# ROLE OF STRUCTURAL FACTORS AND ACIDITY IN CONVERSIONS OF ALKYLAROMATIC HYDROCARBONS ON HIGH-SILICA ZEOLITES

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The interest of research workers in recent years has been greatly aroused by zeolites of the pentasil family, which are distinguished by a high mole ratio  $SiO_2/Al_2O_3$  (> 30) and specific topology of the skeleton. Zeolites of this type have proven to be highly effective catalysts in commercially important processes such as the production of aromatic hydrocarbons and high-octane gasoline from methanol and low-molecular-weight olefins, conversions of alkylaromatic hydrocarbons, and many other reactions [1].

A promising direction in research in this field of catalysis on high-silica zeolites is the investigation of the relationship between the composition of the skeleton, the distribution of the acidic centers, and the catalytic activity of these systems. Earlier, in the example of xylene conversions, differences in catalytic activity and selectivity were found when comparing zeolites with similar composition but different structure: mordenites and USSR analogs of the pentasil-family zeolites, with the code designations TsVK and TsVM [2, 3].

Here we are reporting on a study of the catalytic properties of high-silica zeolites of the TsVK and TsVM types [4], an L zeolite, and mordenites in conversions of o- and mxylenes (OX and MX). The results obtained on the catalytic activity have been compared with data on the acidity as determined from measurements of the heat of adsorption of NH<sub>3</sub>.

#### EXPERIMENTAL

In this work, we used the H forms of the zeolites. Specimens of the superhigh-silica zeolites were prepared by heating for 16 h at  $540^{\circ}$ C to decompose organic components and were then treated with an NH<sub>4</sub>NO<sub>3</sub> solution to remove the Na. The dealuminized mordenites (DM) were prepared by treating the NH<sub>4</sub> form with HCl solutions. In preparing the NH<sub>4</sub> form of the L zeolite, the starting material was the K form. Before use in the catalytic experiments, all zeolite specimens were treated for 4 h at 500°C in a stream of air, and before the calorimetric measurements they were treated in vacuum for 100 h at 480°C. The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ration in these zeolite specimens varied from 5.2 for the L zeolite to 104 for the TsVK (Table 1).

Xylene conversions were studied in a single-pass flow system at atmospheric pressure [2]. The catalytic activity was characterized by the total conversion of xylenes. Also, by graphic differentiation, the initial rates were calculated for the conversion of xylenes into products of isomerization  $(r_i)$  and disproportionation  $(r_d)$ . As a measure of selectivity we used the ratio of concentrations of products of disproportionation and isomerization (d/i). The initial hydrocarbon feed rates were 0.01-0.2 mole/h·g of catalyst. The experiments were performed in a stream of carrier gas (He).

The heats of adsorption of  $NH_3$  (q) were measured at 30° and 300°C in a Calvet type microcalorimeter connected to a vacuum adsorption unit [5].

### DISCUSSION OF RESULTS

The data on the catalytic activity of the high-silica zeolites in OX conversion (Table 1) show that the L zeolite, with an 80% degree of decationization, was completely inactive at 250°C, even though at a higher temperature ( $360^{\circ}$ C) the conversion of OX on this zeolite

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Catalyst	SiO2 Al2O3	T., °C	Conver - sion, %	Product composition, %					
				ben- zene	tol- uene	xylene			
						<i>p</i> -	<i>m</i> -	0-	TIMB
TsVK-1	37	200	33,3	-	0,1	10,7	22,3	66,7	0, <b>1</b>
TsVK-2	60	250 200 250	70,5 23,3 58.2	- -	1,4 	22,0 5,6 17.3	17,7 40.0	23,3 76,7 41.8	1,4  0.4
TsVK-3	104	200 200 250	9,6 49,4	-	0,0  0.2	1,8	7,8 33.1	90,4 50.6	0.2
TsVM	40	200 200 250	6,0 37.6	-	0,1 0,5	1,4	4,5	94,0 62.4	0.5
$\rm NH_4M$	10	200	48,1 82,5		1,1	12,0	38,4	51,9 47.5	1,1
DM <b>-1</b> 4	14	200 200 250	76,6 88,6	0,1 0,5	4,1	17,5	50,3 34.7	23,4	4,6 23,3
DM <b>-1</b> 8	18	200 250	81,1 89.7	0,1	5,8 22,3	18,2 12,4	50,5 29.9	18,9	6,5 24.2
DM-68	68	$200 \\ 250$	59,6 87.2	0.7	4,1 18,9	8,4	41,3 33.6	40,4	15,8 22.1
NH4KL	5,2	250 250 360	<sup>7</sup> 1nact 74,8	ivě ( –	19,4	8,3	30,5	25,2	16,1

