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A Mathematical Theory of Enhanced *para*-Xylene Selectivity in Molecular Sieve Catalysts

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In certain molecular sieve catalysts, such as the zeolite ZSM-5, the diffusivity of *para*-xylene can be more than a thousand times higher than the diffusivities of *ortho*- and *meta*-xylenes. The xylene mixtures produced in such catalysts from alkylation of toluene or from toluene disproportionation can have *para*-xylene concentrations far in excess of the equilibrium concentration. A mathematical theory is developed here to explain this enhancement of *para*-selectivity and the decline of selectivity under increasing conversion.

INTRODUCTION

A mixture of the xylene isomers can be produced by either the alkylation of toluene with methanol,

$$\text{methanol} + \text{toluene} \rightleftarrows \text{xylenes} + \text{water},$$

or by the disproportionation of toluene,

$$2\ \text{toluene} \rightleftarrows \text{benzene} + \text{xylenes}.$$

The *para*-xylene, which is a precursor of polyester resins, is the most valuable product. However, many catalytic reactions produce equilibrium distribution at 22% *ortho*-, 54% *meta*-, and 24% *para*-xylene according to Allen and Yats (*1*).

In recent literature, shape-selective zeolite catalysts have been used to produce xylenes with *para* selectivity above 50% (*2–4*). *para*-Xylene selectivity was enhanced by impregnation with phosphorus and boron compounds and by coating the catalyst surface with polymers. A plausible explanation is that the pores in the ZSM-5 zeolite are approximately 7–8 Å in diameter, which permit the rapid diffusion of toluene and *para*-xylene with molecular diameters of *6.3 Å*, but severely retard the diffusion of *ortho*- and *meta*-xylenes with molecular diameters of *6.9 Å* (*7, 12*). This diffusion takes place in the "configurational" region (*5*). The primary products of alkylation or disproportionation may be near equilibrium in selectivity, but the rapid diffusion of *para*-xylene plus isomerization in the pores would shift the product selectivity.

A quantitative theory will be presented here to account for the observed enhancement of *para* selectivity, and for the decline in *para* selectivity under increased conversion.

XYLENE SELECTIVITY AT ZERO CONVERSION IN ALKYLATION OR DISPROPORTIONATION

Consider the alkylation reaction

$$\text{methanol} + \text{toluene} \xrightarrow{k_a} \text{xylenes} + \text{water}. \quad (1)$$

The reaction takes place with an excess of toluene to suppress the further alkylation of xylenes to trimethylbenzenes. The reaction takes place inside a pore where the concentration gradients of methanol and toluene are negligible. The general mathematical theory for such systems was developed by Wei (*6*). Let the primary distributions of *o*-xylene, *m*-xylene, and *p*-xylene at the catalytic site be given as

$$\mathbf{C}^p = (C_o{}^p, C_m{}^p, C_p{}^p) \qquad \text{mole/cm}^3.$$

As the xylenes diffuse out of the pores, ac-

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cording to the Fickian relations

$$J_i = -D_i \nabla C_i \qquad \text{moles/cm}^2 \cdot \text{sec}, \quad (2)$$

where $D_p \sim 1000\, D_o = 1000\, D_m$, the xylenes also isomerize in the pores,

$$o\text{-xylene} \rightleftarrows m\text{-xylene} \rightleftarrows p\text{-xylene}, \quad (3)$$

so that the material balance in the pore is

$$\frac{d\mathbf{C}}{dx} = \mathbf{0} = q\mathbf{C}^p - \underline{\mathbf{K}}\mathbf{C} + \underline{\mathbf{D}}\nabla^2\mathbf{C}, \quad (4)$$

where q is the rate of xylene formation (1/sec) and $\mathbf{K}$ is the isomerization rate matrix (1/sec).

$$\underline{\mathbf{K}} = k_I \begin{bmatrix} 2 & -1 & 0 \\ -2 & 2 & -2 \\ 0 & -1 & 2 \end{bmatrix}.$$

