(5) are shown in Fig. 2. The results of processing the data obtained by the method of least squares are reported in Table 1. The confidence intervals were calculated with a probability of 0.95. The correspondence of the experimental data with the equation for line (5) indicates the formation of coordination compounds of 1:1 composition.

As Fig. 2 and Table 1 indicate, sorption of KC1, NaC1, RbC1, CsC1, AgNO₃, and T1NO₃ up to a composition of $m_{MAn}/E < 0.5$ is described by Eq. (6), which corresponds to transfer of electrolytes from solutions to the ligand-containing phase according to mechanism (1). Only complexed cations and free anions are thus present in the polymer phase. The absence of anions in the external sphere of the complexes formed causes intensification of the reaction of the crown ethers with the metal cations in the polymer. This is reflected in the large values of the electrolyte transfer constants (Table 1).

CONCLUSIONS

1. Complexing was studied in sorption of KCl, NaCl, RbCl, CsCl, AgNO₃, and TlNO₃ by sorbents containing immobilized dibenzo-18-crown-6 and dibenzo-24-crown-8.

2. The cations are coordinated and the anions are in the free state in the polymer phase.

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EFFECT OF HEAT TREATMENT ON THE CATALYTIC ACTIVITY AND SELECTIVITY OF ACTION OF HIGH-SILICA ZEOLITES IN TRANS-FORMATIONS OF XYLENES

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Isomerization of xylenes takes place with a high selectivity on zeolites of the pentasil family, while xylenes are transformed into products of disproportionation: toluene (T) and trimethylbenzene (TMB) with a high rate on mordenite catalysts [1-3]. In addition, enrichment of the products of isomerization with p-xylene (para-selectivity) is characteristic of pentasils [1-5].

Varying the conditions of preliminary activation can cause a change in the direction of the reaction on zeolites [6]. The catalytic activity and selectivity of action of zeolites of the pentasil and mordenite type treated with air at different temperatures (T_{act}) were compared in the model reaction of isomerization of o-xylene (OX).

EXPERIMENTAL

The following zeolites were used in the study: pentasil NTsVK-30 (Si/A1 = 30, 0.1% Na₂O); dealuminated mordenites DM-7 (Si/A1 = 7) and DM-34 (Si/A1 = 34) [7]; high-silica mordenite NM-10 (Si/A1 = 10) prepared by direct crystallization [8]. The concentration of Na₂O in the mordenites was $\leq 0.15\%$.

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Xylenes, % Tact, K T_{expt}, K T+TMB x, % OX РΧ МΧ $523 \\ 523$ 0,1 523 573 673 15,92,8 13,084,1 33,3 41,1 58,0 $0,4 \\ 0,5 \\ 0,5 \\ 0,5$ 7,9 66,7 25,032.358,95238,3 42,040,0 773 773 52317,5 6,0 3,8 2,7 0,5 0,2 50,120.279,8 23,759819.2 873 59880,8 24.652.4 $25,\!6$ 97359874,4 22,149,660,21073 59839,8 13,7 25,618,26,9 11,1 81,8 117359898,9 0,012735981,1 0,50,6

TABLE 1. Composition of the Products of Transformation of o-Xylene on NTsVK-30 Catalyst

TABLE 2. Composition of the Products of Transformation of o-Xylene on Mordenites (523 K)

T _{act} , K	x, %	Xylenes			T + TMB	D /I					
		PX	MX	ох	1 + 1 1000						
DM~7											
623 673 773 823 873 973 1023 1073 1073 1173		$\left \begin{array}{c} 0,1\\ 2,1\\ 15,3\\ 16,8\\ 12,0\\ 2,0\\ 0,6\\ 0,2\\ 0,0\\ \end{array}\right $	$\left \begin{array}{c} 1.5\\17.8\\39.1\\41.5\\37.7\\18.1\\6.7\\1.9\\0.0\end{array}\right $	$ \begin{vmatrix} 98,4\\79,4\\13,8\\17,2\\28,2\\75,4\\91,3\\97,5\\100,0 \end{vmatrix} $	$\left \begin{array}{c} 0,0\\ 0,7\\ 31,8\\ 24,5\\ 22,1\\ 4,5\\ 1,0\\ 0,4\\ 0,0\\ \end{array}\right.$	$[\begin{array}{c} 0,0\\ 0,04\\ 0,58\\ 0,42\\ 0,22\\ 0,14\\ 0,19\\ 0,0 \end{array}]$					
DM-34											
673 773 823 873 973 973 1073	54,564.755,627,68,34,40,0	9,0 12,4 7,9 3,5 0,7 0,2 0,0	36,8 35,4 37,5 19,7 6,4 3,7 0,0	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\left \begin{array}{c} 8,7\\16,9\\10,2\\4,4\\1,2\\0,5\\0,0\end{array}\right $	$\left \begin{array}{c} 0,19\\ 0,35\\ 0,22\\ 0,19\\ 0,17\\ 0,13\\ 0,0\\ \end{array}\right $					
NM-10 *											
673 723 773 823 873 923 973 1023 1073	22.0 71.1 76.1 78.7 77.2 74.0 74.3 71.1 23.0	$\left \begin{array}{c} 2.5\\ 14.4\\ 19.3\\ 16.4\\ 15.8\\ 13.7\\ 12.9\\ 9.6\\ 3.7\end{array}\right $	$ \begin{vmatrix} 16.9 \\ 44.4 \\ 39.2 \\ 43.4 \\ 41.0 \\ 43.2 \\ 34.2 \\ 33.6 \\ 15.2 \end{vmatrix} $	78.0 28.9 23.9 21.3 22.8 26.0 26.0 28.8 77.0	$ \begin{array}{c ccccc} 2,6\\ 12,3\\ 17,6\\ 18,9\\ 20,4\\ 17,1\\ 26,9\\ 28,0\\ 4,1\\ \end{array} $	$\left \begin{array}{c} 0,13\\ 0,21\\ 0,30\\ 0,32\\ 0,36\\ 0,30\\ 0,57\\ 0,65\\ 0,22\\ \end{array}\right.$					
*T = 623 K.											

