- 180. V. B. Pukhnarevich, S. P. Sushchinskaya, V. A. Pestunovich, and M. G. Voronkov, Zh. Obshch. Khim., 43, 1283 (1973).
- 181. V. B. Pukhnarevich, L. M. Kopylova, B. A. Trofimov, and M. G. Voronkov, Zh. Obshch. Khim., 45, 89 (1975).
- 182. V. Chvalovsky, J. Pola, V. B. Pukhnarevich, L. I. Kopylova, E. O. Tsetlina, B. A. Trofimov, and M. G. Voronkov, Collect. Czech. Chem. Commun., <u>41</u>, 391 (1976).
- 183. M. G. Voronkov, V. B. Pukhnarevich, L. I. Kopylova, V. A. Pestunovich, E. O. Tsetlina, B. A. Trofimov, J. Pola, and V. Chvalovsky, Dokl. Akad. Nauk SSSR, 227, 91 (1976).
- 184. V. B. Pukhnarevich, L. I. Kopylova, B. A. Trofimov, and M. G. Voronkov, Zh. Obshch. Khim., 45, 2638 (1975).
- 185. M. G. Voronkov, S. P. Sushchinskaya, V. B. Pukhnarevich, and V. V. Keiko, Inventor's Certificate No. 765,272 (1980); Byull. Izobr., No. 35, 145 (1980).
- 186. M. G. Voronkov, S. P. Sushchinskaya, and V. B. Pukhnarevich, Zh. Obshch. Khim., <u>51</u>, 242 (1981).
- 187. M. G. Voronkov, S. P. Sushchinskaya, and V. B. Pukhnarevich, Zh. Obshch. Khim., <u>49</u>, 1171 (1979).
- 188. V. B. Pukhnarevich, L. I. Kopylova, E. O. Tsetlina, V. A. Pestunovich, V. Chvalovsky, J. Getfleish, and M. G. Voronkov, Dokl. Akad. Nauk SSSR, 231, 1366 (1976).
- 189. V. B. Pukhnarevich, L. I. Kopylova, M. Chapka, J. Getfleish, E. N. Satsuk, M. V. Sigalov, V. Chvalovsky, and M. G. Voronkov, Zh. Obshch. Khim., <u>50</u>, 1554 (1980).
- 190. L. I. Kopylova, M. V. Sigalov, É. N. Satsuk, M. Chapka, J. Chvalovsky, V. B. Pukhnarevich, E. Ya. Lukevits, and M. G. Voronkov, Zh. Obshch. Khim., <u>51</u>, 385 (1981).
- 191. V. B. Pukhnarevich, I. I. Tsykhanskaya, and M. G. Voronkov, Inventor's Certificate No. 810,706 (1980); Byull. Izobr., No. 9, 93 (1981).
- 192. M. G. Voronkov, V. B. Pukhnarevich, I. I. Tsykhanskaya, and Yu. S. Varshavskii, Dokl. Akad. Nauk SSSR, 254, 887 (1980).
- 193. M. G. Voronkov, S. N. Adamovich, and V. B. Pukhnarevich, Zh. Obshch. Khim., <u>51</u>, 2385 (1981).

CONVERSION OF XYLENES IN THE PRESENCE OF ZEOLITES WITH A HIGH

SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> RATIO

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During a study of the conversion of  $C_3-C_4$  olefins and 1-octene on ultrahigh-silica colites (USZ) it was shown [1, 2] that the ratio of the concentrations of the  $C_8$  aromatic

zeolites (USZ) it was shown [1, 2] that the ratio of the concentrations of the  $C_8$  aromatic hydrocarbons in the reaction products was substantially dependent on the conditions under which the process is carried out and the composition of the catalyst.

In connection with this, we have investigated the conversion of o- and m-xylenes (o-X and m-X) in the presence of the initial and decationized forms of USZ in the present work. For purposes of comparison, the conversion of these same hydrocarbons was studied on decationized mordenite (HM) and on a dealuminated mordenite which had been prepared from it (DM).

## EXPERIMENTAL

Ultrahigh-silica zeolites (USZ) in the initial and decationized forms (Table 1) [3, 4] were employed in the work. A sample of decationized mordenite (HM) with a 95% degree of exchange was prepared by decationization of the Na-form of mordenite, while the dealuminated zeolite was prepared according to the technique described in [5].