These rate constants will lead to an equilibrium of 25% *o*-, 50% *m*-, and 25% *p*-xylenes. $\underline{\mathbf{D}}$ is the diagonal matrix (cm²/sec)

$$\underline{\mathbf{D}} = D_o \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1000 \end{bmatrix}$$

The boundary conditions are

$$\begin{aligned} &x = 0, \quad \nabla\mathbf{C} = \mathbf{0} \qquad \text{due to symmetry,} \\ &x = L, \quad \mathbf{C} = \mathbf{0} \qquad \text{at zero conversion.} \quad (5) \end{aligned}$$

Let the matrix $\mathbf{D}^{-1}\mathbf{K}$ have the diagonal form of

$$\underline{\mathbf{D}}^{-1}\underline{\mathbf{K}} = \underline{\mathbf{M}\boldsymbol{\mu}^2\mathbf{M}^{-1}} \quad (6)$$

where $\underline{\mathbf{M}}$ is the matrix of eigenvectors, $\underline{\mathbf{M}}^{-1}$ is the inverse of $\mathbf{M}$, $\underline{\boldsymbol{\mu}}^2$ is the diagonal matrix of eigenvalues,

$$\{\mu_1^2, \mu_2^2, \mu_3^2\} \qquad (1/\text{cm}^2).$$

The solution to (4) with boundary values (5) is

$$\mathbf{C}(x) = q\underline{\mathbf{M}} \left\{\frac{1}{\mu_i^2}\left(1 - \frac{\cosh \mu_i x}{\cosh \mu_i L}\right)\right\} \underline{\mathbf{M}}^{-1}\underline{\mathbf{D}}^{-1}\mathbf{C}^p \quad (7)$$

where the expression within the braces is a diagonal matrix.

The rate of production of xylenes per length of pore is equal to the rate of diffusive flux through the pore entrance with the composition of

$$\begin{aligned} &-\frac{1}{L}\underline{\mathbf{D}}(\nabla\mathbf{C})_{x=L} \\ &= q\underline{\mathbf{DM}}\left\{\frac{\tanh \mu_i L}{\mu_i L}\right\}\underline{\mathbf{M}}^{-1}\underline{\mathbf{D}}^{-1}\mathbf{C}^p = q\mathbf{C}^s. \quad (8) \end{aligned}$$

The *secondary* distribution, $\mathbf{C}^s$, is the observable selectivity at very low conversion as a result of the primary distribution altered by pore isomerization and filtered by unequal diffusivities. The secondary product distribution is related to the primary distribution by

$$\mathbf{C}^s = \underline{\mathbf{T}}\mathbf{C}^p$$

where $\underline{\mathbf{T}} = \underline{\mathbf{DM}}\{\tanh \phi_i/\phi_i\}\underline{\mathbf{M}}^{-1}\underline{\mathbf{D}}^{-1}$ and $\phi_i = L\mu_i$. The function $\tanh \phi_i/\phi_i$ is an effectiveness factor, when $\phi_i \to \infty$, $\tanh \phi_i/\phi_i \to 1/\phi_i$. In our example

$$\underline{\mathbf{D}}^{-1}\underline{\mathbf{K}} = \frac{k_I}{D_o}\begin{bmatrix} 2 & -1 & 0 \\ -2 & 2 & -2 \\ 0 & -0.001 & 0.002 \end{bmatrix},$$

$$\underline{\mathbf{M}} = \begin{bmatrix} 0.25 & 1 & 1 \\ 0.50 & 1.4125 & -1.4145 \\ 0.25 & -0.00241 & 0.00415 \end{bmatrix},$$

$$\underline{\mathbf{M}}^{-1} = \begin{bmatrix} 0.0040 & 0.0040 & 3.996 \\ 0.5001 & 0.3533 & -1.2066 \\ 0.5009 & -0.3568 & 0.2077 \end{bmatrix},$$

$$\underline{\boldsymbol{\mu}}^2 = \frac{k_I}{D_o}\{\ 0, \quad 0.5875, \quad 3.4145\ \}$$

$$\underline{\boldsymbol{\mu}} = \left(\frac{k_I}{D_o}\right)^{1/2}\{\ 0, \quad 0.7665, \quad 1.8478\ \}$$

$$\left\{\frac{\tanh \phi_i}{\phi_i}\right\} = \left\{1, \frac{\tanh 0.7665\phi}{0.7665\phi}, \frac{\tanh 1.8478\phi}{1.8478\phi}\right\}, \quad (9)$$

where $\phi = L(k_I/D_o)^{1/2}$.

