# DETERMINATION OF THE REACTION REGION FOR ISOMERIZATION

OF XYLENES ON H-FORM Y ZEOLITE

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An important problem in catalysis is the question of the role of diffusion and of the region where reaction takes place. Without a solution to this it is impossible to understand the mechanism of the action of zeolite catalysts and to plan further increases in their effectiveness. The complexity of this problem in the case of zeolites arises from the lack of any experimental criteria for determining the region where the reaction proceeds. We have shown [1] in a study of isomerization and diffusion of xylenes in HY zeolite that the effectiveness factor of the catalyst amounts to 0.1 which points to the diffusion region. It is, however, difficult to reconcile this conclusion with other experimental factors [1]: the isomerization activation energies are different for the different isomers of xylene; the curves of the approach of the reaction system to equilibrium coincide on HY [1] and on Ni/Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub> [2] which differ in pore structure.

We suggested new criteria [3] for determining the reaction region in zeolites, based on the variation of the general and observed specific activity of the catalyst with the number of active centers. The present work is concerned with the determination of the reaction region for the isomerization of xylenes on H-form Y zeolite making use of these criteria.

### EXPERIMENTAL

The xylene isomerization reaction was studied in an impulse microreactor in a current of He (25 ml/min) from which traces of moisture were removed by means of zeolite in a trap at -196°C. The reaction was studied over the temperature range 350-500°C. In the course of the reaction, 4-5 impulses of the initial hydrocarbon (o-, m-, or p-xylene) were applied to the reactor, the volume of each impulse being ~10  $\mu$ l. The reaction products were frozen out in a trap at -196°C, dissolved in n-pentane, and analyzed by GLC. To determine the quantity of the initial hydrocarbon consumed in the formation of coke or high-molecularweight polymeric deposits, n-heptane was added as internal standard. It was shown that 20-30% of the hydrocarbon passing through was converted to coke.

The catalysts studied were NaY zeolites decationated to the extent of 17, 38, 55, 75, and 98%. The quantity of Na<sup>+</sup> cation found in the larger cavities of the zeolite at the different degrees of decationation was determined by extraction with an excess of NH<sub>4</sub>Cl solution at ~20°C [4]. Before the experiment, a weighed sample of the catalyst (15-20 mg) was heated for 1 h in a current of He at 500°C, increasing the temperature from ambient to 500°C at a rate of 20 K/min.

The rate constant k for the xylene isomerization was calculated from the equation used for the impulse method in [5]. The specific activity of the catalyst  $k_{\rm sp}$  was found by dividing k by the number of acidic centers in the larger cavities of the Y zeolite which was taken as the number of Na<sup>+</sup> ions replaced by protons.

## RESULTS AND DISCUSSION

The study showed that the composition of the products formed is practically independent of the number of impulses of hydrocarbon passed through the catalyst. Rate constants for the reaction were calculated on the basis of the yields of reaction products from the isomerization of different xylene isomers. Since these constants were obtained in independent experiments, it was necessary to make sure that the calculated values were correct. It is not difficult to show that for a triangular reaction scheme for xylene isomerization

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Fig. 1. Variation of k (1, 2) and  $k_{sp}$  (3, 4) for xylene isomerizations on HY zeolite at 500°C with  $v_{H}$ +: a) o- to m- (1, 3) and p- (2, 4); b) m- to p- (1, 3) and o- (2, 4); c) p- to m- (1, 3) and o- (2, 4) isomers.



the product of the rate constants on passing round the scheme in a clockwise direction  $(\vec{k})$  must be equal to the product of the rate constants in an anticlockwise direction  $(\vec{k})$ , i.e.,

$$k_{o-m}k_{m-p}k_{p-o} = k_{o-p}k_{p-m}k_{m-o}$$

The experimental results obtained at 500°C are satisfied by this condition (Table 1).

The variations of k (mole/g·sec·MPa) and  $k_{sp}$  (sec<sup>-1</sup>·MPa<sup>-1</sup>) with the average number of protons  $v_{H}$ + in its larger cavities in the isomerization of o- (Fig. 1a), m- (Fig. 1b), and p-xylene (Fig. 1c) provide evidence that diffusion of the hydrocarbon in the pores of the zeolite is without effect on the kinetics of the reaction. If the opposite were the case, k would not depend on the number of acid centers and  $k_{sp}$  would decrease with increase in  $v_{H}$ + [3].

