

# Kinetics of Liquid Phase Xylene Isomerization over H-Mordenite

A study of the kinetics for the liquid phase isomerization of ortho-xylene over *H*-mordenite has been made at 505°K,  $2.76 \times 10^5$  N/m<sup>2</sup>, and 23 mole % toluene diluent. This is the first known study reporting kinetic data for the liquid phase isomerization of xylene over a zeolite catalyst. High activity is indicated by the 80% achievement of para-xylene equilibrium at 505°K,  $2.76 \times 10^5$  N/m<sup>2</sup>, and  $0.767 \times 10^{-3}$  kg/s/kg. Although high selectivity has previously been reported for a specifically prepared zeolite catalyst, the 99+ % selectivity of the isomerization reaction with *H*-mordenite as indicated by no C<sub>9</sub>+ aromatics and less than 0.5 mole % benzene in the product is most significant. Catalyst deactivation was also significant. Reaction rate constants are reported for a first-order reversible triangular model among the xylene isomers with catalyst deactivation incorporated into the model.

J. R. HOPPER  
and  
DENNIS S. SHIGEMURA

Chemical Engineering Department  
Lamar University  
Beaumont, Texas 77710

## SCOPE

Ortho and para-xylene are important chemical intermediates. New catalysts which offer high activity and selectivity can alter the optimum economic decision for their production. The objective of this study was to establish a kinetic model for xylene isomerization over a zeolite catalyst—*H*-mordenite. The study was performed under conditions of liquid phase, toluene diluent, and relatively lower temperature (505°K) for which kinetic data have not been previously reported but for which high activity and selectivity were recently demonstrated with an un-

disclosed zeolite catalyst (Grandio et al., 1971). *H*-mordenite is known to have high initial activity for this reaction (Hansford and Ward, 1968), but the selectivity is not reported. Catalyst deactivation, if it existed, was to be incorporated into the model. The results of this study can provide further insight into the catalytic properties of *H*-mordenite and quantitative kinetic information on the magnitude of the activity, selectivity, and catalyst deactivation which are of major value in process optimization and control evaluations.

## CONCLUSIONS AND SIGNIFICANCE

The isomerization of ortho-xylene over *H*-mordenite was investigated at 505°K,  $2.76 \times 10^5$  N/m<sup>2</sup> and about 23 mole % toluene diluent. The most significant observation was the 99+ % selectivity to the isomerization reaction and no formation of C<sub>9</sub>+ aromatics. The activity was very good with an 80% achievement of para-xylene equilibrium at a space velocity of  $0.767 \times 10^{-3}$  kg/s/kg. Catalyst deactivation was significant. The reaction was modeled by the first-order reversible interconversion triangular reaction scheme among the isomers. The catalyst deactivation was

correlated by an exponential decay function of the feed/catalyst ratio. The model in compact notation is expressed as

$$r_j = \frac{1}{\phi} \sum_{k=1}^6 B_{0k} e^{-\alpha_k(\theta/\tau)} R_{jk} \quad (j = A, B, C)$$

The reaction model constants given in Table 4 show the conversion of ortho to para-xylene occurs primarily by the series of 1, 2 methyl shifts first to meta-xylene and then to para-xylene.

Hydrocarbon isomerization reactions have received considerable attention in the past two decades. Significant progress in paraffin isomerization capability was achieved in the 1960's. This progress resulted from the employment of a crystalline zeolite base in the dual-function type catalyst which classically was defined as a dispersed metal on a high-surface-area amorphous base (Rabo et al., 1961; Voorhies and Beecher, 1969; Voorhies and Bryant, 1968;

Hooper and Voorhies, 1972). Commercial application in the United States was not always justified in the 1960's. These studies have, however, become significant under the present-day demand for low leaded gasoline. Similar trends in commercial demand may occur for aromatic isomerization.

Aromatic isomerization has also received considerable interest. Xylene isomerization has particularly attracted interest since the early 1950's because of the demand for ortho- and para-xylene. Acid halides, amorphous acidic,

D.S. Shigemura is with Hydrocarbon Process Research, Dow Chemical U.S.A., Texas Division, Freeport, Texas 77541.

and dual-function type catalysts have generally been used for aromatic isomerization.

Xylene isomerization studies have been performed in both the liquid and the vapor phase. Liquid phase studies have generally been made with homogeneous acidic halide catalysts such as HF/BF<sub>3</sub> (Allen et al., 1959; Brown and Jungk, 1955; Kemp, 1950; McCaulay, 1964). Liquid phase isomerizations suffer from side reactions, sludge formation, loss of the partially soluble catalyst from the reactor, and resulting corrosion and recovery problems (Condon, 1958). Interest first turned to the heterogeneous silica-alumina catalyst (Hanson and Engel, 1967; Silvestri and Prater, 1964) and then to the dual-function catalyst (Ciapetta and Hunter, 1953; Pitts et al., 1953) to avoid these difficulties. However, vapor phase conditions are required with the heterogeneous catalyst because of the higher temperature needed to obtain the desired activity. The higher temperatures lead to coke formation which lowers the yield of the desired products and requires catalyst regeneration.

The use of the crystalline zeolite catalysts for the aromatic isomerization seemed to be a natural extension because of the success of these catalysts with paraffin isomerization. Hansford and Ward (1969) reported high activity of a large number of zeolites relative to a silica-alumina catalyst. A large conversion to transalkylated products was reported for xylene isomerization with a Type Y zeolite at 573°K and  $35.5 \times 10^5$  N/m<sup>2</sup> (Lanewala and Bolton, 1969); no catalyst deactivation was reported. High activity and good catalyst activity maintenance was reported using a rare-earth-exchanged zeolite X (REX) (Wise, 1968). Substantial C<sub>9</sub>+ aromatics were also observed. Matsumoto et al. (1968) reported on a variable study with several exchanged zeolites in a vapor phase isomerization, and first-order reaction was observed. In most studies reaction rate parameters were not developed, significant C<sub>9</sub>+ aromatics were observed and catalyst deactivation was not reported.

Recently a most important finding was reported (Grandio et al., 1971; Bowes et al., 1971) in which almost total elimination of side reactions and high activity for the xylene isomerization was achieved. The reaction was performed in the liquid phase with a special zeolite catalyst of undisclosed composition; kinetic data were not reported.

In view of this latter result the objective of this study has been to investigate the activity and selectivity of a crystalline zeolite, *H*-mordenite, as a catalyst for the isomerization of ortho-xylene under liquid phase conditions and to develop a kinetic model under these conditions. It was anticipated that *H*-mordenite catalyst would offer high activity (Hansford and Ward, 1968); however, high selectivity had never been reported.

## EXPERIMENTAL SYSTEM

This study was performed in the Reaction Engineering Analysis Laboratory, Chemical Engineering Department, Lamar University. The equipment consisted of a micro-catalytic reactor and auxiliary equipment similar to that previously described (Hopper, 1969; Allan, 1970).