For two examples of primary products $\mathbf{C}^p = (0, 1, 0)$ and $\mathbf{C}^p = (0.6, 0.1, 0.3)$, the results $\mathbf{C}^s$ for a range of values of ϕ are given in Fig. 1. It is seen than for $\phi > 10$, regardless of the primary product distribution $\mathbf{C}^p$, diffusion and isomerization will combine to produce better than 90% selec-

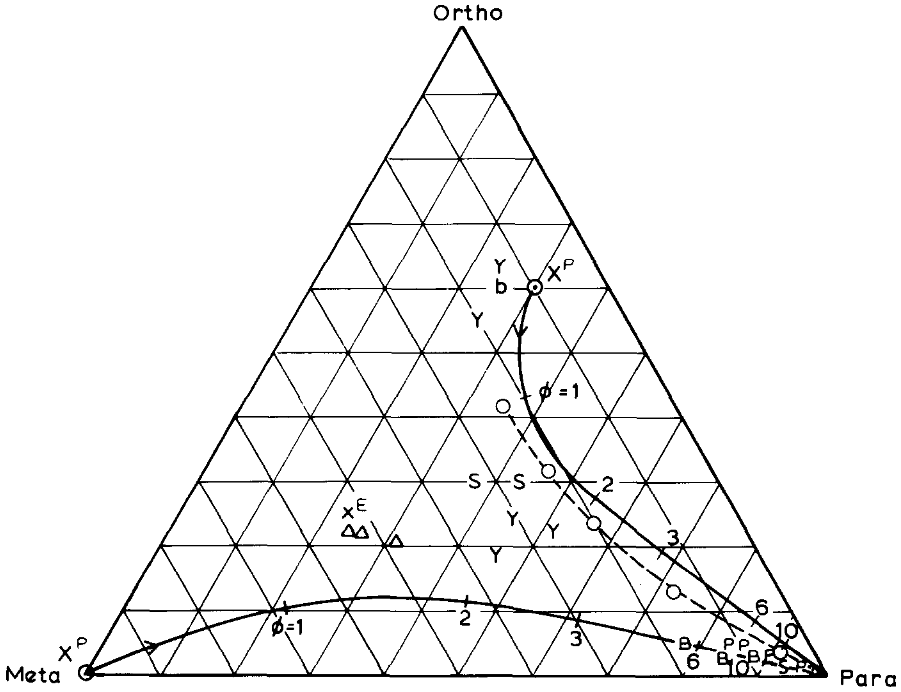

FIG. 1. Xylene selectivity at low conversion. Solid lines are theoretical curves from a primary distribution X^p of (0.6, 0.1, 0.3) and of (0, 1, 0), at a range of values of the Thiele modulus ϕ. E, equilibrium; Y, cation-exchanged zeolite Y, Yashima; b, Friedel–Craft, Allen Yates; X, HZSM5, Kaeding; △, HZSM11, Kaeding; S, carborane-silicone HZSM-5, Kaeding; P, phosphorus HZSM-5, Kaeding; B, boron HZSM-5, Kaeding; O---O, PZSM-5, Young.

tivity of *para*-xylene. This enrichment of *para*-xylene from any primary distribution is made possible by the much greater diffusivity of *para*-xylene. This superior selectivity applies only at zero conversion of toluene to xylenes. As conversion increases, it is expected that *para*-selectivity would decrease.

