JOURNAL OF CATALYSIS 119, 65–70 (1989)

Reactions of Aromatic Hydrocarbons over Zeolite β

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Received January 27, 1989; revised April 13, 1989

The catalytic properties of zeolite β in the isomerization of metaxylene, and the methylation and disproportionation of toluene have been measured and compared with those of other zeolites like ZSM-5, -23, -48, and -50. While zeolite β does not exhibit product shape selectivity among the xylene isomers, it suppresses the formation of the bulky 1.3.5 isomer among trimethylbenzenes leading to high concentrations of the 1.2.4 isomer with the minimum cross section. The disproportionation-to-isomerization ratio in the reactions of metaxylene over these zeolites follows the order

$$\beta > \text{ZSM-50} > \text{ZSM-5} > \text{ZSM-48} > \text{ZSM-23} > \text{ZSM-22}.$$

A comparison of β with ZSM-5 in the xylene isomerization process using industrial feedstock reveals similar trends. The observed shape-selective properties of β in these reactions of aromatic hydrocarbons are explained in terms of its 12-membered three-dimensional pore structure.

INTRODUCTION

Zeolite β was first synthesized by Wadlinger *et al.* (*1*) in 1967. Its framework structure has been elucidated only recently (*2*). The zeolite possesses a three-dimensional, 12-ring pore system. Its framework structure is an intergrown hybrid of two distinct but closely related structures. Both result from the same centrosymmetrical tertiary building unit arranged in layers and both possess three-dimensional 12-ring pore systems. There is a high density of stacking faults in the zeolite structure because successive layers must interconnect in either a left- or a right-handed fashion. Both models of linkages occur with almost equal probability (*2*). The framework and pore structure of zeolite β have several unique and interesting features. It is the only high-silica zeolite to have a fully three-dimensional 12-ring pore system; it is the only large-pore zeolite to have chiral pore intersections. Finally, unlike other zeolites, but like mordenite, it is the only zeolite to have a near-random degree of stacking faults and yet maintain full sorption capacity of about 0.2 ml g^{-1} (*2*, *3*).

There are only a few reports on the catalytic properties of β (*4–9*), especially in the journal literature. One of its potential major applications seems to be in the catalytic hydrodewaxing of petroleum oils where it is able to lower the pour point of the oil (*4*, *5*) by hydroisomerizing the normal paraffins contained therein (and which constitute the wax) to the branched isomers rather than cracking them to lighter paraffins as is done by other zeolites such as ZSM-5 or erionite. The shape-selective catalytic properties of β, especially in the cracking of paraffins and in the isomerization of metaxylene, has recently been investigated by Martens *et al.* (*6–8*) and Corma *et al.* (*9*). However, there are no other detailed reports on the reactions of various aromatic hydrocarbons over this interesting zeolite system.

In the present paper, we report the isomerization of metaxylene, the methylation of toluene, and the disproportionation of toluene over zeolite β. The shape-selective properties of this zeolite, as revealed by the product distribution in these reactions, is found to be consistent with expectations from the size and geometry of its pore system. A comparison of the results of the

0021-9517/89 $3.00

present study with data on other zeolites leads to the conclusion that while β does not exhibit shape selectivity among xylene isomers, it is able to discriminate among isomeric trimethyl benzenes and favors the formation of the 1.2.4 isomer with the minimum cross section.

EXPERIMENTAL

Materials

β zeolites were synthesized hydrothermally from the system $(TEA)_2O$–SiO_2–Al_2O_3–Na_2O–H_2O at 423 K. Three samples, $\beta(28)$, $\beta(44)$, and $\beta(60)$, with SiO_2/Al_2O_3 ratios 28, 44, and 60, respectively, were prepared by mixing appropriate quantities of silica (Sigma 400 Type S-5005), sodium hydroxide (AR grade), sodium aluminate (43.8% Al_2O_3, 39% Na_2O, and 17.2 % H_2O), 40% aqueous tetraethylammonium hydroxide (ALFA), and distilled water. The gel obtained was stirred thoroughly before transferring it to stainless-steel autoclaves. The autoclaves were then kept in an oven maintained at 423 K. After completion of the crystallization (6–9 days), the autoclave was quenched in cold water. The solid material thus obtained was filtered, washed with deionized water, and dried at 393 K. The solids were further calcined in a flow of dry air at 723 K for 20 hr to obtain the sodium form. The molar compositions (anhydrous basis) of the three solid samples were: $\beta(28)$, $28SiO_2 : Al_2O_3 : 0.2Na_2O$; $\beta(44)$m $44SiO_2 : Al_2O_3 : 0.2Na_2O$; and $\beta(60)$, $60SiO_2$; $Al_2O_3 : 0.12Na_2O$. The chemical composition of the zeolites was analyzed by a combination of wet chemical, atomic absorption (Hitachi, Z-8000), and ICP (Jobin-JY-38 VHR) methods. The protonic forms of the zeolite were prepared from the sodium form by ammonium exchange with NH_4Cl solution (5 *N*) until the Na content in the zeolite was less than 100 ppm, to obtain the ammonium form, and then further calcining the latter at 723 K for 20 hr in flowing dry air. For catalytic experiments at atmospheric pressure, 1 g of H-β zeolite (10–20 mesh) was used. The Pt–H–β zeolite used in high-pressure experiments was prepared by ion-exchange of Pt from a solution of chloroplatinic acid. The platinum content was 0.3 wt%. The Pt–H–β powder was mixed with alumina binder (Catapal SB) in a proportion of 20 : 80 by weight and extruded (1.6 mm diameter) for use in catalytic experiments. Metaxylene, toluene, and methanol of high purity (Analar) were used.