Transformations of OX was studied in a flow-type system at ~ 0.1 MPa and experimental temperatures (T) of 523-823 K. Before measuring the catalytic activity, the zeolites were heated in an air current for 6 h at 523-1273 K. The starting hydrocarbon was delivered to the reactor in a current of He (2 liter/h) with a microbatcher (360-720 h⁻¹). The methods of the experiment and chromatographic analysis are reported in [1]. The catalytic activity of the zeolites was estimated by the conversion of OX(x). The catalytic activity of the zeolites was characterized by the ratio of the concentrations of the products of disproportionation and isomerization (D/I) and the selectivity of formation of p-xylene (PX) was characterized by the ratio of p- and m-xylenes, PX/MX.

RESULTS AND DISCUSSION

It follows from a comparison of the data on the change in x as a function of T_{act} (Table 1) that the formation of active centers after heating even at a comparatively low temperature is characteristic of pentasil. Treatment of the catalyst at 523 K resulted in

TABLE 3. Change in the Composition of the Products of Transformation of o-Xylene on Zeolite NTsVK-30 as a Function of the Duration of its Annealing at 1273 K (T = 598 K)

Time, h	x, %	Xylenes, %				DV (MV
		РХ	MX	OX	1 + 1 1910	FA/MA
$\begin{array}{c} 0\\ 1\\ 2\\ 6\end{array}$	79,8 19,8 14,0 1,1	23,7 8,8 6,0 0,5	50,1 10,7 7,9 0,6	20,2 80,2 86,0 98,9	6,0 0,3 0,1 0,0	0,45 0,83 0,76 0,83

the appearance of marked activity: the yield of the products of transformation of OX was $\sim 16\%$ at 523 K. When T_{act} was increased from 523 to 773 K, x increased by more than 3.5 times and remained almost unchanged up to 873 K. An insignificant decrease in the activity was observed for the sample heated at 973 K, and a significant decrease in x (by ~ 2 times) only took place after annealing at 1073 K. More rigorous heat treatment (1273 K) results in almost total deactivation: x = 1.1%.

The appearance of catalytic activity at $T_{act} = 523$ K is due to the partial decomposition of NH₄⁺ ions and the formation of OH groups of the bridge type. The increase in the activity with an increase in T_{act} to 773 K is due to subsequent deammoniation and dehydration of the surface of the pentasil. Since an increase in T_{act} from 773 to 973 K does not cause a significant change in x, it can be assumed that these processes are completed at $T_{act} < 773$ K, and the active centers formed exhibit elevated thermal stability. The analysis of the DTA curves showed that the adsorbed H₂O is totally eliminated from the surface of pentasils at \sim 673 K and the products of decomposition of NH₄⁺ ions and organic cations are eliminated at \sim 753 K [9].

The data on the effect of T_{act} on the acid and sorption properties of pentasil [8] permit hypothesizing that the decrease in the activity after treatment at $T_{act} = 973$ K is only due to a decrease in the number of acid centers, since the degree of crystallinity of the zeolite does not change in these conditions. It is well-known that high-temperature treatment is accompanied by intense dehydroxylation of the surface of zeolites and the formation of Lewis acid centers: coordination-unsaturated Al atoms and Si ions. As demonstrated in [10], the total acidity decreases significantly after annealing of a sample of NTsVK-30 at 1073 K, and not only the concentration of Brönsted acid centers also decreases. The decrease in the number of aprotic centers is apparently due to exit of Al from the pentasil lattice at high T_{act} . A conclusion concerning the partial dealumination of pentasils in high temperature treatment was also drawn as a result of the study of zeolites of this type by diffuse scattering IR spectroscopy [11].