Figure 1 also shows the experimental data of xylene selectivity at low conversions from methanol alklyation of toluene and from toluene disproportionation. The Friedel–Craft (*1*) and zeolite Y (*2, 3*) results are much lower in *meta*-xylene than the equilibrium value. The unmodified HZSM-5 and HZSM-11 results (*7*) are close to equilibrium. Modifications of the HZSM-5 by carborane-siloxant coating, phosphorous treatment, and boron treatment greatly increased the *para*-xylene selectivity to above 97%.

The data of Young *et al.* (11) was obtained over phosphorus modified ZSM-5 by varying the temperature from 400 to 600°C while keeping the toluene conversion below 16%. As temperature increased, the value of ϕ also increased, and the result was a dramatic increase of *p*-xylene selectivity in parallel with the theoretical line.

SUBSEQUENT XYLENE ISOMERIZATION

When the concentration of xylenes outside of the pore is not zero, reentry of xylenes inside the pore and isomerization also take place. The boundary condition (*5*) is modified to

$$x = 0,\ \mathbf{C} = \mathbf{0}$$
$$x = L,\ \mathbf{C} = \mathbf{C}^a.$$

In this case, the solution is

$$\mathbf{C}(x) = q\underline{\mathbf{M}}\left\{\frac{1}{\mu_i^2}\left(1 - \frac{\cosh \mu_i x}{\cosh \mu_i L}\right)\right\}\underline{\mathbf{M}}^{-1}\underline{\mathbf{D}}^{-1}\mathbf{C}^{\mathrm{p}} + \underline{\mathbf{M}}\left\{\frac{\cosh \mu_i x}{\cosh \mu_i L}\right\}M^{-1}\mathbf{C}^{\mathrm{a}}. \quad (10)$$

The rate of production of xylene per length of pore is

$$-\frac{1}{L}\underline{\mathbf{D}}(\nabla\mathbf{C})_{x=L} = q\underline{\mathbf{T}}\mathbf{C}^{\mathrm{p}} + \underline{\mathbf{K}}^{+}\mathbf{C}^{\mathrm{a}}.$$

The first term is the secondary distribution from alkylation or disproportionation; the second term is the subsequent isomerization of xylenes upon reentry into the pores, described by a diffusion-disguised rate matrix $\underline{\mathbf{K}}^{+}$, where

$$\underline{\mathbf{K}}^{+} = \underline{\mathbf{DM}}\{\phi_i \tanh \phi_i\}\underline{\mathbf{M}}^{-1}/L^2. \quad (11)$$

The function $\phi_i \tan \phi_i$ is proportional to $(\phi_i^2 D/L^2)$ $(\tanh \phi_i/\phi_i)$, a rate constant multiplied by an effectiveness factor.

In the absence of diffusion effects, the rate matrix $\underline{\mathbf{K}}$ has eigenvectors and eigenvalues

$$\underline{\mathbf{X}} = \begin{bmatrix} 0.25 & -0.25 & -0.25 \\ 0.50 & 0 & -0.50 \\ 0.25 & 0.25 & -0.25 \end{bmatrix},$$

$$\underline{\mathbf{X}}^{-1} = \begin{bmatrix} 1 & 1 & 1 \\ -2 & 0 & 2 \\ 1 & 1 & -1 \end{bmatrix},$$

$$\underline{\Lambda} = k_1\{0, \quad 2, \quad 4\}.$$

When diffusion effects are present, the diffusion-disguised rate matrix is given by Eq. (11).

As $\phi_i \to \infty$,

$$\{\phi_i \tanh \phi_i\} \to \{\phi_i\} = \phi\{0, 0.7665, 1.8478\},$$

$$\underline{\mathbf{K}}^{+} = \frac{(D_0 k_1)^{1/2}}{L} \begin{bmatrix} 1.3089 & -0.3884 & -0.5411 \\ -0.7678 & 1.3151 & -1.8493 \\ -0.5409 & -0.9264 & 2.3899 \end{bmatrix} \mathrm{1/sec}.$$