Procedures

The zeolites were characterized by XRD (Philips, PW 1710, Cu$K\alpha$), scanning electron microscopy (Cambridge), and gravimetric adsorption techniques. The catalytic activity measurements at ambient pressures were carried out in a tubular, downflow reactor and the products were analyzed on-line by gas chromatography (Shimadzu) using 5% diisodecyl pthalate and 5% bentone-34 on chromosorb W column (2 m). The reproducibility of the data was about $\pm 0.3\%$. Experiments at high pressures were carried out in a catatest unit (Model B, Geomecanique, France). The procedures adopted and the apparatus used have been described earlier (*10, 11*).

RESULTS AND DISCUSSION

Physicochemical Characterization

The crystallinity and phase purity of the three zeolite samples as well as the absence of amorphous matter within their pore structures were first ensured. The XRD pattern of $\beta(28)$, $\beta(44)$, and $\beta(60)$, shown in Fig. 1, matched with that published earlier (*12*). No extraneous peaks are present. The scanning electron micrographs showed the absence of amorphous matter *external* to the zeolite crystals. All the samples consisted of crystals of about 0.3–0.5 μm in dimension. They were cubic in shape. The adsorption (at 198 K and P/Po = 0.5) of H_2O, *n*-hexane, cyclohexane, and *m*-xylene on $\beta(28)$ was 21.3, 19.0, 10.5, and 25 wt%, respectively. The corresponding values for

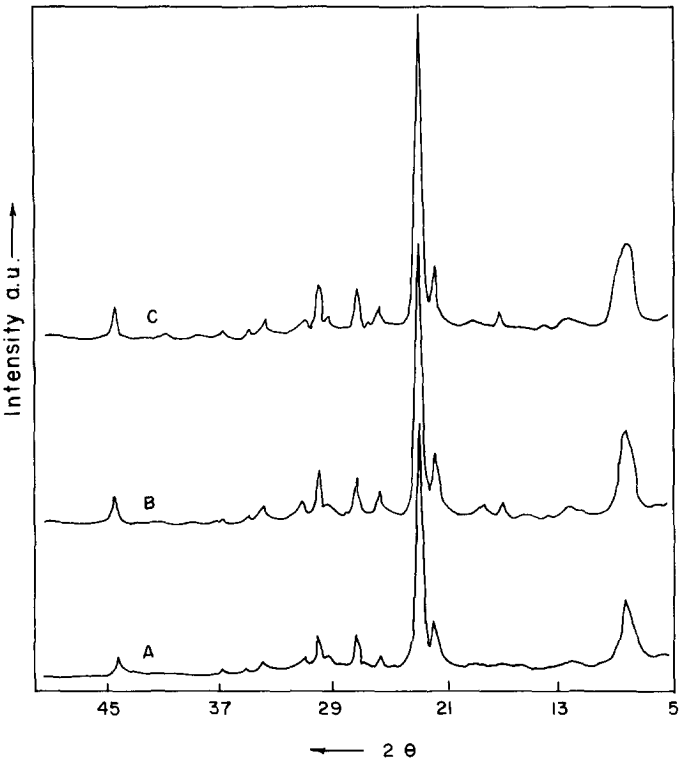

FIG. 1. XRD patterns of zeolite β (28), (44), and (60) (curves A–C, respectively).