A simplified flow diagram is shown in Figure 1. The basic system consisted of a Ruska pump for liquid metering, a fluidized sand bath to maintain isothermal reactor conditions, a back-pressure regulator in the effluent line, a liquid product collecting system, and a wet-test meter for possible vapor products measurement. A gas metering system was provided for catalyst activation and flexibility in the reactor system.

A cross-sectional view of the reactor in the fluidized sandbath is shown in Figure 2. The top and bottom sections of the bath were flanged to support porous stainless steel plates which allowed passage of air and supported the sand particles.

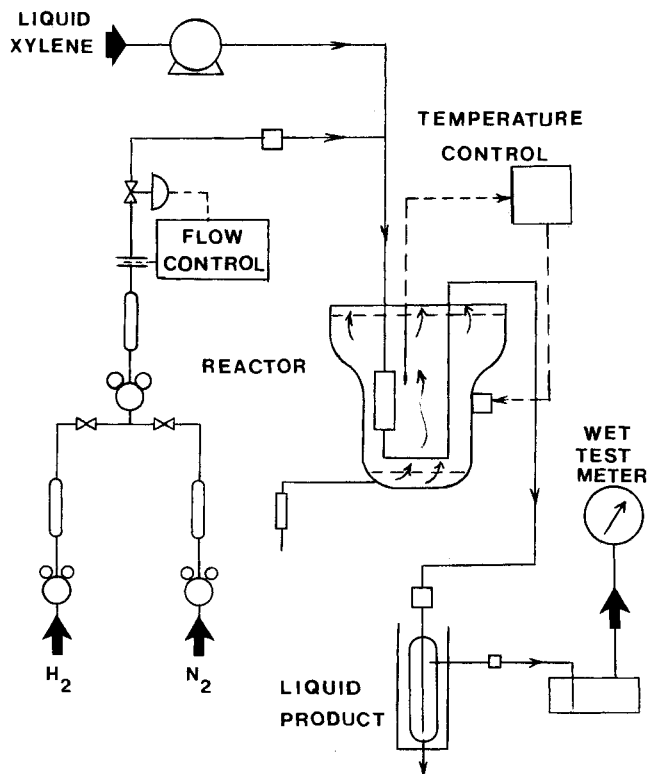


Fig. 1. Simplified flow diagram of the equipment.

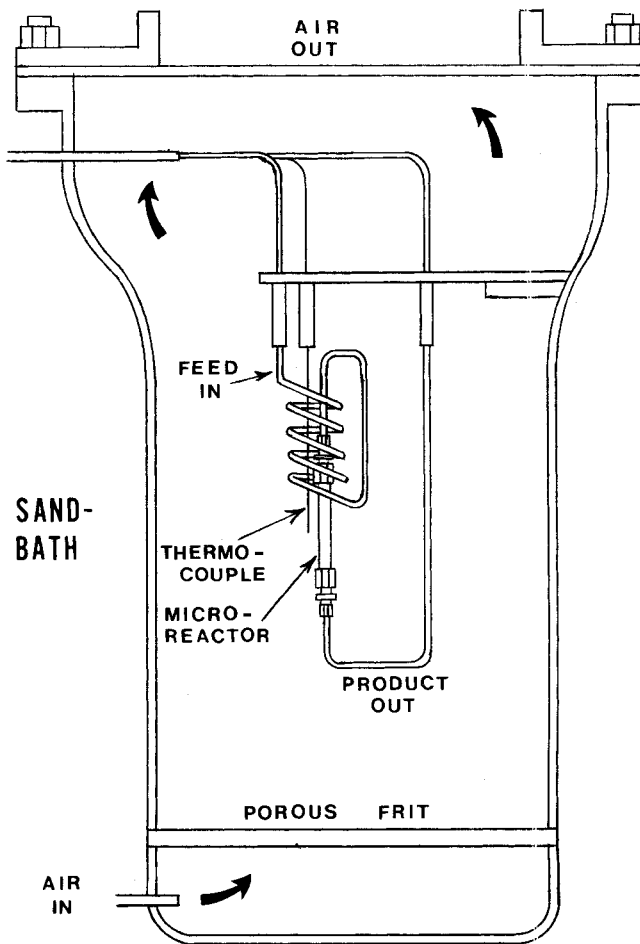


Fig. 2. Cross-sectional view of reactor in fluidized sand bath.

The micro-reactor is shown in Figure 3 (Harrison et al., 1965). It was made from a 7-in. section of 3/8-in. O.D. 316 stainless steel tubing and usually contained 5g of catalyst. The reactor was provided with specially machined reducing unions to allow space for 10 micron porous stainless steel disks used to contain the catalyst in the reactor. Feed flowed downward to the reactor and from the reactor in 1/8-in. tubing with a preheat section provided prior to the reactor inlet. Feed and product were analyzed by a gas chromatograph using a 1/8-in. O.D. stainless steel thin-wall tubing, 20 ft. long, packed with 5% Bentone-34 and 6% diethylene glycol succinate on 60-80 mesh Chromosorb W.

The catalyst used was a Zeolon 900 *H*-mordenite obtained from the Norton Company. The catalyst was calcined over a period of 20 hours at progressively increased temperature levels up to 810°K in the presence of air. A catalyst activation procedure typical of that employed for a metal dispersed catalyst was used by heating the catalyst in situ at 644°K in the presence of hydrogen. Hydrogen was flushed from the reactor with nitrogen prior to the reaction. Several properties for this catalyst are shown in Table 1 (Schneider, 1971). Silica and alumina were not determined but the theoretical mole ratio is shown. Complete details of the entire experimental system and procedure are available (Shigemura, 1972).