The eigenvectors and eigenvalues of $\underline{\mathbf{K}}^{+}$ are

$$\mathbf{X}^{+1} = \begin{bmatrix} 0.250 & -2.860 & 0.231 \\ 0.500 & 2.163 & 2.163 \\ 0.250 & 0.697 & -2.394 \end{bmatrix},$$

$$(\underline{\mathbf{X}}^{+})^{-1} = \begin{bmatrix} 1 & 1 & 1 \\ -0.2613 & 0.0987 & 0.0639 \\ 0.0289 & 0.1337 & -0.2963 \end{bmatrix},$$

$$\underline{\Lambda}^{+} = \frac{(D_0 k_1)^{1/2}}{L}\{0, \quad 1.7343, \quad 3.2796\}.$$

The ratio of $\lambda_3/\lambda_2 = 4/2 = 2$ has declined to $\lambda_3^{+}/\lambda_2^{+} = 3.2796/1.7343 = 1.891$. The eigenvectors, and consequently the straight line reaction paths, have rotated. Figure 2 shows the rotation of straight line reaction paths, and the changes in reaction paths from initial concentrations of pure *o*-xylene, of pure *m*-xylene, and of pure *p*-xylene.

The position of the equilibrium is at 25% *ortho*-, 50% *meta*-, and 25% *para*-xylene. When the value of ϕ is greater than 10, there is no further change in the reaction paths. Experimental data on the isomerizations of a pure xylene isomer over a number of catalysts are shown in Fig. 3, where the equilibrium is at 23% *ortho*, 53% *meta*, and 24% *para*. The data from nonselective catalysts are for silica–alumina (*2*, *3*, *8*, *9*), for Y-zeolites (*2*, *3*). They agree very well with the three curves for $\phi = 0$ in Fig. 3. Two selective catalysts were prepared by modification of ZSM-5 with phosphorus and with magnesium (*11*). The results showed a dramatic change in selectivity in excellent agreement with the three curves for $\phi > 10$ in Fig. 3.

XYLENE SELECTIVITY AT FINITE CONVERSION IN ALKYLATION OR DISPROPORTATION

In an integral reaction, toluene is converted to xylenes in the pores as $\mathbf{C}^{\mathrm{p}}$, and is modified by isomerization and diffusion in the pores to emerge as $\mathbf{C}^{\mathrm{s}} = \underline{\mathbf{T}}\mathbf{C}^{\mathrm{p}}$. After a while the concentration of toluene and methanol declines, so that the production of $\mathbf{C}^{\mathrm{s}}$ decreases; but as the concentration of xylene in the reactor increases, the isomeri-