β(44) were 19.9, 15.9, 18.3, and 20, respectively. The average pore volume (assuming liquid density for the adsorbates) was 0.26, 0.23, and 0.22 ± 0.03 ml/g, for β(28), β(44), and β(60), respectively. These values match well with the literature data of 0.2 ml/g (*2*) and establish the absence of amorphous matter in the *internal* pore volume of the zeolite samples.

Catalytic Properties

Isomerization of m-xylene. The influence of temperature and space velocity on product distribution in the isomerization of *m*-xylene over β(28) at a time-on-stream of 1 hr is shown in Tables 1 and 2. The ratio of para- to orthoxylene in the product was 1.0 ± 0.1 in all cases, close to the equilibrium value. Zeolite β, hence, does not exhibit any product shape selectivity in this reaction. This is not surprising in view of the 12-membered pore openings present in this zeolite. In addition to isomerization, xylene molecules may also undergo bimolecular disproportionation to toluene and trimethylbenzenes. The disproportionation reaction, requiring a bulkier transition state

TABLE 1

Isomerization of *m*-Xylene over H-β(28): Influence of Temperature

Temp. (K)	473	488	518	548	578
Conversion (%)	5.6	15.0	22.3	36.5	51.9
Products (wt%)					
Toluene	0.6	2.4	3.5	6.8	12.9
p-Xylene	2.3	5.8	7.7	11.1	13.2
m-Xylene	94.4	85.0	77.7	63.5	48.1
o-Xylene	2.2	4.8	7.1	10.6	12.3
1.3.5 TMB[a]	0.1	0.5	1.1	2.2	3.7
1.2.4 TMB	0.4	1.3	2.6	5.2	8.7
1.2.3 TMB	0.0	0.2	0.3	0.6	1.1
1.3.5/1.2.4 TMB	0.25	0.38	0.42	0.42	0.42
Disp./isom.[b]	0.098	0.0167	0.239	0.326	0.468

Note. Feed = *m*-xylene + H_2 (1 : 4 mole). WHSV: 3.5 hr^{-1}.

[a] TMB, trimethylbenzene.

[b] TMB/(*p*- + *o*-xylene), mole.

TABLE 2

Isomerization of *m*-Xylene over H-β(28): Influence of WHSV

WHSV (hr^{-1})	3.5	5.2	7.0	8.7	13.0
Conversion (%)	22.3	16.9	15.3	11.1	8.1
Products (wt%)					
Toluene	3.5	2.6	2.2	1.6	1.0
p-Xylene	7.7	6.2	5.5	4.2	3.0
m-Xylene	77.7	83.1	84.7	88.9	91.9
o-Xylene	7.1	5.4	4.9	3.7	2.8
1.3.5 TMB[a]	1.1	0.7	0.7	0.4	0.3
1.2.4 TMB	2.6	1.8	1.8	1.1	0.9
1.2.3 TMB	0.3	0.2	0.2	0.1	0.1
1.3.5/1.2.4 TMB	0.42	0.39	0.39	0.36	0.33
Disp./Isom.[b]	0.240	0.210	0.220	0.178	0.182

Note. Feed: *m*-xylene + H_2 (1 : 4 mole). Temperature: 518 K.

[a] TMB, trimethylbenzene.

[b] TMB/(*p*- + *o*-xylene) mole.

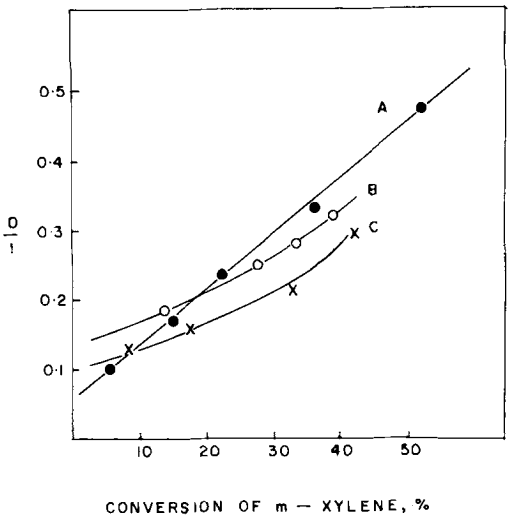

FIG. 2. The variation of disproportionation/isomerization (*D*/*I*) ratio with *m*-xylene conversion; curves A–C refer to β (28), (44), and (60), respectively.