At the same time, it should be said that the curves obtained (Fig. 1) do not correspond with any exactness to those theoretically predicted [3] for a kinetic region for the course of the reaction where k must increase in proportion to the number of active centers N, and  $k_{sp}$  remain constant. It can be suggested that the more rapid increase of k with N and the increase in  $k_{sp}$  which are observed (Fig. 1) are explained by non-uniformity of the acidic centers of the zeolite, and particularly by the increase in the strength of the acidic centers with increase in decationation; the activation energy of the isomerization reaction must drop with increase in the extent of decationation.

To verify this suggestion we studied the isomerization of m-xylene in the temperature range 350-500°C. The activation energy of the isomerization of m- to o- and p-xylenes was calculated from the temperature dependence of the rate constant for this reaction and it was shown that the activation energy decreases with increase in  $v_{\rm H}$ + or, in other words, with increase in the extent of decationation of the zeolite (Fig. 2).



Fig. 2. Variation of the activation energy for the isomerization of mxylene to o- (1) and p- (2) isomers with  $v_{\rm H}$ +.

TABLE 1. Rate Constants for Xylene Isomerization at 500°C

Extent of decation- ation, %	k·10°, mole/g • sec • MPa								
	<sup>k</sup> o-m	$k_{m-p}$	<sup>k</sup> p-0	k	<sup>k</sup> o-p	<sup>h</sup> p-m	<sup>k</sup> m-0	k	
17 38 55 75 98	4,86 9.30 12.00 16.00 47,00	0,89 3.90 4.90 8,10 18,20	0,33 1,50 1.40 3.70 12,90	1,43 54.40 82,30 479.50 11034,70	$\begin{array}{c} 0.60 \\ 1.50 \\ 2.50 \\ 4.10 \\ 23.00 \end{array}$	$2.00 \\ 7,00 \\ 6,80 \\ 15,40 \\ 34,70$	1,60 3,70 4,20 6.80 15,90	1.92 38.80 71.40 429,30 12689,80	

Thus, the manner in which k and  $k_{SP}$  vary with the number of acidic centers points to a kinetic region for the course of the isomerization of xylenes on HY zeolite. Other experimental factors also agree with such a conclusion: activation energies for different xylene isomers differ considerably one from another; from o- and p-xylenes, m-xylene is formed in the first instance and this is subsequently isomerized into p- and o-xylenes respectively; the lower temperature range at which thermal desorption of xylenes takes place from HY zeolite compared with the reaction temperature [1].

The low values of the effectiveness factors  $\eta$  in the isomerization of xylenes on HY zeolite seem to point to the so-called pseudodiffusion region for the reaction [3]. The different correlations between the regions in which the reaction proceeds found from  $\eta$ and through the dimensions of the reaction zone  $l_r$  [3] in relation to the general and specific activities of the catalyst and also to the number N are given in Table 2. It can be seen that with small N, with a high  $k_{SD}$  (Table 2, No. 1), and with large N, with a reduced activity (Table 2, No. 4), the regions in which the reaction proceeds, based on  $\eta$  and on  $l_r$  are not in agreement. In [3], these cases were classed as pseudokinetic and pseudodiffusion regions, respectively. Two other cases, namely, low  $k_{sp}$  with small N (No. 2) and high  $k_{sp}$  with large N (No. 3), are correctly evaluated from both  $\eta$  and  $l_r$ . The guestion arises, to what extent are cases 1 and 4 likely to exist for nonzeolite catalysts. Since the coefficient of Knudsen diffusion amounts on average to  $10^{-3}$  to  $10^{-2}$  cm<sup>2</sup>/sec [6] (in comparison with  $10^{-14}$  to  $10^{-10}$  cm<sup>2</sup>/sec for diffusion in microporous zeolites [6]), it is clear that  $l_r$  for the usual porous catalysts will be greater by several orders of magnitude than  $l_r$  for the case of zeolites. Hence there is a small probability of the existence of pseudokinetic and pseudodiffusion regions of reaction in the case of nonzeolite porous catalysts. It should be noted, however, that the presentation given is of a qualitative nature and each case requires more detailed consideration.