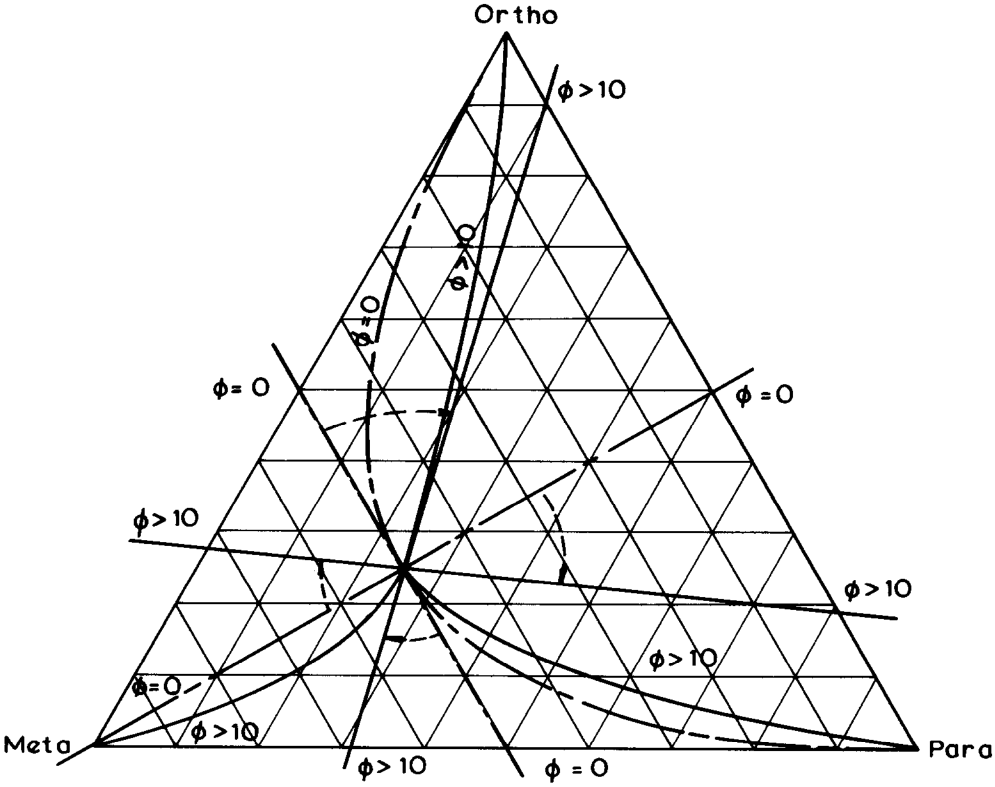

FIG. 2. Theoretical reaction paths in xylene isomerization: – – –, in the absence of diffusion effects, or $\phi = 0$; ——, with very severe diffusion effects, or $\phi > 10$.

zation of $\mathbf{C}^s$ by the diffusion-disguised rate matrix $\underline{\mathbf{K}}^+$ will become more important. Let the rate of production of new xylene be given by

$$q(t) = q^0 e^{-k_a t}.$$

The mass balance equation is

$$\frac{d\mathbf{C}}{dt} = q(t)\mathbf{C}^s - \underline{\mathbf{K}}^+\mathbf{C} \qquad t = 0, \mathbf{C} = \mathbf{0},$$

where the solution is

$$\mathbf{C}(t) = q^0 X^+ \left\{ \frac{e^{-k_a t} - e^{-\lambda_i^+ t}}{\lambda_i^+ - k_a} \right\} (\underline{\mathbf{X}}^+)^{-1}\mathbf{C}^s \quad (13)$$

where $\underline{\mathbf{X}}^+$ and λ_i^+ are the eigenvectors and eigenvalues of $\underline{\mathbf{K}}^+$.

The low conversion product $\mathbf{C}^s$ would be very *para*-selective for catalysts with $\phi > 10$. But as conversion of toluene increases, much of the *p*-xylene would isomerize and thus lower the *para*-selectivity. The relation between *para*-selectivity and toluene conversion depends on the competitive rates of alkylation and isomerization, or the ratio $k_a/k_I^{1/2}$. A superior catalyst has a very high alkylation activity but low isomerization activity.

In toluene disproportionation, thermodynamic equilibrium limits the conversion of toluene to 50%. Let us assume that the secondary distribution $\mathbf{C}^s = (0, 0, 1)$, i.e., pure *p*-xylene. When the toluene conversion is over, and xylene isomerization has run its courses, the percentage *para*-xylene in the xylene mixture will fall to the equilibrium value of 25%. The results for $k_a/k_I^{1/2}$ of 1 and 10 are shown in Fig. 4, as well as literature data (*11*, *12*). The unmodified HZSM-5 gave no enhancement of *para*-selectivity at any level of toluene conversion in disproportionation. The magnesium-modified ZSM-5 gave a much more favorable *para*-

