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Selectivity for *para*-Xylene in the Isomerization of Xylenes Catalyzed by Zeolites with Ten-Ring Windows

DUNCAN SEDDON[1]

Petrochemicals and Plastics Division, ICI (PLC), P.O. Box 90, Wilton, Cleveland, United Kingdom

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The selectivity of xylene isomerization over a ferrierite zeolite, Fu-9, is described. The formation of *para*-xylene from *meta*-xylene is strongly favored. In some instances, products were obtained in which the *para*-xylene content was greater than predicted from the position of thermodynamic equilibrium. Diffusion effects can account for much of this *para*-xylene selectivity, but selectivity is probably enhanced further by transition state selectivity favoring *para* over *ortho* formation, and by xylene loss reactions which affect *ortho*-xylene in particular.

INTRODUCTION

The isomerization of xylenes, particularly *meta*-xylene, is of great commercial importance. One major interest is the maximization of the *para*-xylene isomer. The ten-ring window zeolite ZSM-5 is widely used for this process (*1–3*), the selective properties of which give products of xylene isomerization characterized by high *para*-xylene contents and low levels of disproportionated products. Young *et al.* (*4*) have described the shape selective properties of ZSM-5 in xylene isomerization and have demonstrated that *meta*-xylene is isomerized on a more selective path than is the case with amorphous catalysts. The isomerization pathway of ZSM-5 did not result in products being formed in concentrations greater than that predicted from the position of thermodynamic equilibrium; that is, the yields of the isomers being formed appeared limited by the position of thermodynamic equilibrium of the three xylene isomers. However, there have been reports that nonequilibrium ratios of *para*-xylene from *para* lean feeds is possible (*5*).

The selective alkylation of toluene with methanol to give *para*-xylene over ZSM-5 catalysts has been described (*4, 6*). A mathematical theory for this reaction based on very high rates of diffusion of *para*-xylene versus the *meta* and *ortho* isomers has been developed by Wei (*7, 8*). This theory included the possibility of subsequent isomerization following the alkylation step. From this it can be deduced that high *para*-xylene selectivities in xylene isomerization over ZSM-5 due to the very high diffusion rate of the *para* isomer, but this point has not been unequivocally demonstrated.

The zeolite ferrierite is similar to the zeolite ZSM-5 in containing ten-ring windows. A synthetic ferrierite, Fu-9, is characterized by a high silica/alumina ratio (typically ca. 25) with an essentially fault-free structure. The ten-ring windows of Fu-9 are smaller in diameter than those of ZSM-5. The zeolite is readily transformed into hydrogen form and is active for a wide variety of Brønsted acid-catalyzed conversions. It has been found that in xylene isomerization, Fu-9 produces very high levels of *para*-xylene from the *meta* isomer. The paper describes this reaction.

EXPERIMENTAL

(*a*) *Zeolite synthesis*. The zeolite Fu-9 synthesized by the published procedure (*9*), which involved the crystallization of alkaline gels containing tetramethylammonium

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[1] Present address: BHP Co. Ltd., Melbourne, Research Laboratories, 245 Wellington Road, Mulgrave, Victoria, 3170, Australia.

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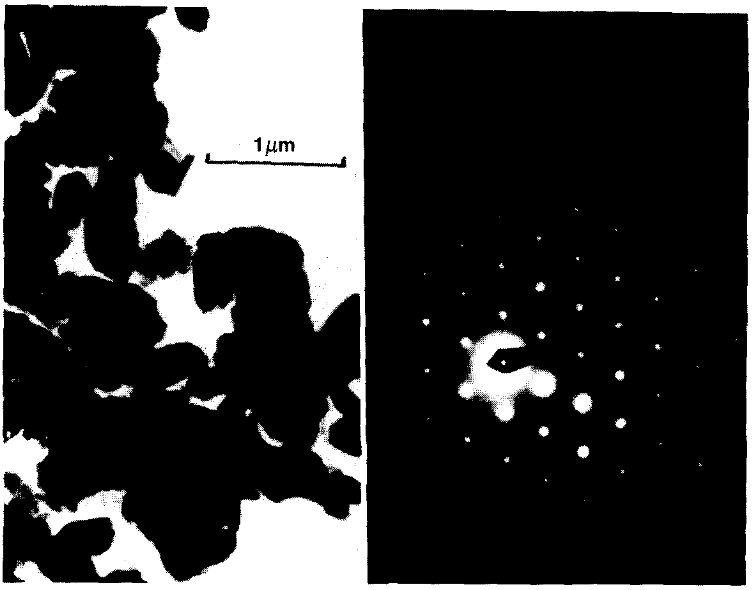