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Catalyst	Conventional symbol	$\frac{\rm SiO_2}{\rm Al_2O_3}$	A mount of Na <sub>2</sub> O, %
Initial form of the ultrahigh- silica zeolite	Na-USZ	70,5	0,7
Decationized ultrahigh-silica zeolite	H-USZ	60,3	0,1
Decationized mordenite Dealuminated mordenite	HM ·DM	10,0 68,0	0,45 0,03

TABLE 1. Some Characteristics of the Zeolite Catalysts

The conversions of o- and m-xylene were studied in a flow system at  $150-550^{\circ}$ C and atmospheric pressure. Before the experiments, the catalysts were activated with air (500°C, 3 h). The initial xylenes were fed into the reactor by means of a microdosimeter. The experiments were carried out in a current of He at a He:hydrocarbon ratio of 5.5 and a hydrocarbon feedstock space velocity of 180 h<sup>-1</sup>. The duration of the experiments was usually 20 min. The stability of the catalyst was checked in experiments lasting 120 min. The reaction products were analyzed by means of GLC at 70°C using a capillary column (50 m) with squalane (5%).

The purity of the initial m-xylene was 98.4% and the amount of impurities in the o-xylene did not exceed 0.1%.

## DISCUSSION OF RESULTS

It follows from a comparison of the data on the change in the overall conversion of oxylene as a function of temperature (Fig. 1) that the Na-USZ catalyst is the least active and the DM zeolite is the most active. A value for the overall conversion of o-xylene equal, for example, to 50% is achieved on Na-USZ at 440°C, on H-USZ at 240°C, and on DM and HM at 195 and 200°C, respectively. The Na- and H-USZ catalysts, as well as DM, possess satisfactory stability. The yield of products remained constant over a period of 120 min. Unlike this, the stability of HM, which is similar to DM with respect to its activity, was found to be low. After 70 min, its activity was lowered by a factor of two. The data for this catalyst shown in Fig. 1 therefore corresponds to the first 20 min of the experiment.

The conversion of the xylenes on the catalysts which were studied took place along two pathways: 1) isomerization with the formation of the corresponding isomers and 2) disproportionation of the initial xylene and the products of its isomerization into toluene and



Fig. 1. The temperature dependence for the conversion of oxylene on various zeolite catalysts: 1) DM; 2) HM; 3) H-USZ; 4) Na-USZ.

Fig. 2. The change in the ratio of the concentrations of the disproportionation products of o-xylene and its isomerization products (D/I) on various zeolites as a function of temperature: 1) DM; 2) HM; 3) H-USZ; 4) Na-USZ.



Fig. 3. The change in the ratio of the isomerization products of o-xylene (p-xylene/m-xylene) as a function of the conversion: 1) H-USZ; 2) Na-USZ; 3) HM; 4) DM.

Fig. 4. The change in the ratio of the isomerization products of m-xylene(p-xylene/o-xylene) as a function of the conversion: 1) H-USZ; 2) DM.

and trimethylbenzenes. In order to estimate the selectivity in the conversion of the xylenes in the above-mentioned directions, the ratio of the concentrations of the disproportionation and isomerization products (D/I) was used.

It follows from Fig. 2 that o-xylene solely undergoes isomerization on the Na-USZ catalyst (D/I = 0 at 300-500°C). In addition to isomerization, disproportionation of the initial o-xylene and of the isomers of this molecule which are formed is also observed to some extent on the H-USZ catalyst (D/I  $\approx$  0.12 at 360°C, curve 3). Appreciable quantities of toluene and trimethylbenzenes are found in the conversion products of o-xylene on the HM catalyst (D/I = 0.3 at 250°C, curve 2). Isomerization occurs with the least selectivity on the DM catalyst. The D/I ratio increases from 0.2 at 200°C up to 1.4 at 300°C (curve 1). Similar results were obtained for the conversions of m-xylene on the above-mentioned catalysts.

A substantial difference was also observed in the ratio of the isomerization products of xylenes on USZ and mordenites. The amount of conversion was varied by changing the reaction temperature at a constant space velocity of feed of the initial xylene. It follows from Fig. 3 that, in the case of the Na- and H-USZ, the values of the p-xylene/m-xylene ratio are the same (curve 1) and that they significantly exceed the corresponding values for HM and DM (curve 2) and, as the degree of conversion increases, they approach far more rapidly to the equilibrium value (the broken line). Hence, for the same degree of conversion of the initial xylene, the concentration of p-xylene in the products of the reaction on Na-USZ is always significantly higher than on the mordenites. Judging from the nature of curve 2 in Fig. 3, the formation of p-xylene from o-xylene on mordenites takes place sequentially (o-xylene  $\neq$  m-xylene  $\neq$  p-xylene), which is in agreement with the data given in [6].