TABLE 1. Isomerization of o-Xylene on High-Silica Zeolite Catalysts ( $U_{OX} = 0.01 \text{ mole/h} \cdot g$ )

\*Trimethylbenzenes.

was approximately 75%. Far more active were the TsVK and TsVM zeolites, among which the highest activity was manifested by the TsVK-1 sample with a mole ratio  $SiO_2/Al_2O_3 = 37$ . Increases in this ratio to 68 and 104 gave lower activities.

The conversion of OX at 250°C on the TsVM zeolite synthesized without any organic cation was approximately one-half that on the TsVK-1 sample, which contained the same amount of aluminum in the skeleton. Further investigation is required to resolve the question of how the method of synthesis influences the formation of the active centers of pentasil-family catalysts.

A comparison of zeolites of different structural types indicates that the mordenite catalysts have the highest activity in xylene conversion. For example, with the decationized mordenite, the OX conversion at only 200°C was found to be 48.1%. After removal of approximately 20% of the Al from this zeolite, the OX conversion increased to 76.6%. Among the mordenites, the highest activity has been observed for samples with an approximately 50% dealuminization [3]. The mordenite catalyst DM-68 was lower in activity than the samples with higher contents of Al (DM-14 and DM-18) but was considerably more active than the TsVK-2, which had approximately the same composition.

The data of Table 1 indicates substantial differences in the ratio of concentrations of reaction products from isomerization disproportionation reactions on zeolitic catalysts of different types. In the presence of the L zeolites and mordenites, the isomerization is accompanied by considerable disproportionation, the contribution of which to the overall conversion increases with increasing reaction temperature, amounting to 20-48%. A picture of the changes in selectivity of conversion is given by plots of the ratio of disproportionation and isomerization product concentrations (d/i) as a function of the total conversion of OX (Fig. 1). As can be seen from Fig. 1 and the data reported in [3], on the zeolites of the pentasil family, the OX is subjected mainly to isomerization; the formation of small quantities of toluene and trimethylbenzenes is observed only in the high-conversion region. On the mordenites, disproportionation products appear even at fairly low conversions; on the L zeolites, even in the low-conversion region, the isomerization of the OX is accompanied by considerable disproportionation. Also shown in Fig. 1 are comparative data for Y zeolite [6], on which the disproportionation products are formed in large quantities even at low conversions; at OX conversions of approximately 30%, the values of d/i are near unity. The high activity of the Y zeolites in the disproportionation of toluene has been noted previously in [7].

From a comparison of the selectivities of the different zeolites at the same level of conversion of the original OX, we can conclude that the ratio of the isomerization and disproportionation rates is very much dependent on the structure of the zeolite skeleton.



Fig. 1. Ratio of concentrations of products from disproportionation and isomerization of o-xylene (d/i) as a function of conversion: 1) TsVK-2; 2) DM-68; 3) NH<sub>4</sub>KL; 4) REE-Y (data from [6]).

According to data obtained by x-ray structure analysis, the effective section of the wide straight channels in pentasils is no greater than 5.7 Å; for the mordenites it is approximately 6.5 Å, and for the L zeolites approximately 7.0 Å; for the faujasites, the diameter of the entrance apertures to the large void spaces is close to 8.2 Å [8]. The yields of disproportionation products increase in this same order. The absence of any disproportionation activity for the pentasils is probably related to the molecular sieve effect in the zeolites of this type. It has been suggested [6, 9] that disproportionation of OX is a bimolecular reaction proceeding through the intermediate formation of compounds of the diphenylalkane type. Apparently, the limited size of the channels and void spaces in the TsVK and TsVM zeolites can prevent the formation of such intermediate compounds, thus lowering the rate of this process and also the rate of desorption of the trimethylbenzenes that are formed. In the case of the wide-pore zeolites, the rates of formation and desorption of the disproportionation products are probably not limited by the dimensions of the channels and void spaces.