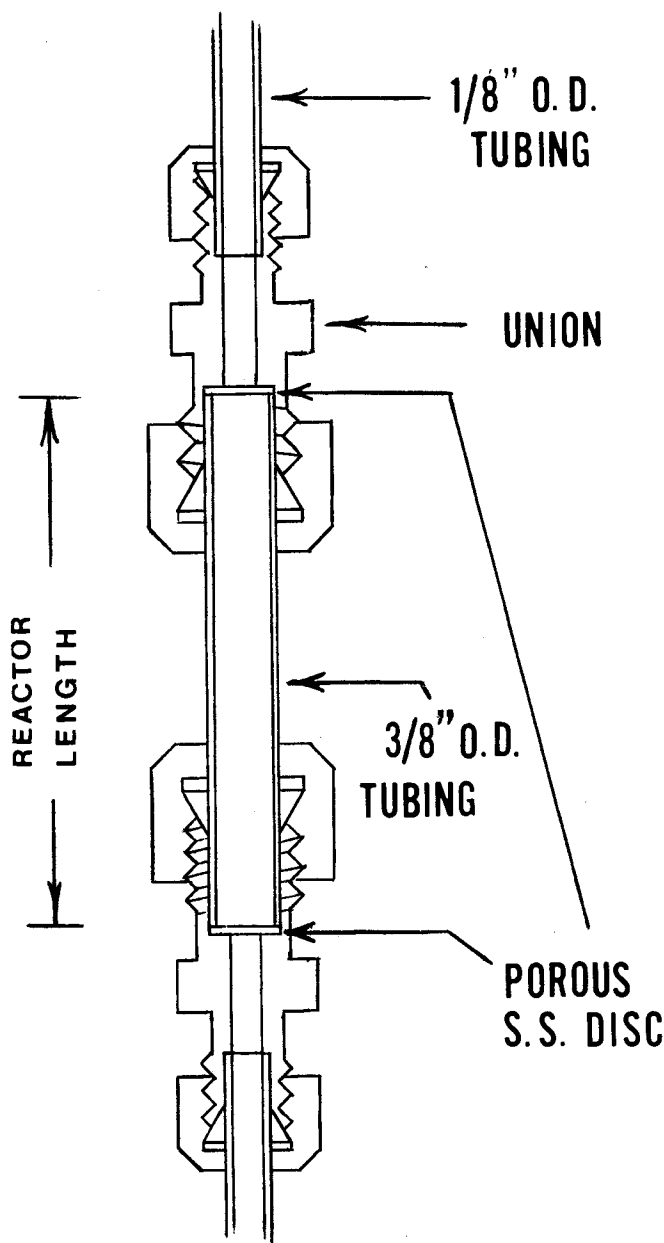


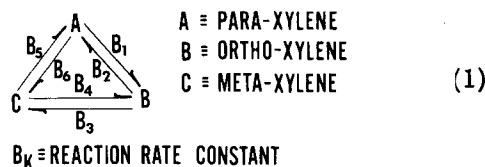
Fig. 3. Micro reactor.

TABLE I. *H*-MORDENITE PROPERTIES

Theoretical mole ratio, SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	10/1
Pore volume, cm <sup>3</sup> /g	0.208
Particle porosity	0.274
Surface area, m <sup>2</sup> /g	386

#### KINETIC MODEL

Mass transfer resistance as bulk diffusion resistance and macropore diffusion resistance were initially established to be negligible in the overall reaction before considering the chemical resistances. Bulk diffusion resistance was demonstrated to be negligible by observing no increase in reactant conversion or selectivity for an increase in superficial velocity by a factor of three while maintaining constant values for space velocity, pressure and temperature. Macropore diffusion was shown to be negligible by observing no change in reactant conversion or selectivity for a change in the catalyst particle mean diameter by a factor of two. A simplified reaction scheme for the xylene isomerization is illustrated in Equation (1).



This scheme represents a general three-component unimolecular reaction system with interconversion among all three isomers. This scheme was previously proposed for a vapor-phase isomerization study (Amemiya, 1961). A modification of this scheme for which there is no interconversion between the ortho- and para-isomers was proposed for the vapor phase isomerization over silica-alumina (Hanson and Engel, 1967) and for the acidic halide catalyzed liquid phase isomerization (Brown and Jungk, 1955).

A kinetic model based on this scheme which uses a first-order reversible reaction among the three isomers was assumed. The rate of disappearance of each isomer ( $i$ ) expressed as gram-moles reacted per second ( $N_i$ ) per kilogram of catalyst ( $W_c$ ) as a function of concentration ( $C_i$ ) and reaction rate constant ( $B$ 's) can be written as follows:

$$\begin{aligned}
 -\frac{dN_A}{dW_c} &= B_1 C_A - B_2 C_B + B_6 C_A - B_5 C_C \\
 -\frac{dN_B}{dW_c} &= B_2 C_B - B_1 C_A + B_3 C_B - B_4 C_C \\
 -\frac{dN_C}{dW_c} &= B_4 C_C - B_3 C_B + B_5 C_C - B_6 C_A
 \end{aligned}
 \quad (2)$$

Since there is no change in the number of moles during the reaction, these equations can also be expressed in terms of the toluene-free mole fraction of each isomer ( $X_i$ ), the space time ( $\tau$ ), an average reaction system density ( $1/\phi$ ), and the equilibrium constant ( $K$ ) as follows:

$$\begin{aligned}
 -\phi \frac{dX_A}{d\tau} &= B_1(X_A - X_B/K_1) - B_5(X_C - X_A/K_5) \\
 -\phi \frac{dX_B}{d\tau} &= -B_1(X_A - X_B/K_1) + B_3(X_B - X_C/K_3) \\
 -\phi \frac{dX_C}{d\tau} &= -B_3(X_B - X_C/K_3) + B_5(X_C - X_A/K_5)
 \end{aligned}
 \quad (3)$$

where

$$\phi = \frac{W_A}{\rho_A} + \frac{W_B}{\rho_B} + \frac{W_C}{\rho_C} + \frac{W_T}{\rho_T}$$

and

$$K_m = \frac{B_m}{B_{m+1}} \quad (m = 1, 3, 5)$$

Catalyst deactivation must also be incorporated into this model when it becomes significant to the catalyst activity. It is well known that carbon formation in catalytic cracking is responsible for loss in activity and must be incorporated into kinetic models for catalytic cracking. However, carbon formation which is the primary cause for catalytic deactivation in the cracking reaction is also considered to be the cause for deactivation of this isomerization reaction. Voorhies (1945) was the first to consider catalyst deactivation and incorporate it into a reaction model. More recently others, including Weekman and Nance (1970) and Ozawa and Bischoff (1968), have considered catalyst deactivation. These studies have generally assumed the deactivation function to be independent of the total feed over the catalyst. However, in this study it was observed that the activity and therefore the rate constant  $B_i$  could be best correlated with the expression

$$B_i = B_{0i} e^{-\alpha(\phi/\tau)} \quad (4)$$

for a given process time  $\theta$ , space time  $\tau$ , and initial rate constant  $B_{0i}$ . This expression is a function of the total feed which passes over the catalyst.

The objective of the experimental study was to obtain data for concentration (or toluene-free mole fraction) of system components as a function of space time which could be used with Equations (3) and (4) to establish the model parameters.

## EXPERIMENTAL RESULTS

### Isomerization

Experimental tests were made at fixed conditions of 505°K,  $2.76 \times 10^5$  N/m<sup>2</sup> and constant feed mole composition near 76% ortho-xylene and 24% toluene. Possible variations in catalyst activity from sample to sample were evaluated by repeating several experiments with different samples. Results indicated no change in catalyst activity from sample to sample. Each individual experiment was selected for a different space velocity  $1/\tau$  (kg/s/kg). Product samples were collected over a period of time from the beginning of the experiment and analyzed. This defined the relationship between the toluene-free mole fraction of each isomer and the oil throughput  $\theta/\tau$ . Thus each experiment resulted in a graph of mole fraction versus  $\theta/\tau$  for each isomer.