than isomerization, would be facilitated by the availability of a large void space around the active, acidic site (*8*). In Tables 1 and 2, the ratio of disproportionation to isomerization (*D*/*I*) increases with increasing temperature and contact time. In Fig. 2, the variation of *D*/*I* with *m*-xylene conversion is illustrated for β(28), β(44), and β(60). The results include data at different temperatures and contact times. There are three features of Fig. 2 worth noting: (1) at a given conversion level of *m*-xylene, the *D*/*I* ratio decreases with increasing SiO_2/Al_2O_3 ratio of the zeolite; (2) the increase in the *D*/*I* ratio with increasing conversion for β(28) is more pronounced than that for β(44) and β(60); and (3) the *D*/*I* ratio increases with conversion for all three zeolites. These observations are really not surprising and have been observed in other zeolite systems like mordenite (*13*) and ZSM-5 (*11*). The tendency of β to disproportionate (rather than isomerize) the xylenes is compared with that of other zeolites in Table 3. In this table, while the data for β is from the present study, the others are taken from Ref. (*14*). Both β and ZSM-50 have the highest value of *D*/*I* (0.13). ZSM-5 and ZSM-48 have similar, intermediate values while ZSM-22 and -23 have negligible values of *D*/I.

These observed differences can be rationalized on the basis of differences in pore geometry of the various zeolites. Two parameters, the diameter of the channels and the presence of large cavities, in the

TABLE 3

Influence of Pore Geometry on Shape Selectivity in the Isomerization of *m*-Xylene

Zeolite	Pore diameter (nm)	Characteristics	Disp/Isom
12-Membered ring pores			
β	0.57 × 0.75 0.56 × 0.65	Linear channels Tortuous channels	0.135
10-Membered ring pores			
ZSM-50	0.58 × 0.41 0.68 × 0.58 × 0.81	Unidim. elliptical channel, side cavities	0.133
ZSM-5	0.54 × 0.56 0.55 × 0.51	Circular, straight; elliptical, sinusoidal, bidim. with large intersections	0.022
ZSM-48	0.53 × 0.56	Unidim. circular	0.021
ZSM-23	0.56 × 0.45	Unidim., tear drop	0.008
ZSM-22	0.55 × 0.45	Unidim., elliptical	0

Note. Feed: *m*-xylene + H_2 (1 : 4 mole). Conversion of *m*-xylene = 10 + 2%.

TABLE 4

The Xylene Isomerization Process: Comparison of β(44) with ZSM-5

Zeolite	Feed	β		ZSM-5	
Pressure (bar)		6	6	6	18
WHSV (hr^{-1})		6	10	10	10
EB conversion (wt%)		49	43	21	49
Xylene loss (wt%)		3.4	1.8	0.7	2.1
Composition (wt%)					
C_8^- aliphatics	8.0	10.5	11.3	11.4	17.2
Benzene	3.6	4.8	4.3	4.9	6.2
Toluene	6.0	8.2	7.0	5.1	4.6
Ethylbenzene	22.4	11.3	12.8	17.6	11.4
p-Xylene	8.8	13.1	13.0	12.8	12.9
m-Xylene	47.4	31.5	33.7	35.0	32.3
o-Xylene	3.7	12.0	11.4	11.9	13.2
Ethyltoluene	—	1.5	1.4	—	—
1.3.5 TMB	—	1.0	0.7	—	—
1.2.4 TMB	0.1	2.7	1.9	0.1	0.4
1.2.3 TMB	—	1.2	1.1	0.8	1.1
C_{10}^+ aromatics	—	1.7	1.3	0.1	0.2

Note. Temperature: 655 K. H_2/oil (mole): 6.

form of either pore intersections (β) or side pockets (ZSM-50), influence the *D/I* ratio. Zeolite β has channels consisting of 12-membered rings. In addition, it possesses large voids at the intersections of the three-dimensional channel system. ZSM-50 contains large side pockets (0.68 × 0.58 × 0.81 nm). Hence, the disproportionation reaction is favored in these zeolites leading to the high *D/I* values of around 0.13.

In the industrial process for xylene isomerization, the feedstock contains significant quantities of ethylbenzene. The activity of the catalyst is evaluated (*11*) from its ability to eliminate ethylbenzene from the feedstock and its selectivity from its capacity to achieve this objective at a minimum loss of xylenes. The performance of β(44) is compared with a ZSM-5(SiO_2/Al_2O_3 = 50)-based catalyst in Table 4. The zeolite and platinum contents in both the samples were similar. The feedstock was obtained from a petrochemical complex. The zeolites are compared at (1) a constant ethylbenzene conversion level of 49% (columns 1 and 4) and (2) constant reaction conditions (columns 2 and 3). At a similar activity level, the xylene loss (from disproportionation reactions) is higher over β than over ZSM-5. At similar reaction conditions, β is more active than ZSM-5. Similar results were observed in the isomerization of *m*-xylene also. The latter feature is probably due to the lower diffusional resistance encountered by the feed molecules in the larger, three-dimensional pore system of β. The results of Table 4 are quite consistent with those obtained from the *m*-xylene test reaction and illustrate the utility of such simple model reactions.