Another manifestation of molecular sieve effects in the pentasils is found in the higher selectivity of p-xylene (PX) formation. A comparison of the PX yields in the isomerization of OX on the zeolites TsVK-2, DM-14, and DM-68 (Fig. 2) shows that at identical levels of conversion of the original isomer, the fraction of PX in the reaction products on the pentasil type zeolite is considerably higher than on the mordenites. The distribution of MX isomerization products also proved to be different for the DM-68 and TsVK-2. As can be seen from Fig. 3, with the TsVK-2 catalyst, the concentration ratio PX/OX is considerably different from the equilibrium value, particularly at low conversions. For the dealuminized mordenite, this ratio is constant and is essentially equal to the equilibrium value, over a broad range of MX conversions.

The differences in distribution of the xylene isomerization products and in the reaction selectivity on the pentasils and the mordenites become more understandable if we examine the results from the standpoint of a limitation on the reaction rate by diffusion into the bulk. For zeolites, reactions typically proceed in this regime, where the diffusion rate is determined by the shape and dimensions of the reacting molecules and the channels of the zeolite (configurational diffusion) [10]. In such a case, the higher selectivity for the p-isomer can be explained by the higher diffusion rate in the channels of the pentasil in the case of the PX molecules, which have a smaller kinetic diameter (7.0 Å) than those of the MX and OX molecules (7.6 Å). Therefore, the PX molecules are more readily desorbed into the gas phase in comparison with the MX and OX, and the latter two molecules will stay longer in the zeolite pores and will be subjected to further isomerization. In contrast, in the channels of the DM, the diffusion rates of the PX, MX, and OX molecules are considerably higher than in the pores of the pentasil. Moreover, for all three of the isomers, the rates will show smaller differences from each other. As a result, we do not observe enrichment of the reaction products in the p-isomer on the mordenite catalysts.

These results may be compared with data on acidity of the catalysts, as determined by adsorption calorimetry (Fig. 4). With increasing  $SiO_2/Al_2O_3$  mole ratio in the zeolite skeleton, the strength of the acidic centers increases, and the number of these centers decreases. Bands with identical heat of adsorption are present in the spectra of zeolites of different compositions and structures. This means that the positions of the bands in the



Fig. 2. Yield of p-xylene (relative to hydrocarbon passed through) as a function of o-xylene conversion: 1) DM-68; 2) DM-14; 3) TsVK-2 ( $T_{act} = 500^{\circ}C$ ); 4) TsVK-2 ( $T_{act} = 1000^{\circ}C$ ).

Fig. 3. Ratio of m-xylene isomerization products (PX/OX) as a function of conversion: 1) TsVK-2; 2) DM-68.

spectra are not random, but are rather due to the existence of centers of different types in the zeolites. In the decationized L zeolite we can distinguish three types of strong acidic centers with heats of adsorption approximately 100, 110, and 120 kJ/mole; these centers are absent from the original KL sample. The appearance of these centers is related to the formation of strong acidity upon removal of the  $K^+$  ions. In the H form of the mordenites, centers with q > 120 kJ/mole appear, these centers being absent from the NH\_KL zeolite; also, there is an increase in the total number of acidic centers with q > 90 kJ/mole. The result is an increase in the total acidity and also in the number of strong acidic centers. Upon dealuminization of the mordenites, the total number of acidic centers is reduced, but their strength increases. In the dealuminized samples, we do not find any centers with q < 120 kJ/mole, but considerably stronger centers appear, with q > 140 kJ/mole. A comparison of the acidity spectra of the mordenites and pentasils shows that in the zeolites of these two types, strong acidic centers with q > 120 kJ/mole are present. However, in contrast to the mordenites, in the TsVK and TsVM type zeolites, we find no centers adsorbing NH<sub>3</sub> with q > 130 kJ/mole. The spectra of the TsVK and TsVM zeolites are similar, although in the sample synthesized without an organic cation, no centers with q > 125 kJ/mole could be detected. The absence of such centers is probably responsible for the lower activity of the TsVM zeolite in OX conversion. The higher activity of the dealuminized mordenites in comparison with the other high-silica zeolites can be explained by the fact that the mordenites have acidic centers with  $q \ge 140$  kJ/mole.