A plot of the logarithm of the mole percent ortho-xylene remaining in the product versus oil throughput  $\theta/\tau$  is shown in Figure 4. The data are shown plotted for several values of liquid space velocity kg/s/kg over a range from  $0.286 \times 10^{-3}$  to  $3.823 \times 10^{-3}$ . The increasing concentration of ortho-xylene in the product at increasing values of  $\theta/\tau$  is indicative of the decreasing activity of the catalyst. The reason for the change in slope is possibly due to a difference in activity of the active sites on the catalyst and the rate of carbon deposited on these catalyst sites. A similar experimental observation was made by Ozawa and Bischoff (1968) in a catalytic cracking deactivation study. For future investigation it may also be of significance to observe that the change in slope appears to be a function of space velocity as it occurs at lower

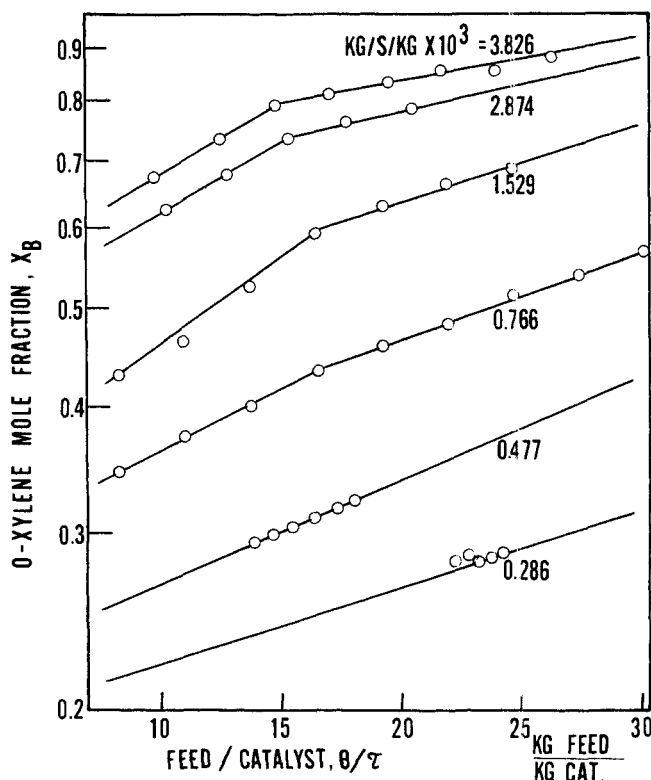


Fig. 4. O-Xylene composition versus feed/catalyst ratio for various space velocities.

values of oil throughput as the space velocity is increased. A plot of the logarithm of the mole percent meta-xylene formed in the product versus oil throughput  $\theta/\tau$  is shown in Figure 5. These data correspond to the same conditions for ortho-xylene as shown in Figure 4. Similar data for para-xylene are shown in Figure 6.

### Selectivity

One of the most significant experimental results obtained was the high selectivity of the catalyst system to the isomerization reaction at the exclusion of the transalkylation or disproportionation reaction. This high selectivity had not been observed with *H*-mordenite previously (Bowes, et al., 1971) when it was observed with other special zeolites. There were no trimethylbenzene compounds detected in any of the products analyzed. The only component which appeared in the product other than xylenes or toluene was benzene. A plot of benzene composition in the product as a function of process time is shown in Figure 7. The level of benzene produced showed only a slight trend as the activity of the catalyst changed. An indication of the level of benzene being produced and the toluene level in the products is illustrated in Figure 8. The line-bar indicates the range of values observed and the point represents the average over the process time at the particular space velocity. The dashed line shows the feed composition. There was a very slight (but not significant) indication of a decrease in toluene composition from feed to product analysis. It is felt that the small amount of benzene and carbon formed result from the disproportionation of toluene initially present.

## ANALYSIS OF RESULTS

Data in the form of mole fraction as a function of space time at a constant level of deactivation were required before Equation (3) could be applied to the analysis.

These data were obtained from the previously described experimental results in the following manner. Values of isomer mole fraction and space velocity were determined

from Figures 4, 5, and 6 at constant values of oil throughput ( $\theta/\tau$ ). The values of isomer mole fraction were then

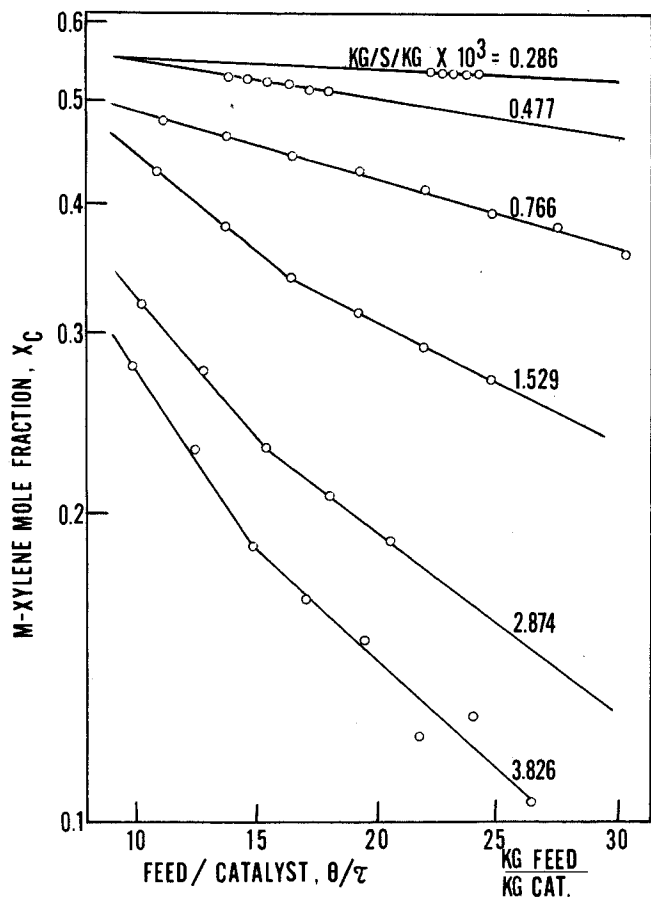


Fig. 5. M-Xylene composition vs. feed/catalyst ratio for various space velocities.

