—
Benzene	0.1	0.3	2.0
Toluene	84.6	81.4	65.7
Ethylbenzene	0.1	0.1	0.1
<i>p</i> -Xylene	4.3	6.2	6.8
<i>m</i> -Xylene	1.9	5.8	13.9
<i>o</i> -Xylene	1.5	1.8	5.6
<i>p</i> -Ethyltoluene	0.1	0.2	0.6
<i>m</i> -Ethyltoluene	—	0.1	1.1
<i>o</i> -Ethyltoluene	—	—	0.2
1,3,5-TMB ^b	—	—	0.3
1,2,4-TMB	0.2	0.7	2.8
1,2,3-TMB	—	—	0.1
C ₁₀ aromatics	0.2	0.4	0.5
Xylene isomers (%)			
<i>Para</i>	56	45	26
<i>Meta</i>	25	42	53
<i>Ortho</i>	19	13	21
Sel. xyl. ^c	91.7	88	77

^a Toluene/methanol = 3.5, mole.

^b See footnote to Table 2.

^c Selectivity to xylenes in product aromatics.

zeolites in the methylation of toluene with methanol. The results over H-ZSM-5 are similar to those obtained by Kaeding *et al.* (11, 12). Near-equilibrium distribution of the three xylene isomers was observed especially for small crystallites of the zeolites (11, 12). In contrast, both ZSM-22 and ZSM-23 exhibit a higher shape selectivity and yield larger amounts of the *para* isomer (56 and 45% compared to 26% for ZSM-5). The amounts of C₉ and C₁₀ aromatics formed are also lower (Table 6) over ZSM-22 and ZSM-23. The conversion of toluene, of course, decreases in the order ZSM-5 > ZSM-23 > ZSM-22. The selectivity to total xylenes in the product follows the reverse order ZSM-22 ≈ ZSM-23 > ZSM-5. The influence of contact time on product distribution over ZSM-22 and -23 is shown in Tables 7 and 8, respectively. Both toluene and methanol conversions are higher over ZSM-23 than ZSM-22, presumably due to the larger adsorption volume in the former (Table 1). Even though the pores in both the zeolites consist of 10-membered rings, the effective diameter of the pores is slightly larger in the former compared to the latter (0.56 × 0.45 vs 0.55 × 0.45 nm, respectively). Moreover, while the pores in the former are like a teardrop in shape the

TABLE 7

Methylation of Toluene over H-ZSM-22:
Influence of WHSV

Feed: toluene + CH ₃ OH (4:1, mole)				
Temp (K):	683			
WHSV (hr ⁻¹):	3.5	7.0	13.2	17.6
Conversion (% wt):				
Toluene	12.2	11.0	9.2	7.3
Methanol	94.0	91.0	88.0	87.0
Products (% wt)				
Aliphatics	5.5	4.7	3.5	3.0
Methanol	1.5	2.3	3.0	3.2
Benzene	0.1	0.1	—	—
Toluene	84.6	85.7	87.5	89.3
Ethylbenzene	0.1	0.1	0.1	—
<i>p</i> -Xylene	4.3	4.0	3.4	2.6
<i>m</i> -Xylene	1.9	1.5	1.2	0.9
<i>o</i> -Xylene	1.5	1.2	1.0	0.7
<i>p</i> -Ethyltoluene	0.1	0.1	0.1	0.1
<i>m</i> -Ethyltoluene	—	—	—	—
<i>o</i> -Ethyltoluene	—	—	—	—
1,3,5-TMB ^a	—	—	—	—
1,2,4-TMB	0.2	0.1	0.1	0.1
1,2,3-TMB	—	—	—	—
C ₁₀ aromatics	0.2	0.1	0.1	0.1
Xylene isomers (%)				
<i>Para</i>	56	60	61	62
<i>Meta</i>	25	22	21	21
<i>Ortho</i>	19	18	18	17
Sel. xyl. ^b	92	93	93.5	93.5

^a See footnote to Table 2.^b See footnote to Table 6.

TABLE 8

Methylation of Toluene over H-ZSM-23:
Influence of WHSV

Feed: toluene + CH ₃ OH (4:1, mole)			
Temp (K):	683		
WHSV (hr ⁻¹):	3.5	13.2	17.6
Conversion (% wt):			
Toluene	15.5	15.3	14.7
Methanol	100	98.8	96.8
Products (% wt)			
Aliphatics	3.0	1.5	1.0
Methanol	—	0.3	0.8
Benzene	0.3	0.2	0.1
Toluene	81.4	81.6	82.2
Ethylbenzene	0.1	0.1	0.2
<i>p</i> -Xylene	6.2	9.7	9.8
<i>m</i> -Xylene	5.8	3.7	2.9
<i>o</i> -Xylene	1.8	1.8	2.1
<i>p</i> -Ethyltoluene	0.2	0.1	—
<i>m</i> -Ethyltoluene	0.1	—	—
<i>o</i> -Ethyltoluene	—	—	—
1,3,5-TMB ^a	—	—	—
1,2,4-TMB	0.7	1.0	0.8
1,2,3-TMB	—	—	—
C ₁₀ aromatics	0.4	0.1	0.1
Xylene isomers (%)			
<i>Para</i>	45	64	66
<i>Meta</i>	42	24	20
<i>Ortho</i>	13	12	14
Sel. xyl. ^b	88	91.5	92.5

^{a,b} See Table 7.

pores in ZSM-22 are elliptical. These apparently minor differences in the shape of the pores give rise to the differences in activity and shape selectivity of these zeolites in catalytic reactions.

SUMMARY

The shape selective properties of three medium pore zeolites namely ZSM-22, -23, and -5, with comparable Si/Al ratio and crystallite size, are studied using *m*-xylene isomerization, and toluene methylation as model reactions. The activity of these zeolites in *m*-xylene isomerization decreases in the order ZSM-5 > ZSM-23 > ZSM-22, while the selectivity for isomerization (rather than disproportionation) follows the reverse order. In toluene methylation, ZSM-22 and ZSM-23 exhibit superior shape selectivity compared to ZSM-5, both in the formation of the *para* isomer (*para* selec-

tivity) and in the yield of xylenes. The xylene loss on ZSM-22 is mainly due to dealkylation while on ZSM-5 transalkylation is the main cause for xylene loss. ZSM-23 occupies an intermediate position.

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