Thus, a comparison of the catalytic and acidic properties of zeolites differing in structure and composition leads us to the conclusion that there is a direct relationship between the activity in xylene conversion and the content of strong acidic centers. The concentration of acidic centers depends not only on the composition of the skeleton, but also on the conditions of pretreatment. In particular, one of the most important factors determining the catalytic properties of zeolites is the temperature interval of formation and destruction of the active centers. This interval can be determined by studying the relationship between the catalytic activity and the activation temperature (T<sub>act</sub>) of a zeolitic catalyst. From plots of the activity of mordenites as a function of T<sub>act</sub> (Fig. 5), it can be seen that in the 350-500°C region there is a sharp increase in activity, related to decomposition of NH4<sup>+</sup> ions and dehydration of the zeolites. In the 500-550°C interval, the activity of the DM-14 sample changes but little. With higher levels of T<sub>act</sub>, the OX conversion is much lower. This sort of change in the catalytic activity corresponds to the temperature regions for the existence of adsorbed water (< 350°C) and NH4<sup>+</sup> and OH groups (450-600°C) [11].

The sharp decrease in activity with  $T_{act} > 550^{\circ}C$  is probably related to removal of OH groups. It is known [11] that as the Al is removed from a zeolite, the bonding strength of



Fig. 4. Acidity spectra of zeolites, calculated from heats of adsorption of  $NH_{a}$  at 30°C.

adsorbed water decreases, and its desorption from dealuminized mordenites is completed at  $\sim 100^{\circ}$ C. From a comparison of the curves shown in Fig. 5 for the DM-14 and DM-68, we can assume that with increasing degree of dealuminization, the thermal stability of the hydroxyl cover decreases with a decrease in the content of the OH groups that are the carriers of Brønsted acidity. According to data obtained by diffuse scattering IR spectroscopy, the dehydroxylation of dealuminized mordenites proceeds at lower temperatures (< 480°C) in comparison with the dehydroxylation of the H form of mordenite (550-600°C) [12]. The mechanism of dehydroxylation of dealuminized mordenite includes simultaneous removal of a nonacidic OH group bonded to Si atoms and a proton of an acidic OH group of the bridge type. The mordenite skeleton is preserved up to at least 1000°C [11].

In contrast to the dealuminized mordenites, the TsVK is characterized by a broader temperature interval for the formation and destruction of the active centers (Fig. 5, curve 1). The increase in catalytic activity of this zeolite when it is calcined at 300-500°C is related, the same as for the mordenites, to the decomposition of NH<sub>4</sub><sup>+</sup> ions at these temperatures and the appearance of acidic centers. Heat-treatment at 500-700°C does not change the activity; only after raising T<sub>act</sub> to 800°C is there a significant decrease in OX conversion.

The conversion of OX at 250°C on the TsVK-2 sample calcined at 1000°C was no greater than 1%. This catalyst manifested appreciable activity only when the reaction temperature was raised to 300-400°C. Here we observed an increase in the selectivity with respect to PX formation. The yields of PX on the sample calcined at 1000°C, at all levels of OX conversion, were considerably higher than on the catalyst calcined at 500°C (Fig. 2, curve 4). In previous studies, an analogous increase in PX selectivity was observed for TsVK-2 calcined at 1000°C in the aromatization of C<sub>4</sub> olefins [13, 14]. The PX/MX ratio in the C<sub>8</sub> alkylbenzene fraction was 2-4 times the equilibrium value. The observed change in selectivity can be explained by a reinforcement of diffusional hindrance for the OX and MX molecules in connection with the decrease in the zeolite pore diameter after high-temperature treatment. Such a narrowing of the channels may be due, in particular, to deposition of Al<sub>2</sub>O<sub>3</sub> particles in the pores at the expense of the Al atoms removed from the zeolite skele-



Fig. 5. Total conversion of o-xylene at 250°C (on three different zeolites) and concentration of acidic centers (in the case of the TsVK-2 zeolite) as functions of catalyst pretreatment temperature: 1) TsVK-2; 2) DM-68; 3) DM-14.