A different type of change in x as a function of T_{act} is observed on mordenites (Table 2). The stability of the catalytic activity is a function of both the degree of dealumination of these zeolites and the method of preparation of the samples with a low concentration of aluminum (extraction of Al by acid treatment or direct crystallization of the reaction mixture enriched with Si).

The formation of a significant number of active centers in isomerization of OX on the surface of DM-7 mordenite only takes place after $T_{act} > 623$ K. In the region of $T_{act} = 673$ -773 K, the yield of products of the reaction increases sharply, which is due to decomposition of NH₄⁺ ions and dehydration of the zeolite, as in the case of pentasil. In the range of $T_{act} = 773-873$ K, the activity of the catalyst changes insignificantly, and x decreases rapidly at higher T_{act} .

For the sample of DM-34, the optimum T_{act} is 773 K, treatment at 873 K causes a decrease in the activity by more than two times, and after annealing at 973 K, x decreased to 4.4%. This type of change in the catalytic activity is in agreement with the results in [12], in which the temperature regions of the existence of adsorbed H₂O (< 623 K), NH₄⁺ ions, and OH groups (723-973 K) were found.

It is very probable that the sharp decrease in the activity of DM-34 and DM-7 at T_{act} > 823 K and > 873 K is due to an increase in the degree of surface dehydroxylation in these conditions. It is known [12] that the strength of binding of adsorbed H₂O decreases as Al is eliminated from mordenites and its desorption from the surface ends at \sim 373 K. According



Fig. 1. Change in the para-selectivity (1) and D/I (2) as a function of $\rm T_{act}$ (NTsVK-30; 598 K).

Fig. 2. Change in conversion of o-xylene (1) and para-selectivity (2, 3) as a function of the temperature. 1, 2) NTsVK-30 ($T_{act} = 1273$ K), 3) 2.8% V/NTsVK-30 ($T_{act} = 773$ K).

to the diffuse scattering IR spectroscopic data, DM is dehydroxylated at lower temperatures (\sim 753 K) than the hydrogen form of mordenite (823-873 K) [13]. The mechanism of dehydroxylation of DM and the formation of Lewis acid centers includes simultaneous elimination of non-acid hydroxyl groups bound with Si atoms and the proton of the bridge acid OH group. The participation of aprotic acid centers in the reaction of isomerization of xylenes was discussed previously in [7]. Although the contribution of these centers to the total activity is low, it can be hypothesized that the decrease in the yield of isomeric xylenes after annealing of DM at 823-873 K is not only due to dehydroxylation of the surface but also to destruction of the Lewis acid centers as a result of dealumination of the zeolites.

The activity of zeolite NM-10 synthesized by direct crystallization was significantly inferior to the activity of DM (Table 2). The temperature at which the same x was attained (75-80%) was 523 K for DM-7 and 623 K for NM-10. These data are in agreement with the results in [14], in which it was concluded that the volume of the intracrystalline space of the mordenites increases during dealumination and the number of active centers accessible to the molecules of aromatic hydrocarbons correspondingly increases. However, the sample of NM-10 is close to NTsVK-30 zeolite with respect to the thermal stability of the active centers and significantly exceeds DM-7 and DM-34. After annealing of NM-10 at 1023 K, x decreased by \sim 7%, while DM-7 retained only \sim 10% of the initial activity after the same treatment and DM-34 was totally deactivated at 973 K.

The results obtained show that during direct synthesis and subsequent decationization of high-silica pentasils and mordenites, active centers which are very resistant to heat treatment are formed. At the same time, preparation of high-silica mordenites by dealumination results in a decrease in the thermal stability of these centers.

Two basic factors which determine the character of the dependence of the catalytic activity of pentasils and mordenites on T_{act} can thus be distinguished. They are dehydroxylation of the surface of the zeolites and partial dealumination after heating at high temperatures. Let us examine how these processes affect the selectivity of transformation of xy-lenes into products of isomerization and disproportionation.

As noted above, isomerization of xylenes on dealuminated mordenites is accompanied by significant disproportionation: the yield of T and TMB increases with an increase in x and attains $\sim 32\%$ on zeolite DM-7. On the whole, the data on the composition of the products of the reaction on mordenites indicate the insignificant effect of heat treatment on the select-ivity of formation of the products of isomerization. This is in agreement with the results in [7], in which it was shown that the ratio of the initial rates of disproportionation and isomerization is not a function of the composition of the mordenites and is $\simeq 0.2$.