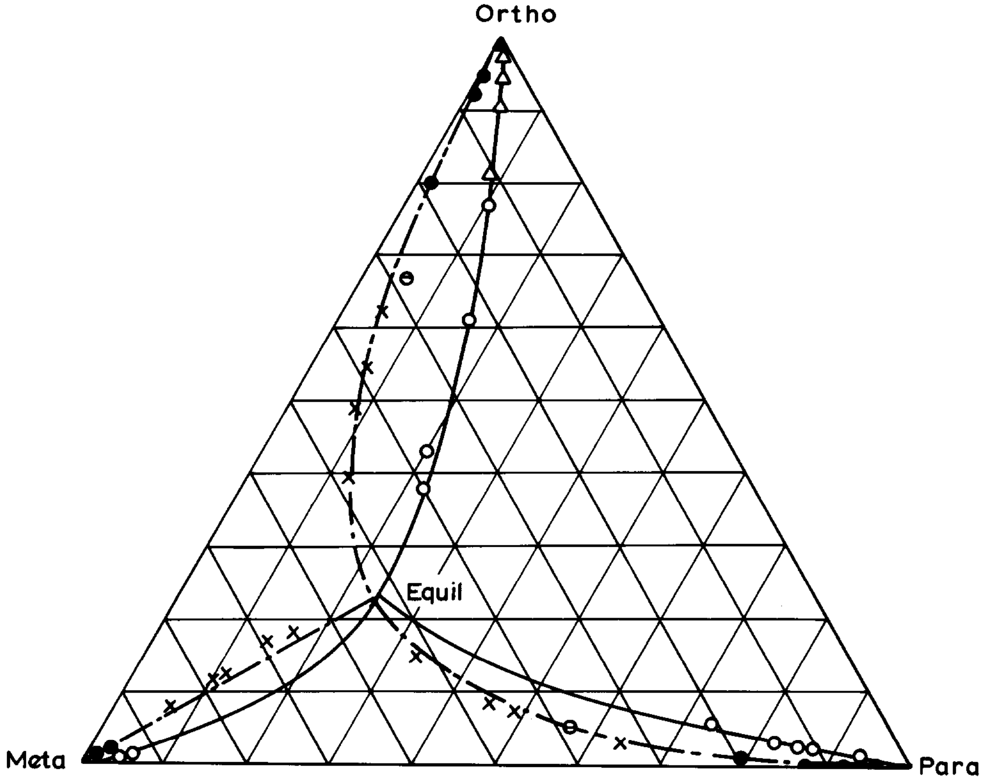

FIG. 3. Reaction path data with xylene isomerization over nonselective catalysts: ●, silica–alumina, Henson and Engel; X, silica-alumina, Silvestri and Prater; θ, silica–alumina, Yashima; and over selective catalysts: O, PZSM-5, Young; △, MgZSM-5, Young.

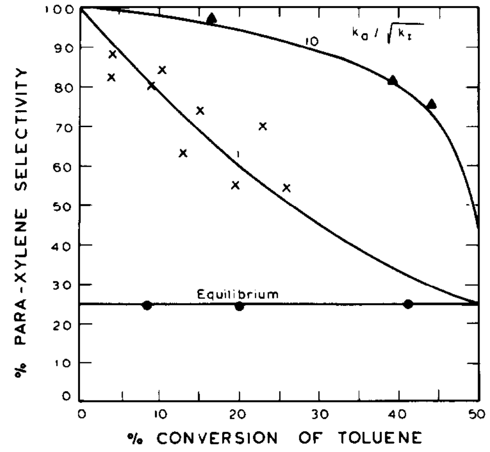

FIG. 4. The relation between the percentage *para*-selectivity and percentage toluene conversion in toluene disproporationation. ——, Theoretical curves for $k_a/k_I^{1/2}$ of 1 and 10. ●, HZSM-5, disproportionation, Young; X, MgZSM-5, disproportionation, Young; ▲, PZSM-5, methanol alkylation, Young.

selectivity, which declined with increasing toluene conversion, following approximately the theoretical curve for $k_a/k_I^{1/2} = 1$. The data on toluene–methanol alkylation over phosphorus-modified ZSM-5 gave excellent *para*-selectivity in agreement with the theoretical curve for $k_a/k_I^{1/2} = 10$.

CONCLUSION

In a molecular sieve catalyst where molecular dimensions have profound effects on diffusivity, the primary product distribution at the catalytic sites can be modified by isomerization and selective diffusion to produce secondary product distributions that highly favor the fast diffusing species. Available experimental data agree very well with the mathematical theory developed here.

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