Fig. 6. Acidity spectra of TsVK-2 zeolite calcined at different temperatures.

ton at high temperatures. The conclusion as to partial dealuminization of pentasil type zeolites with the formation of A1-OH groups was also drawn in [15, 16] from a study of diffuse scattering IR spectra of the H form of ZSM-5 zeolite that had been heat-treated at 950°C.

The changes in activity of the TsVK-2 zeolite with increasing  $T_{act}$  correlate well with the results obtained in the measurements of acidity. From an examination of the acidity spectra of this catalyst, calcined at 480°, 650°, and 800°C (Fig. 6), it follows that during the course of heat treatment, the contents of both the strong and the weak acidic centers decrease. In the 480-650°C interval, however, these changes are small; the increase of  $T_{act}$  to 800°C is accompanied by an almost threefold decrease in the concentration of the centers. Nonetheless, heat treatment, even under such severe conditions, does not eliminate the acidity completely. In the spectrum of the TsVK-2 that has been calcined at 800°C, the concentrations of centers adsorbing NH<sub>3</sub> with q = 110 and 130 kJ/mole are 0.11 and 0.04 mmole/g, respectively. These data are consistent with our previous conclusion that the catalytic activity of zeolites of the pentasil family comes from a small number of OH groups, which apparently enter into the composition of the active centers and can be removed as a result of destruction of these centers during heat treatment [13].

Thus, reduction of the Al content in the skeleton by acid treatment (dealuminization) lowers the thermal stability of the hydroxyl cover, as is observed in the case of mordenite catalysts. On the other hand, as a result of direct crystallization of the zeolites with decreasing concentration of Al in the skeleton, as in the synthesis of pentasils, the OH groups that are formed are more heat-resistant.

According to the data from x-ray structure analysis, the skeleton of the DM and TsVK zeolites does not break down, all the way to  $T_{act} = 1000$  °C. However, the stability of catalytic activity is related more to the stability of the hydroxyl cover than to the thermal stability of the skeleton. For example, in an investigation of decationized L zeolites, it was shown that in the interval  $T_{act}$  300-450 °C, their skeleton does undergo partial breakdown. Nonetheless, the catalytic activity in OX isomerization appeared only after calcining the samples at 400 °C, i.e., when the decomposition of NH4<sup>+</sup> ions has been completed [17].

A comparison of the activity in conversion of xylenes with the distribution of acidic centers according to strength reveals certain relationships in the course of catalytic reactions on zeolites of different structural types. Differences in the pore structure provide an explanation for the selectivity of conversions and the formation of specific products.

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Catalyst	SiO2/Al2O3	SiO <sub>2</sub> /A <b>l</b> <sub>2</sub> O <sub>3</sub>	Number of centers (1 indicated NH <sub>3</sub> adso mole	of Brønsted nmoles) with I heat of rption, kJ/	Catalytic activity at 250°C, mmoles/h•g•10 <sup>2</sup>		
					OX isomerization		OX dispropor-
			$130\pm10$	$150 \pm 10$	experi- ment	calcula- tion	(experiment)
HM DM-14 DM-18 DM-68 TsVM TsVK-2*	10 14 18 68 40 60	0,0 0,35 0,18 0,05 0,03 0,20	$1,5 \\ 0,60 \\ 0,50 \\ 0,23 \\ 0,47 \\ 0,34$	0,0 0,0 0,12 0,07 0,0 0,0	0,50 2,05 2,56 1,10 0,40 1,00	- - 1,18 0,31 1,17	0,09 0,50 0,58 0,20 0,0 0,0

TABLE 2. Content of Acidic Centers in High-Silica Zeolites and the Catalytic Activity of These Zeolites in o-Xylene Conversion

\*Heats of adsorption of NH3 determined at 30°C.

However, the level of catalytic activity must be determined by the concentration of active centers and also the ratio of numbers of active centers of different types.