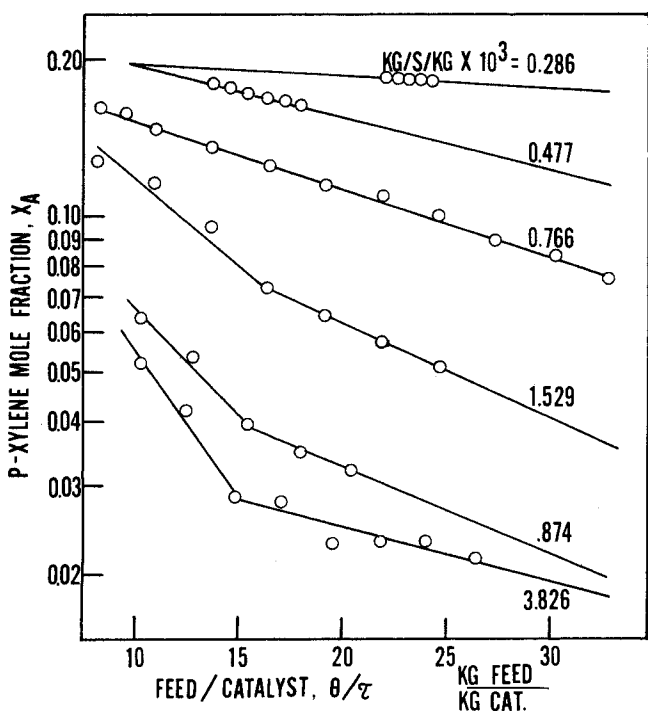


Fig. 6. P-Xylene composition vs. feed/catalyst ratio for various space velocities.

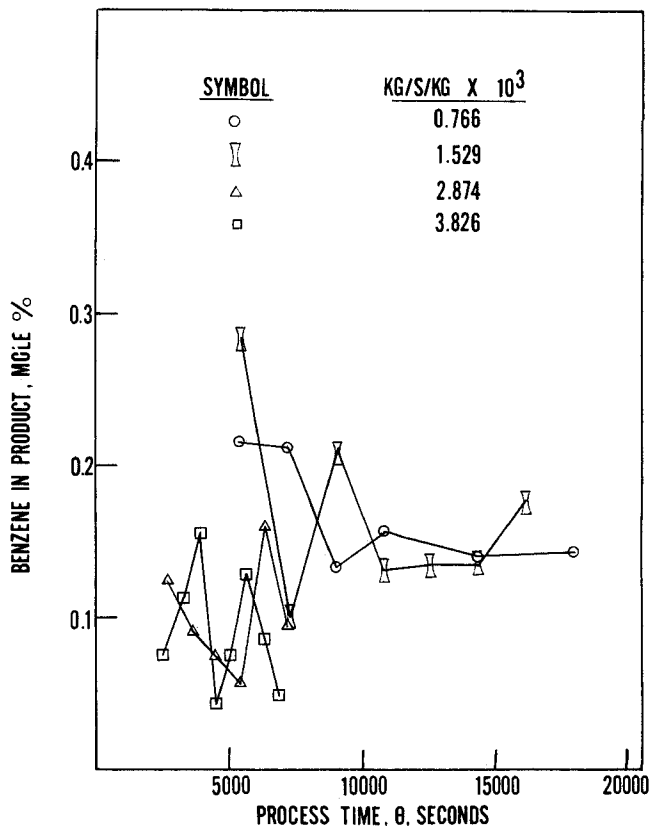


Fig. 7. Benzene composition in products vs. process time.

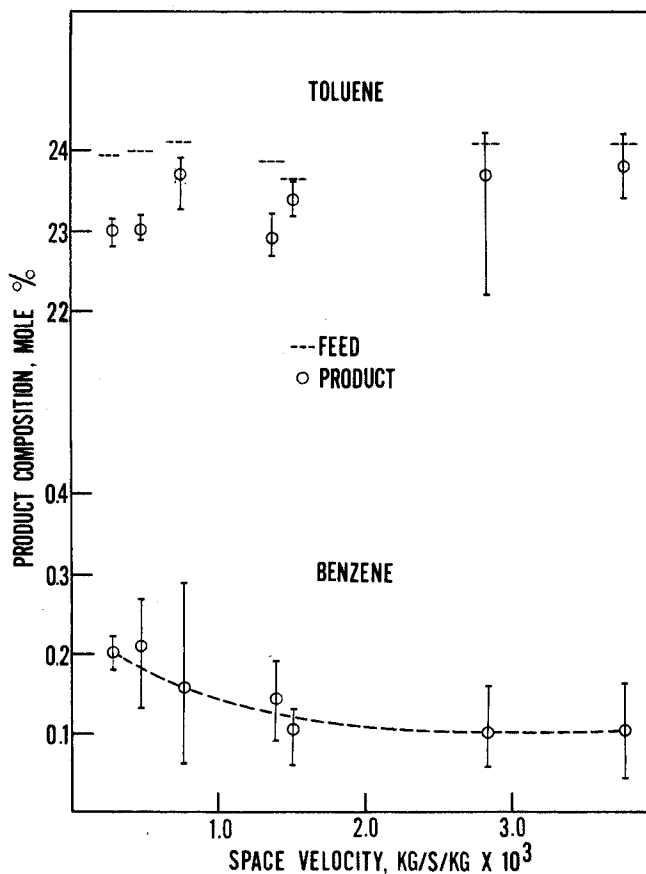


Fig. 8. Benzene and toluene product distribution vs space velocity.

plotted versus space time and a smooth curve mechanically placed through the points. A plot of such a set of data at a value of  $(\theta/\tau)$  of 10 is shown in Figure 9. This plot shows the rate of disappearance of ortho-xylene and the rate of appearance of meta-xylene and para-xylene as a function of reactor space time. These curves show that the rate of formation of meta-xylene is much greater than the rate of formation of para-xylene. Note for this value of  $(\theta/\tau)$  the system is approaching thermodynamic equilibrium at high values of space time. An 80% achievement of para-xylene equilibrium was obtained at a space velocity of  $0.766 \times 10^{-3}$  kg/s/kg and a process time of 7200 sec. This type of plot was repeated at selected values of  $(\theta/\tau)$  from 10 to 30. A similar plot at  $(\theta/\tau) = 25$  is shown in Figure 10. A comparison with Figure 9 shows the effect of catalyst deactivation. The system is farther away from achieving equilibrium because of the catalyst deactivation.

#### Solving the Rate Equations for the Best Parameter Values

Values for the rate constants were determined using the method and a modified form of the Fortran code supplied by Himmelblau et al. (1967). For this method the system of rate equations of Equation (3) can be written in a more compact notation as

$$\frac{dX_j}{d\tau} = \sum_{k=1}^6 B_k R_{jk} \quad (j = A, B, C) \quad (5)$$

where  $R_{jk}$  represents the function of mole fraction corresponding to each rate constant for each equation.