A change in the T_{act} of pentasil NTsVK-30 affects the value of D/I, and the selectivity with respect to isomerization decreases with an increase in the temperature and correspondingly the degree of transformation of OX. At 523 K, the total concentration of PX and MX is \sim 100 times higher than the concentration of T and TMB. At 598 K, the contribution of the disproportionation reaction to the total transformation of OX increases: 6% of the total yield of products of the reaction per fraction of T and TMB (see Table 1). As T_{act} increases from 773 to 973 K, the value of D/I linearly decreases (Fig. 1, curve 2) and x is almost unchanged. The centers responsible for the occurrence of the disproportionation reaction could primarily be destroyed during such high-temperature treatment of pentasil, and the centers on which OX is transformed into isomers could be unaffected. The selectivity with respect to isomerization of xylenes increases with no change in the overall activity of the zeolite. Destruction of the active centers of isomerization only begins after $T_{act} > 973$ K.

Another more probable cause of the decrease in the yield of the products of disproportionation as T_{act} increases consists of narrowing of the channels of the pentasil under the effect of the high temperatures. It is known [2-5] that transformations of alkylbenzenes on pentasils take place in configuration diffusion conditions. For this reason, even a small decrease in the pore diameter of the pentasil can either result in a significant decrease in the rate of desorption of large molecules of TMB or in general to total blockage of the channels of the zeolite and cessation of diffusion of these substances into the gas phase.

The molecular sieve properties of pentasils are even more clearly manifested by an increase in the selectivity of formation of PX. For example, in reactions of isomerization of OX and MX with the same x, the proportion of the p-isomer in the products of the reaction on pentasils is significantly higher than on mordenites or faujasites [1-3]. As a result, the gas phase is enriched with the p-isomer, which results in a "superequilibrium" ratio of the concentrations of xylenes formed. The value of this ratio can be used as a measure of the para-selectivity.

Heat treatment of the NTsVK-30 catalyst at $T_{act} > 973$ K causes a significant increase in the para-selectivity. The PX/MX ratio increases from 0.45 (which approximately corresponds to the equilibrium value) for the zeolite activated at 773 K to 0.83 after annealing at 1273 K (Fig. 1, curve 1). The duration of treatment at 1273 K does not affect the value of the para-selectivity (PX/MX remains unchanged, ~ 0.8), but decreases the yield of the products of isomerization to a significant degree (Table 3).

The NTsVK-30 catalyst annealed at 1273 K for 1 h exhibited significant activity when the temperature was increased to 598-673 K and $x \sim 50\%$ was only attained at 773 K (Fig. 2, curve 1). The PX/MX ratio was 1.5-2 times higher than the equilibrium value in the entire temperature range studied (598-823 K) and insignificantly decreased with an increase in the reaction temperature (Fig. 2, curve 2). This increase in the para-slectivity, like inhibition of the disproportionation reaction, was apparently due to intensification of diffusion hindrances due to partial exit of Al from the lattice and an increase in the difference in the rates of diffusion of isomeric xylenes from the channels of the zeolite into the gas phase. Similar effects were previously observed in aromatization of C₄ olefins on NTsVK-30 annealed at 1273 K [6] and in studying the transformations of i-C₄H₈ and OX on the same zeolite modified with vanadium [15]. The PX/MX ratio on pentasil containing V is almost three times higher than the equilibrium value and decreases insignificantly with an increase in the temperature (Fig. 2, curve 3). It can be concluded that high-temperature treatment and modification of PX due to a change in the pore structure.

In contrast to pentasils, high-temperature treatment of mordenites did not result in the appearance of molecular sieve selectivity but only caused a sharp decrease in the catalytic activity. This is apparently also due to the diffusion character of transformations of xylenes on zeolites [3-5]. The diameter of the wide channels in mordenite is ~ 0.15 nm greater than the pore diameter of pentasil [3]. For this reason, the rate of diffusion of molecules of PX, MX, and OX in the channels of DM should be significantly higher and should be dependent on the value of their kinetic diameter to a lesser degree. As a result, enrichment of the products with the p-isomer does not take place on DM even after high-temperature treatment. Since the selectivity in the disproportionation reaction also changed very little after annealing, it can be concluded that the change in the pore structure of DM under the effect of high temperatures does not affect the rate of desorption of molecules of TMB.

CONCLUSIONS

1. In studying the isomerization and disproportionation of xylenes, the temperature range of the formation and destruction of active centers in zeolites of the pentasil and mordenite type was established. Active centers resistant to heat treatment at 973-1073 K are present on the surface of zeolites prepared by direct synthesis.

2. After treatment of zeolite of the pentasil type with air at 1073-1273 K, the selectivity with respect to formation of p-xylene increased significantly, and the reaction of disproportionation of the xylenes with a decrease in the total catalytic activity was inhibited.

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