Calorimetric measurements of the heat of NH<sub>3</sub> adsorption at 300°C [18] and a study of the IR spectra [12] provided a basis for determining, in each zeolite, the number of Brønsted acid centers of different strengths and the number of Lewis acid centers (Table 2). It was found that the decationized mordenite that had been heated at T  $\leq 500$ °C did not contain any Lewis acid centers, which appeared only after removal of approximately 20% of the Al from the skeleton. As the degree of dealuminization was increased, it was found that the concentrations of Lewis and strong Brønsted centers pass through a maximum. The highest concentration of Lewis acid centers was found in the DM-14 sample, and the highest concentration of strong Brønsted centers in the DM-18. Measurements of the initial rates of OX isomerization in the presence of the dealuminized mordenites with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratios shows that the DM-18 catalyst, which contained one-half the Al in the original decationized sample, had the highest activity (Table 2).

On the basis of the data on the acidity of the dealuminized mordenites, using the method of regional rates, we calculated the rate of OX isomerization on the acid centers of different types. Here it was assumed that the reaction proceeds at its own specific rate on the centers of each type, and that the contribution of these centers to the total rate is proportional to the number of centers and to the specific rate:  $r_{tot} = \Sigma r_{i}n_{i}$ . Since the HM zeolite contains only Brønsted acid centers with q = 120-140 kJ/mole, it is easy to determine that their activity is  $0.55 \cdot 10^{-23}$  mole/h center. Deducting the rate on such centers from the total rate of isomerization on the DM-14 zeolite, we can calculate the reaction rate on the Lewis centers:  $8.8 \cdot 10^{-23}$  mole/h center. Such a calculation for the DM-18 zeolite shows that on the Brønsted centers with  $q = 150 \pm 10$  kJ/mole, the isomerization rate is  $20 \cdot 10^{-23}$  mole/h center.

From these data we can calculate the rates of OX isomerization on DM-68, TsVM, and TsVK-2 zeolites and compare these results with the experimentally determined reaction rates. As can be seen from Fig. 2, the experimental and calculated rates of OX isomerization are in satisfactory agreement for these three catalysts. The calculation shows that the weakest Brønsted centers are approximately 16 times less active than the Lewis centers, and approximately 36 times less active than the strong Brønsted centers. However, the contribution of the weak centers to the overall reaction rate cannot be neglected. In the TsVM zeolite, half of the total activity pertains to these centers; and in the HM zeolite, these centers completely determine the isomerization rate.

These data also show that in zeolites of the pentasil type, there are acidic centers that are similar in heat of  $NH_3$  adsorption and in catalytic activity to the centers present in dealuminized mordenites. The only differences between the zeolites of these structural types are (a) that the pentasils do not contain any strong Brønsted acid centers with q =  $150 \pm 10 \text{ kJ/mole}$ , and (b) the slightly higher catalytic activity of the mordenites.

From these studies we can conclude that the isomerization of xylenes proceeds not only on Brønsted centers, but also on Lewis acid centers, and that the reaction rate depends on the concentrations of centers of different types. As regards the activity of these catalysts in xylene disproportionation and the differing selectivity with respect to formation of the p-isomer, we find that in this particular case, in addition to the role of the acidity, an important role is played by the pore structure of the zeolites, determining the presence or absence of diffusional hindrance for the molecules of the original hydrocarbons or the conversion products. In particular, the comparatively small decrease in the effective diameter of the channels when the change is made from mordenite to zeolites of the pentasil family leads to a considerable molecular sieve effect, manifested in a low disproportionation activity and a higher selectivity with respect to p-xylene.

# CONCLUSIONS

1. On high-silica zeolites of the pentasil family, xylenes are converted to isomerization products with high selectivity. In the presence of wider-pore zeolites, the isomerization is accompanied with a considerable degree of disproportionation, the contribution of which increases with increasing diameter of the zeolite pores.

2. The hydroxyl cover in the pentasils has a far higher thermal stability than in the mordenites; and as a consequence, the pentasils retain high catalytic activities even when heat-treated at 700°C.

3. The acidic centers of zeolites of the pentasil and mordenite types are similar in heats of ammonia adsorption and in their specific activity in xylene conversion.

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