FIG. 1. TEM of Fu-9 crystals (left) and electron diffraction pattern of an individual crystal (right).

chloride and trimethylamine hydrochloride at temperatures over 220°C. Silica/alumina ratio (molar) of the product zeolite was typically ca. 25; it was not possible to prepare the zeolite with silica/alumina ratios greater than 30 or less than 20, and thus, Fu-9 appears to be an example of a zeolite existing over a restricted silica/alumina range. This is in contrast to ZSM-5 which exists over a very wide silica/alumina range (from about 35 to infinity). The as-synthesized Fu-9 zeolite was transformed into the hydrogen form by calcination (in moist air at 500°C for ca. 16 h) followed by ammonium ion exchange or acid exchange. The zeolite was found to be stable to acids, no apparent leaching of aluminum being observed. The zeolite ZSM-5 was synthesized by the published procedures (*10*).

(*b*) *Zeolite characterization.* The zeolite Fu-9 is distinguished from natural ferrierite and other synthetic analogs of ferrierite (e.g., ZSM-35) by a powder X-ray diffraction pattern which is very similar to the calculated pattern derived from the structure of ferrierite, solved by Vaughan (*11*). That Fu-9 has a near perfect ferrierite structure is illustrated in Fig. 1, which shows crystal diffraction patterns obtained by transmission electron microscopy. This is in contrast to the faulted nature of natural ferrierites (*12*).

(*c*) *Xylene Isomerization.* Catalysts (5 g) as $\frac{1}{8}$-in.-diameter binder free pellets (Fu-9) or alumina-bond zeolite (ZSM-5 alumina, 1/27, wt/wt[2]) were charged into a downflow tubular reactor fitted with reactant vaporizer, thermocouples, and product condensation system. Feed was pumped from burets via a peristaltic pump to the vaporizer. Condensed liquids were analyzed off-line by GLC.

RESULTS

The reaction pathway for *meta*-xylene isomerization over H-ZSM-5 is illustrated in Fig. 2, which shows that the position of equilibrium is approached at a *para*-xylene level in the product very near to 100% of the equilibrium level. The zeolite shows pronounced selectivity in favoring the *para* versus the *ortho* isomer. These results are in accord with Young *et al.* (*4*).

The zeolite H-Fu-9 isomerizes xylenes

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[2] Alumina, in relation to ZSM-5, is inert for xylene isomerization.

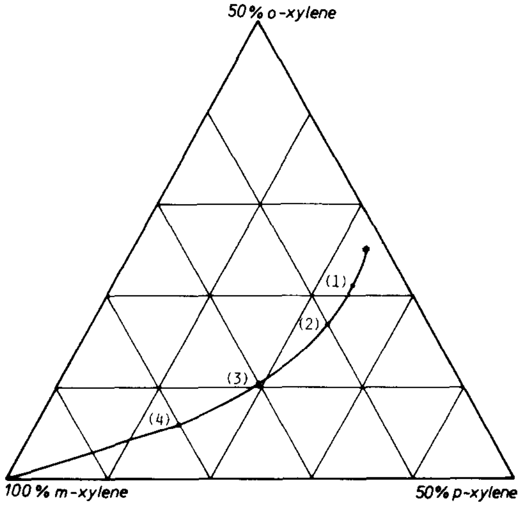

FIG. 2. Reaction pathway for *meta*-xylene isomerization over H-ZSM-5. WHSV = (1) 1.0, (2) 2.1, (3) 5.1, (4) 10.4. * = Equilibrium.

well at temperatures over about 380°C. Like most other zeolites which are active for this reaction, progressive coking with time on stream occurs. The zeolite H-ZSM-5 is unusual in this regard, showing a very low coking rate.