Each of Equations (5) may be integrated with respect to space time from  $\tau_0$  to  $\tau_i$  to give

$$X_j(\tau_i) - X_j(\tau_0) = \sum_{k=1}^6 B_k \int_{\tau_0}^{\tau_i} R_{jk} d\tau \quad (6)$$

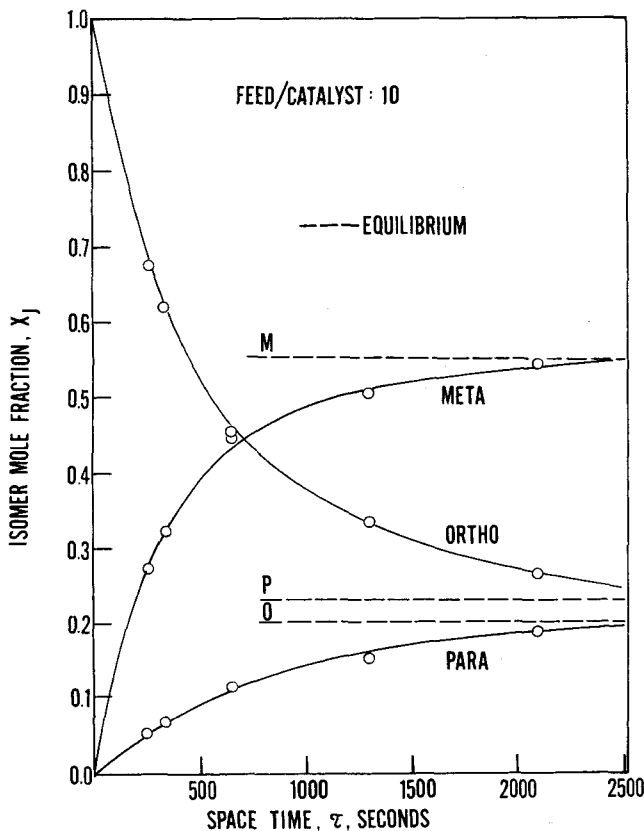


Fig. 9. Xylene composition vs space time at  $\theta/\tau = 10$ .

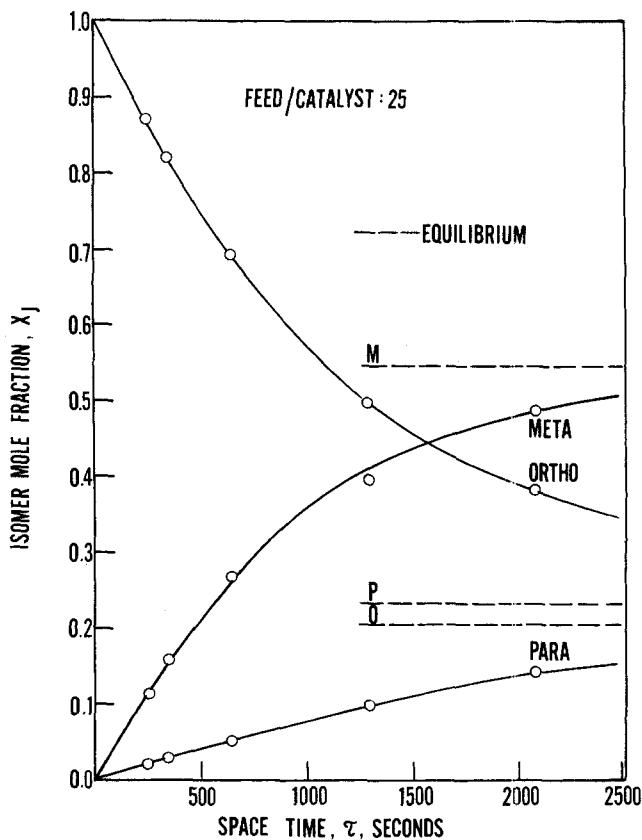


Fig. 10. Xylene composition vs. space time at  $\theta/\tau = 25$ .

$$(i = 1, 2, \dots, P)$$

$$(j = A, B, C)$$

where  $P$  is the number of time intervals between the times at which the mole fractions were evaluated and  $B_k$  is assumed constant even though it is a slowly varying function of  $\tau$ .

Equation (6) can be written as

$$Z_{ij} = \sum_{k=1}^6 B_k \int_{\tau_0}^{\tau_i} R_{jk} d\tau \quad (7)$$

where

$$Z_{ij} = X_j(\tau_i) - X_j(\tau_0)$$

The best value of the coefficients  $B_k$ 's can be estimated by minimizing the sum of the squares of the deviations between the measured value of mole fraction change  $Z_{ij}$  and the calculated value of mole fraction change  $\hat{Z}_{ij}$  for each equation and each time increment as indicated in Equation (8).

$$\text{Minimize } \sum_{i=1}^P \sum_{j=A}^C [(Z_{ij} - \hat{Z}_{ij})]^2 \quad (8)$$

Each of the figures of mole fraction versus space time were used to obtain the data introduced into the computer program described. A large number of space time increments were chosen to obtain the maximum accuracy in representing the smoothed curves.

The rate constants obtained from each of the plots of mole fraction versus space time, each for a different value of  $(\theta/\tau)$ , are given in Table 2. The sum of the squares of the difference between measured and calculated values of mole fraction change are also shown for each value of

$(\theta/\tau)$ . The range of values of the sum of the squares of the deviations of  $10^{-3}$  to  $10^{-5}$  show a very good agreement between the model and the data introduced into the analysis.

#### Interpretation of Results

A comparison of the values of the constants  $B_3$  and  $B_2$  in Table 3 shows that the rate of isomerization of ortho-xylene to meta-xylene ( $B_3$ ) is initially 12 times the magnitude of the rate of isomerization of ortho-xylene to para-xylene ( $B_2$ ) but is reduced to half this magnitude as the catalyst deactivates.

A comparison of the values of the constants  $B_6$  and  $B_1$  shows that the rate of isomerization of para-xylene to meta-xylene ( $B_6$ ) is initially about ten times the rate of para-xylene to ortho-xylene ( $B_1$ ) but decreases to half of this magnitude over this period of catalyst deactivation.

Meta-xylene reacts at about the same rate to both ortho-xylene ( $B_4$ ) and para-xylene ( $B_5$ ) with possibly a slightly greater rate to the ortho-xylene as indicated by a comparison of the values for  $B_4$  and  $B_5$ . In contrast to the two previous comparisons, in which the ratio of the constants being compared became smaller with deactivation, there is a trend in the data indicating the ratio of  $B_4$  to  $B_5$  to be getting larger as the catalyst deactivates. The magnitude of the change is considerably less than observed for  $B_3/B_2$  and  $B_6/B_1$ .