In the case of zeolites, the diffusion coefficient D and the true  $k_{sp}$  can depend on N in a different way. Thus, for example, in a narrow-pore zeolite such as mordenite or pentasil, D can depend on the presence or absence of alkali metal cations in their channels and in the case where the acidic centers are nonuniform this leads to a change in the true ksp. An analogous situation can arise in metal zeolite catalysts when the contents of the metal are increased; this leads to diffusion problems and also a change in the true ksp as a result of a change in the dispersion of the metal. In the light of this it was thought desirable to examine the different variants of the dependence of k and the observed  $k_{sp}$  of zeolites on N.



Fig. 3. Dependence of k (I) and  $k_{SP}$  (II) for a catalyst on the number of active centers (III) for different variants of kinetic and diffusion regions for the reaction on zeolites (Table 3).

TABLE 2. Variation of Catalyst Effectiveness Factors and Reaction Region with General and Specific Activities, Reaction Zone Dimensions, and Number of Active Centers\*

No.	k	<sup>k.</sup> sp	Ν	<sup>l</sup> r	η	Reaction region based on l <sub>r</sub>
1	S	L	S	<p< td=""><td>1</td><td>D</td></p<>	1	D
2	S	S	S	>p	1	K
3	L	L	L	<p< td=""><td>0</td><td>D</td></p<>	0	D
4	L	S	L	>p	0	K

\*S = small value, L = large value,  $\rho$  = zeolite crystal dimensions, D = diffusion region, K = kinetic region.

In Table 3, we consider the following variants of the changes in D and the true  $k_{\rm Sp}$  on increasing N: constant, increasing (+) and decreasing (+). In addition, for the true  $k_{\rm Sp}$  passage through a maximum ( $\Lambda$ ) or a minimum (V) is also added. The figures in the Table correspond to the numbers of the variants. To simplify the analysis we shall consider only the forward and reverse proportional dependence of D and the true  $k_{\rm Sp}$  on N. We shall make the same stipulation for the ascending and descending branches in the case of extreme dependence. To clarify the nature of the dependence of k and the observed  $k_{\rm Sp}$  on N one should take account of the fact that under constant conditions the reaction rate in the diffusion region is proportional to  $\sqrt{kD}$  [7], and in the kinetic region it is proportional to k and clearly does not depend on D.

The variation of k and the observed  $k_{sp}$  with N, with allowance for the assumptions which we have made, are set out in Fig. 3. The numbers under the diagrams correspond to the variant numbers in Table 3. As can be seen, several variants give identical diagrams (for example 1, 7, 9, and 3, 8, 10) for the variation of k and  $k_{sp}$  with N. In these cases it is also desirable to clarify the nature of the change of D with N and the reaction rate with D.

TABLE 3. Variants in the Dependence of the True Specific Activity and Diffusion Coefficient in Kinetic (Numerator) and Diffusion (Denominator) Reaction Regions on Zeolites

	<sup>k</sup> sp							
D	const	Ţ	Ļ	│ <u>∧</u>	$\sim$			
const	<u>1</u> 6	<u></u> 9	$\frac{3}{10}$	4-11	$\frac{5}{12}$			
Ť	$\frac{1}{7}$	$\frac{2}{13}$	$\frac{3}{14}$	$\frac{4}{15}$	<u> </u>			
ţ	$\frac{1}{8}$	$\frac{2}{17}$	$\frac{-3}{-18}$	4	$\frac{5}{20}$			

The dependence of k and  $k_{sp}$  on the number of acidic centers found in the case of xylene isomerizations on HY zeolite (Fig. 1) corresponds to variant 2, i.e., to a kinetic region for the reaction with the true  $k_{sp}$  increasing with N. The slight difference here between the observed curve of  $k_{sp}$  against N (Fig. 1) and the predicted curve (Fig. 3, variant 2) is explained by the decrease in activation energy for xylene isomerization as N increases, i.e.,  $k_{sp}$  changes exponentially with N, and not proportionately as was assumed for variant 2.

# CONCLUSIONS

1. Intracrystal diffusion of the reagent molecules does not constitute a limiting factor in the isomerization of xylenes on HY zeolite in an impulse microreactor at 350-500°C.

2. The different variants of the dependence of the general and observed specific activities of a zeolite catalyst on the number of active centers have been considered and it has been shown that on the basis of the criteria suggested one can in most cases reliably judge whether the reaction is proceeding in the kinetic or the diffusion region.

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