Results for the isomerization of pure xylene isomers over Fu-9 at 400°C are given in Table 1. For H-Fu-9 the reaction pathways for the isomerization of pure xylene isomers, illustrated in Fig. 3, is very different from that of ZSM-5 for *meta*- and *para*-xylene isomerization. For the *ortho* isomer, the reaction pathway is similar to that reported for the H-ZSM-5 zeolite (*4*). For *meta*-xylene isomerization, there is a pronounced selectivity for the *para* isomer. The *meta*-xylene reaction pathway was found to be dependent upon time on stream, which may be interpreted as dependent upon the extent of coking, as well as other reaction variables such as space velocity and temperature. This is better illustrated in Fig. 4, which shows the reaction pathways for *meta*-xylene isomerization at 450°C; pertinent details of individual points are given in Table 2. At high severities (low

TABLE 1

Isomerization of Xylene Isomers over Fu-9 at 400°C[a]

WHSV	θ^b (h)	*meta*-Xylene			WHSV	θ^b (h)	*para*-Xylene			WHSV	θ^b (h)	*ortho*-Xylene		
		meta	*para*	*ortho*			*meta*	*para*	*ortho*			*meta*	*para*	*ortho*
1.0	1	58.0	25.0	17.0	1.0	1	54.2	27.2	18.6	1.3	1	46.4	19.0	34.6
	2	60.3	25.0	14.7		2	55.2	29.8	15.0		2	43.8	17.2	39.0
	3	62.2	24.8	13.0		3	56.0	31.5	12.5		3	42.0	16.1	41.9
	4	63.5	24.3	12.2		4	56.0	33.5	10.5		4	39.5	15.5	45.0
	5	65.5	24.0	10.5		5	56.0	34.9	9.1		5	37.5	14.0	48.5
	6					6	56.0	35.8	8.2		6	35.5	12.7	51.8
2.2	1	65.9	22.0	12.1	2.1	1	46.4	47.1	6.5	2.2	1	33.1	12.9	54.0
	2	69.0	21.0	10.0		2	43.8	51.6	4.6		2	30.6	10.9	58.5
	3	71.0	20.9	8.1		3	41.0	55.2	3.8		3	27.6	9.8	62.6
	4	72.2	20.1	7.7		4	39.7	57.1	3.2		4	25.9	9.0	65.1
	5	73.4	19.6	7.0		5	38.2	59.5	2.3		5	24.6	8.0	67.4
	6	74.0	19.2	6.8		6	36.4	61.5	2.1		6	22.0	7.0	71.0
5.0	1	75.9	16.9	7.2	4.3	1	31.4	67.4	2.2	4.2	1	24.0	5.4	70.6
	2	79.6	14.8	5.6		2	28.0	70.6	1.4		2	21.7	5.0	73.3
	3	81.2	13.9	4.9		3	25.2	73.6	1.2		3	19.0	4.2	76.8
	4	82.7	13.0	4.3		4	23.4	75.5	1.1		4	16.5	3.5	80.0
	5	83.5	12.5	4.0		5	22.5	76.6	0.9		5	14.5	2.9	82.6
	6					6	22.0	77.1	0.9		6	10.0	2.0	88.0
10.1	1	82.9	11.5	5.3	9.8	1	24.8	74.0	1.2	11.3	1	17.8	4.0	78.2
	2	86.1	9.5	4.4		2	20.8	78.1	1.1		2	13.0	3.0	84.0
	3	88.0	8.3	3.7		3	19.1	79.6	1.3		3	11.0	2.5	87.5
	4	89.0	7.9	3.1		4	17.5	82.0	0.5		4	9.3	1.8	88.9
	5	90.2	7.0	2.8		5	16.6	82.9	0.5		5	7.8	1.5	90.7
	6					6	15.9	84.0	0.1		6	6.0	1.0	93.0

[a] Thermodynamic equilibrium at 400°C; *meta*, 52.4%, *para*, 23.5%, *ortho*, 24.0%.