The results are consistent with the picture of a system in which the isomerization easily takes place in a series of 1, 2-methyl shifts (that is, meta to ortho and meta to para) but occurs with difficulty in the 1, 3-methyl migration (that is, para to ortho). Similar results have been observed with two different catalyst systems (Brown and Jungk, 1955; Silvestri and Prater, 1964). The observed change in the relative rates among the isomers with cata-

TABLE 2. RATE CONSTANTS FOR ORTHO-XYLENE ISOMERIZATION ( $m^3/kg-s$ )  $\times 10^6$

$\theta/\tau$	$B_1$	$B_2$	$B_3$	$B_4$	$B_5$	$B_6$	$\Sigma(Z - \hat{Z})^2$
10	0.146	0.166	1.879	0.726	0.657	1.488	$1.1 \times 10^{-3}$
15	0.095	0.108	1.320	0.510	0.532	1.211	$3.4 \times 10^{-4}$
20	0.109	0.124	0.985	0.380	0.328	0.748	$1.0 \times 10^{-4}$
25	0.101	0.114	0.797	0.308	0.248	0.564	$4.9 \times 10^{-5}$
30	0.087	0.099	0.656	0.253	0.207	0.472	$2.7 \times 10^{-5}$

TABLE 3. RATE CONSTANT RATIOS FOR ORTHO-XYLENE ISOMERIZATION

$\theta/\tau$	$B_3/B_2$	$B_6/B_1$	$B_4/B_5$
10	11.3	10.2	1.10
15	12.2	12.7	0.96
20	7.95	6.87	1.16
25	6.97	5.61	1.24
30	6.63	5.43	1.22

TABLE 4. DECAY MODEL CONSTANTS FOR ORTHO-XYLENE ISOMERIZATION (505°K,  $2.76 \times 10^5 N/m^2$ , 23 mole % toluene, H-mordenite)

	$\alpha \times 10^8$	$B_{0i}, (m^3/kg-s) \times 10^6$
$B_1$	-0.703	0.186
$B_2$	-0.703	0.211
$B_3$	-1.45	2.900
$B_4$	-1.45	1.154
$B_5$	-1.706	1.222
$B_6$	-1.706	2.781

lyst deactivation could indicate that the 1, 2-methyl shifts are occurring on relatively more active sites and the 1, 3-methyl migration occurs on relatively less active sites and the rate of deactivation is greater with the more active site.

#### Correlation for Catalyst Deactivation

The model for catalyst deactivation can be written in a linear form as

$$\ln B_i = \ln B_{0i} - \alpha(\theta/\tau)$$

If this model is representative of the experimental results, a linear curve should result from a plot of  $\ln B_i$  versus  $(\theta/\tau)$ . A plot of the calculated values for  $B_1$ ,  $B_3$  and  $B_5$  is shown in Figure 11. The calculated values do follow the linear plot of the model satisfactorily and the model is therefore accepted as being representative of the observed data. The deactivation constant is obtained from the slope of the linear plot and the initial value of the reaction rate constant  $B_{0i}$  is obtained from the intercept. Values of  $\alpha$  and  $B_{0i}$  for each rate constant are given in Table 4.

It has previously been observed that the conversion of meta to para and meta to ortho occurs more easily than the conversion between ortho and para. This was indicated by the magnitude of  $B_3$ ,  $B_4$ ,  $B_5$ , and  $B_6$  relative to  $B_1$  and  $B_2$ . Also the values of  $\alpha$  associated with  $B_3$ ,  $B_4$ ,  $B_5$ , and  $B_6$  are all of approximately the same magnitude and are about twice the magnitude of the  $\alpha$  values associated with  $B_1$  and  $B_2$ . Thus this indicates that the rate of deactivation of  $B_3$ ,  $B_4$ ,  $B_5$ , and  $B_6$  is greater than  $B_1$  and  $B_2$ .

These observations are again consistent with a picture of the 1, 2 methyl shifts occurring on relatively more active catalyst sites and the 1, 3 methyl migration occurring on less active sites with the rate of deactivation being

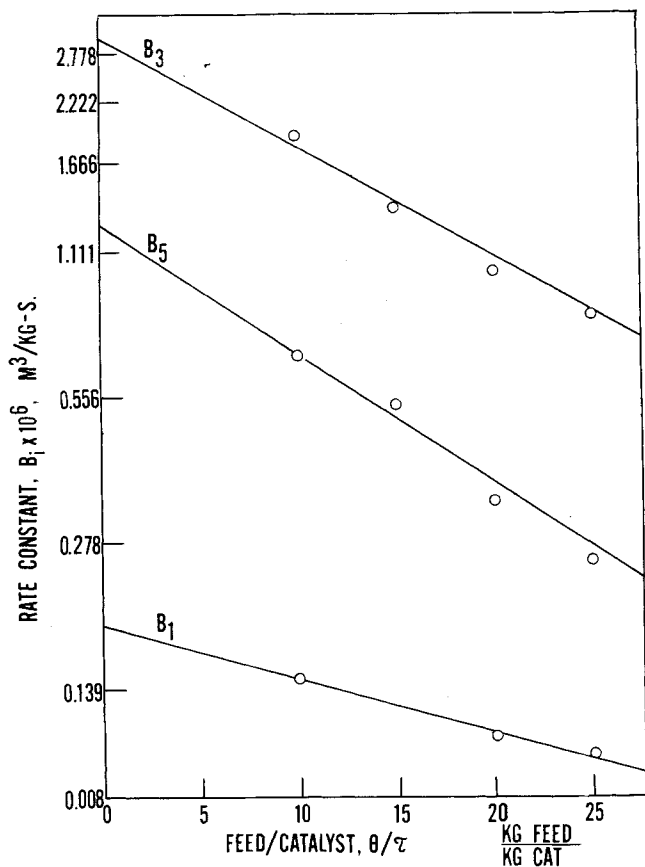


Fig. 11. Catalyst deactivation as a function of oil/catalyst throughput.

greater with the more active site.

The final kinetic model incorporating reaction rate constants and catalyst deactivation parameters can be expressed in the compact form as

$$r_j = \frac{1}{\phi} \sum_{k=1}^6 B_{0k} e^{-\alpha_k(\theta/\tau)} R_{jk} \quad (j = A, B, C) \quad (10)$$

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#### NOTATION

- A = para-xylene symbol  
 B = ortho-xylene symbol  
 $B_k$  = reaction rate constant,  $m^3/kg\cdot s$   
 C = meta-xylene symbol  
 $C_j$  = isomer concentration, moles/ $m^3$   
 $N_j$  = isomer flow rate, moles/s  
 P = number of time intervals between which mole fractions were evaluated  
 $r_j$  = rate of appearance of  $j$ , (moles  $j$ )/(kg cat) (s)  
 $R_{jk}$  = function of mole fraction corresponding to each rate constant, moles  $j$   
 $W_c$  = catalyst weight, kg  
 $W_j$  = weight fraction, kg/total kg  
 $X_j$  = isomer mole fraction, moles/(total moles xylene)  
 $Z_{ij}$  = measured value of mole fraction change  
 $\hat{Z}_{ij}$  = calculated value of mole fraction change