Methylation and disproportionation of toluene. The methylation of toluene over β(44) is illustrated in Table 5. As expected, no shape selectivity is observed in the xylenes' fractions. However, among the trimethylbenzene isomers, the formation of the bulkiest 1.3.5 isomer is suppressed. The 1.2.4 isomer with minimum cross section is formed predominantly. A similar trend could also be seen in the isomerization of *m*-xylene (Tables 1 and 2). The 12-membered channels of β, while unable to discriminate among xylene isomers, are able to do so for the trimethylbenzenes.

TABLE 5

Methylation of Toluene over H-β(44): Influence of Temperature

Temp. (K)	548	598	648
Toluene conversion (%)	17.4	26.0	27.2
Methanol conversion (%)	100	100	100
Products (wt%)			
Aliphatics	0.5	0.3	0.3
Benzene	0.4	1.0	2.1
Toluene	79.5	71.3	70.1
p-Xylene	4.4	5.3	5.0
m-Xylene	4.4	10.7	11.3
o-Xylene	5.1	4.9	4.7
p-Ethyltoluene	0.1	0.1	0.1
m-Ethyltoluene	0.1	0.2	0.1
o-Ethyltoluene	—	—	—
1.3.5 TMB[a]	0.9	1.5	1.5
1.2.4 TMB	2.8	3.5	3.7
1.2.3 TMB	0.4	0.5	0.5
Durene	1.4	0.7	0.6
1.3.5/1.2.4 TMB	0.32	0.43	0.40

Note. Feed: toluene + methanol (4:1 mole). WHSV: 3.5 hr^{-1}. Pressure in atmospheres.

[a] TMB, trimethylbenzene.

TABLE 6

Disproportionation of Toluene over H-β(28): Influence of Temperature

Temp. (K)	608	638	668	713
Toluene Conversion (%)	5.8	8.9	13.2	18.1
Products (wt%)				
Aliphatics	0.1	0.1	0.1	0.1
Benzene	2.3	3.8	6.6	9.6
Toluene	94.2	91.1	86.8	81.9
p-Xylene	0.8	1.2	1.5	1.9
m-Xylene	1.7	2.5	3.2	4.0
o-Xylene	0.7	1.1	1.4	1.8
Ethyltoluene	0.1	0.1	0.1	0.1
1.3.5 TMB	—	—	—	0.1
1.2.4 TMB	0.1	0.1	0.1	0.4
1.2.3 TMB	—	—	0.2	0.1

Note. Feed: toluene + H_2 (1 : 4 mole). WHSV: 3.5 hr^{-1}. Pressure in atmospheres.

TABLE 7

Disproportionation of Toluene over H-β(28): Influence of WHSV

WHSV (hr^{-1})	3.5	5.2	7.0	8.7	13.0
Toluene conversion (%)	15.8	12.6	9.6	8.2	4.9
Products (wt%)					
Benzene	6.8	5.4	4.1	3.4	2.0
Toluene	84.2	87.4	90.3	91.8	95.1
p-Xylene	2.1	1.7	1.3	1.2	0.7
m-Xylene	4.5	3.5	2.8	2.4	1.5
o-Xylene	2.0	1.6	1.2	1.1	0.7
1.3.5 TMB	—	0.1	0.1	0.1	—
1.2.4 TMB	0.3	0.2	0.1	—	—
1.2.3 TMB	0.1	0.1	0.1	—	—

Note. Feed: toluene + H_2 (1 : 4 mole). Temperature: 698 K. Pressure in atmospheres.

The disproportionation of toluene over β(28) at various temperatures and space velocities is shown in Tables 6 and 7, respectively. The absence of shape selectivity in the xylenes' fractions and its presence in the trimethylbenzenes is again observed.

CONCLUSIONS

The isomerization of metaxylene and the methylation and disproportionation of toluene over the large-pore zeolite β have been studied. The results are compared to those obtained for various medium-pore zeolites. It is concluded that while zeolite β does not exhibit any product shape selectivity for the isomerization reaction due to the large pores, shape selectivity is observed in the methylation (of toluene) and disproportionation (of *m*-xylene and toluene) reactions. Zeolite β is able to discriminate among the trimethylbenzenes and suppresses the formation of the bulkier 1.2.3 and 1.3.5 isomers.

ACKNOWLEDGMENT

The work was funded in part by UNDP.

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