[b] Time on line.

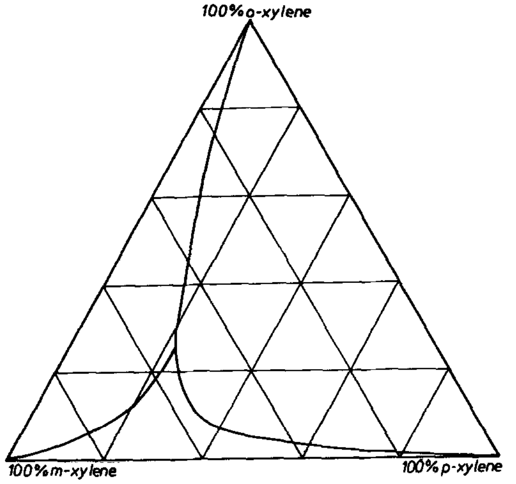

FIG. 3. Reaction pathways for the isomerization of pure xylene isomers over H-Fu-9.

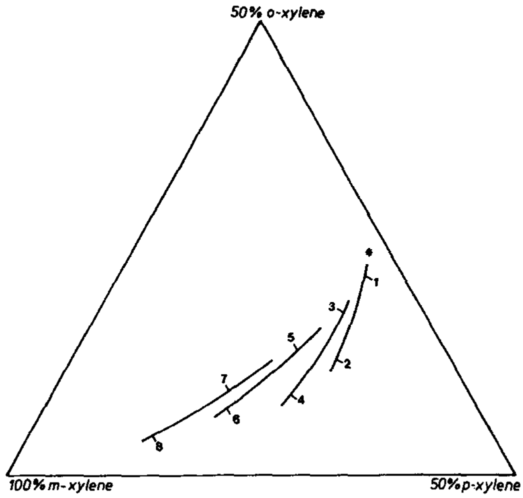

FIG. 4. Reaction pathways for *meta*-xylene isomerization over H-Fu-9. Different lines are from isomerization at different space velocities at 450°C. Further details are given in Table 2.

space velocity, high temperature) the reaction pathway for *meta*-xylene isomerization gives a product with a *para*-xylene level well beyond the position of thermodynamic equilibrium (e.g., 26% *para*-xylene versus an equilibrium value of 23.4%). As the results in Table 1 illustrate, high *para*-xylene concentrations are accompanied by high xylene losses, mainly to disproportionated products, toluene and C_9 aromatics, and to high *ortho*-xylene concentrations, although not up to the equilibrium position.

The reaction pathway for *para*-xylene isomerization is again highly distorted relative to that reported for the H-ZSM-5 zeolite (*4*). Progressive coking does not markedly move the observed products away from the reaction pathway shown (Fig. 3).

TABLE 2

Isomerization of *meta*-Xylene over H-Fu-9 at 450°C[a]

Point[a]	WHSV (h^{-1})	Time on stream (h)	Normalized xylene isomer concentration (wt%)			Xylene loss (wt%)
			meta	*para*	*ortho*	
1	1.0	1.0	54	25	21	11.4
2	1.0	6.0	60	26	14	5.9
3	2.2	1.0	58	25	17	5.5
4	2.2	5.0	66	24	10	3.3
5	4.4	1.0	63	22	15	2.9
6	4.4	5.0	75	18	7	1.6
7	9.9	1.0	74	17	9	1.5
8	9.9	7.0	84	12	4	1.5

[a] Thermodynamic equilibrium at 450°C; *meta*, 51.9%; *para*, 23.4%; *ortho*, 24.7%.

DISCUSSION

The zeolite H-Fu-9 is able to isomerize *meta*-xylene to a product in which the *para*-xylene concentration in the product is greater than the concentration at thermodynamic equilibrium. This occurs with concomitant high xylene losses. A similar situation occurs for the isomerization of *para*-xylene to *meta*-xylene. If *meta*-xylene isomerization initially yields an equilibrium mixture of *ortho* and *para* isomers within the zeolite then, as Wei suggested (*7*), the dominant isomer observed will be *para*-xylene because of its faster diffusion rate through the zeolite. This effect would be enhanced if the zeolite underwent coking, which would explain the variation with time on stream. However, the analysis would appear to fall short of explaining how the *para* isomer could be formed in concentrations greater than thermodynamic equilibrium concentrations.