#### Greek Letters

- $\alpha$  = catalyst deactivation constant  
 $\theta$  = process time, s  
 $\rho_j$  = density,  $kg/m^3$   
 $\tau$  = space time, (kg cat) (s)/(kg feed)  
 $\phi$  =  $1/\text{average density}$ , defined in Equation (3)

#### Subscripts

- $i$  = time interval index  
 $j$  = component index  
 $k$  = rate constant index  
 $m$  = index on rate constant to define equilibrium constant  
 A, B, C, T = component index for para-, ortho-, and meta-xylene and toluene  
 0 = parameter for fresh catalyst, or initial time

#### LITERATURE CITED

- Allan, D. E., "The Dehydrogenation and Isomerization of Cyclohexane Over a Platinum Alumina Mordenite Catalyst," Ph.D. dissertation, Louisiana State Univ., Baton Rouge (1970).  
 Allen, Robert, and Larry Yats, "Kinetics of Three-Compound Equilibria. II. The Isomerization of Xylene," *J. Am. Chem. Soc.*, **81**, 5289 (1959).  
 Amemiya, Tozo, "Catalytic Isomerization of Xylenes," *Bull. Japan Petrol. Inst.*, **3**, 14 (1961).  
 Bowes, Emmerson, and J. J. Wise, "Isomerization and Disproportionation of Aromatic Hydrocarbons," U.S. Patent 3,578,723 (1971).  
 Brown, Herbert, and Hans Jungk, "The Isomerization of O- and P-Xylenes and some Related Alkybenzenes Under the Influence of Hydrogen Bromide and Aluminum Bromide; the

- Relative Isomerization Aptitudes of Alkyl Groups," *J. Am. Chem. Soc.*, **77**, 5579 (1955).  
 Condon, F. E., "Catalytic Isomerization of Hydrocarbons," in *Catalysis*, Ch. 6, Reinhold, New York (1958).  
 Ciapetta, F. G., and J. B. Hunter, "Isomerization of Saturated Hydrocarbons, Paraffins," *Ind. Eng. Chem.*, **45**, 147 (1953).  
 Grandio, P., F. H. Schneider, A. B. Schwartz, and J. J. Wise, "Xylene Isomerization Over Zeolite Catalysts," paper presented at Am. Chem. Soc. Meeting, Div. Petrol. Chem., Atlantic City (1971).  
 Hansford, R. C. and J. W. Ward, "The Nature of Active Sites on Zeolites," *J. Catal.*, **13**, 316 (1969).  
 Hanson, L. L., and A. J. Engel, "Kinetics of Xylene Isomerization Over Silica-Alumina Catalyst," *AIChE J.*, **13**, 260 (1967).  
 Harrison, D. P., J. W. Hall, and H. F. Rase, "An Automatic Precision Microreactor," *Ind. Eng. Chem.*, **57**, 18 (1965).  
 Himmelblau, D. M., C. R. Jones and K. B. Bischoff, "Determination of Rate Constants for Complex Kinetic Models," *Ind. Eng. Chem. Fundamentals*, **6**, 539 (1967).  
 Hopper, J. R., "A Study of the Catalytic Hydroisomerization Reactions of N-Pentane and Cyclohexane Over Structurally Modified Mordenites," Ph.D. dissertation, Louisiana State Univ., Baton Rouge (1969).  
 ———, and Alexis Voorhies, Jr., "Hydroisomerization of Cyclohexane and n-Pentane Over Series of Mordenite Catalysts of Varying Silica-Alumina Ratio," *Ind. Eng. Chem. Product Research Develop.*, **11**, 294 (1972).  
 Kemp, J. D., "Manufacture of Xylene Isomers," U.S. Patent 2,527,824 (1950).  
 Lanewala, M. A. and A. P. Bolton, "The Isomerization of the Xylenes Using Zeolite Catalysts," *J. Org. Chem.*, **34**, 3107 (1969).  
 Matsumoto, H., and Y. Mortia, "Zeolite Catalysts for the Reaction of Aromatic Hydrocarbons," *Bull. Jap. Petrol. Inst.*, **10**, 8 (1968).  
 Matsumoto, H., J. Take and Y. Yoneda, "Linear Free Energy Relationships in Heterogeneous Catalysis VIII. Isomerization of Alkybenzenes Over Solid Acid Catalysts," *J. Catal.*, **11**, 211 (1968).  
 McCaulay, D. A., *Friedel Crafts and Related Reactions*, **2**, Interscience, N. Y. (1964).  
 Ozawa, Y. and K. Bischoff, "Coke Formation Kinetics on Silica-Alumina Catalyst," *Ind. Eng. Chem. Process Design Develop.*, **7**, 67 (1968).  
 Pitts, P. M., J. E. Conner, Jr. and L. N. Leum, "Isomerization of Alkyl Aromatic Hydrocarbons," *Ind. Eng. Chem.*, **47**, 770 (1955).  
 Rabo, J. A., P. E. Pickert, and R. L. Mays, "Pentane and Hexane Isomerization," *Ind. Eng. Chem.*, **53**, 733 (1961).  
 Shigemura, D. S., "A Kinetic Study of the Catalytic Isomerization of Xylene Over Hydrogen Mordenite," M.E.S. thesis, Lamar Univ., Beaumont, Texas (1972).  
 Schneider, F. H., private communication of catalyst analysis (1971).  
 Silvestri, A. J. and C. D. Prater, "Kinetic Studies of the Selectivity of Xylene Isomerization Over Silica-Alumina Catalyst," *J. Phys. Chem.*, **68**, 3268 (1964).  
 Taylor, W. J., D. D. Wagman, M. G. Williams, K. S. Pitzer, F. D. Rossini, "Heats, Equilibrium Constants, and Free Energies of Formation of the Alkylbenzenes," *J. Research Natl. Bur. Standards*, **37**, 95 (1946).  
 Voorhies, A., Jr., "Carbon Formation in Catalytic Cracking," *Ind. Eng. Chem.*, **37**, 318 (1945).  
 ———, and R. G. Beecher, "Hexane Isomerization," *Ind. Eng. Chem. Product Research Develop.*, **8**, 366 (1969).  
 Voorhies, A., Jr., and P. A. Bryant, "Hydroisomerization of Normal Pentane Over a Zeolite Catalyst," *AIChE J.*, **14**, 852 (1968).  
 Weekman, V. W., Jr. and D. M. Nace, "Kinetics of Catalytic Cracking Selectivity in Fixed, Moving, and Fluid Bed Reactors," *AIChE J.*, **16**, 397 (1970).  
 Wise, J. J., "A Study of the Catalytic Hydroisomerization Reactions of N-Pentane and Cyclohexane Over Structurally Modified Mordenites," U. S. Patent 3,377,400 (1968).

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