High *para*-xylene levels could be further enhanced by several causes. First, formation of the *ortho*-xylene isomer may proceed "normally" at the active centers within the zeolite channels, but because of steric constraint—extremely low diffusion rate—this isomer is converted by disproportionation into nonxylene products. Studies on the larger pore LaY zeolite showed that *ortho*-xylene disproportionates more rapidly than does *meta*- or *para*-xylene (*13*). This was not observed in H-Fu-9, but it is the reactivity of *ortho*-xylene at an internal active center which may be critical for subsequent rapid loss to lighter and heavier products.

A second possibility is that formation of *para*-xylene at the isomerization center is more facile than formation of the *ortho* isomer. In such a situation the fast rate of diffusion of the *para* relative to *ortho* isomer would enhance the selectivity of *para*-xylene formation over a wide range of conversions (approach to equilibrium). Following the work of Spencer (*14*) it can be concluded that such kinetic control at the isomerization center can explain *para*-xylene formation with greater than thermodynamic equilibrium compositions. Spencer (*14*), developing an earlier argument by Wei and Prater (*15*), has discussed the thermodynamic constraints of multicomponent systems and showed that no other constraints exist for a system moving toward thermodynamic equilibrium within the restriction that the free energy of the system must decrease. This leads to the view that isomerization of *meta*-xylene to a product with more than the thermodynamic equilibrium concentration of *para*-xylene is feasible, provided the appropriate kinetic control is present. Figure 5 illustrates the reaction pathway found for *meta*-xylene isomerization over H-Fu-9, overlayed on contours of equal free energy for xylene mixtures. This shows that the *para*-xylene product can be greater in concentration than for thermodynamic equilibrium.

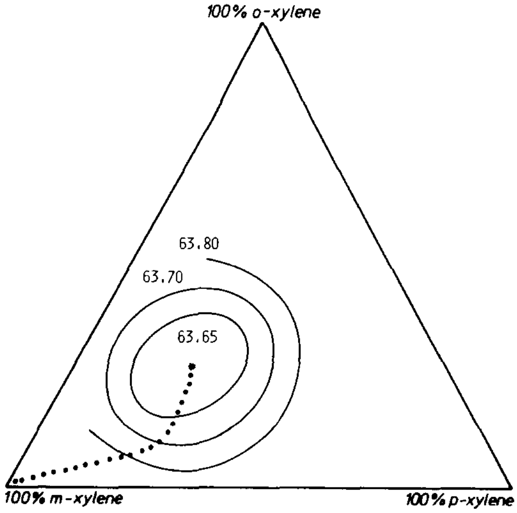

FIG. 5. Free-energy contours for xylene isomers. Plotted course is for *meta*-xylene isomerization over H-Fu-9 (determined at various space velocities) at 450°C; time on stream = 2 h.

At this stage it is not possible to differentiate between the factors discussed above. Thus, very high selectivity to the sterically smaller xylene isomers may arise by a combination of the schemes discussed, namely, (i) very low rates of diffusion for the *ortho*-xylene isomer made even lower as coking increases, (ii) transition state selectivity favoring *para*- or *meta*-xylene, and (iii) a xylene loss mechanism which specifically favors the *ortho* isomer.

The reaction pathway for *para*-xylene isomerization is different from that of ZSM-5, but unlike the isomerization pathway for *meta*-xylene, it is not as dependent on time on stream (coking). This suggests that the course of this reaction pathway is governed by stereo-control at the isomerization center, and that formation of *ortho*-xylene is being blocked rather than being rapidly converted to other products or relative *para*-xylene diffusion rates progressively increasing with extent of coking. Intuitively this would be predicted from a 1,2-shift mechanism for xylene isomerization. The formation of *ortho*-xylene from *para*-xylene requires two consecutive 1,2 shifts, the second one, *meta* to *ortho*, being considerably more difficult.

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