The distribution of the products of the isomerization of m-xylene on USZ and mordenite (DM) was also found to be different (Fig. 4). In the presence of USZ, the p-xylene/o-xylene ratio is significantly greater than the equilibrium value, and, moreover, as the degree of conversion decreases from 50 to 15% this ratio increases from 1.5 to 3.6. In the case of DM, the p-xylene/o-xylene ratio was constant and practically corresponds to the equilibrium value over a wide range of degrees of conversion of m-xylene (15 to 55%).

The constancy of the values for the p-xylene/o-xylene ratio is indicative of the parallel nature of the formation of p-xylene and o-xylene in the presence of DM (m-xylene  $\stackrel{\text{//}}{\approx} \text{ p-xylene}$ ), which is in accord with the generally accepted ideas concerning this reaction [6, 7].

The differences in the distribution of the products of the isomerization of xylenes and in the selectivity of the process on USZ and mordenites can be explained by invoking the idea that the reaction takes place under an internal diffusion regime. The internal diffusion region is characterized by a number of features including a change in the selectivity of the process [8]. Limitation of a reaction by diffusion in the bulk is very typical of zeolites with pores of a much smaller diameter than in the case of the usual oxide catalysts [9]. In the case of zeolites with entrance windows with dimensions similar to the diameter of the reactants, the rate of diffusion is determined by the shape and sizes of both the channels in the zeolite and of the reactants, which can lead to the selective formation of a specific reaction product, i.e., to shape-selectivity [10].

Apparently, the isomerization of xylenes on USZ takes place under a regime of shapediffusion and, moreover, the rate of diffusion of p-xylene from the channels of such a zeolite is significantly greater than the rates of diffusion of m-xylene or o-xylene, the molecules of which have a greater diameter than the p-xylene molecules [11]. Unlike this, the rates of diffusion of o-, m-, and p-xylene molecules in the channels of mordenite are appreciably higher than in the pores of USZ and approximately the same for all of the isomeric xylenes. Hence, the p-xylene molecules can readily diffuse from the channels of USZ into the gas phase while the o-xylene and m-xylene molecules will be situated in the voids in the zeolite for a longer period of time and undergo further isomerization. As a result of this, the products from the reaction of USZ may be enriched in p-xylene as demonstrated above. The scheme proposed for this process, based on the decisive role played by shape-diffusion, is found to be in accord with the results, summarized in [10], on the selective formation of p-xylene during the disproportionation of toluene and during its methylation with methanol on zeolites of the ZSM type.

The different selectivity of USZ and mordenites with respect to the isomerization and disproportionation of xylenes is probably also due to structural factors. It is postulated in [7] that the disproportionation reaction takes place via the intermediate formation of compounds of the diphenylalkane type. Apparently, the restricted dimensions of the channels and the cavities in USZ may be the reason for the reduction in the rate of formation of such intermediate compounds as well as for the reduction in the rate of desorption of the trimethyl-benzenes which are formed. Meanwhile, in the case of the mordenites, the rates of formation and desorption of the disproportionation products are unlikely to be limited by the dimensions of the channels and cavities. The very fact that DM exhibits a very high activity in this reaction may be associated with the increase in the pore size in mordenite as a result of its dealumination [12].

It has already been pointed out above that, under the conditions used for the conversion of xylenes, USZ possess a higher stability than the mordenites and, moreover, DM is more stable than HM. The low stability of A, X, Y, and M zeolites was observed by us previously [13] during conversions of the lower olefins and it was explained by the intense occurrence of coke formation. It is known [14] that the rapid deactivation of HM is associated with the blocking of its one-dimensional pore structure by ion-radicals and other strongly adsorbed molecules. The dealumination of mordenites leads to an increase in their stability, which is usually attributed to the reduction in the density of acid centers leading to a reduction in the rate of condensation of the products into high-molecular-weight compounds in comparison with the rate of desorption of these products [12].

It may therefore be postulated that the high stability of USZ is attributable to the following principal factors: 1) the reduced density of acid centers as in the case of the dealuminated mordenites, and 2) the specific features of the structure of USZ which reduce the rate of formation of the large molecules which are the precursors of coke.

## CONCLUSIONS

1. A study has been made of the conversion of m- and o-xylenes in the presence of an ultra-high silica zeolite in the initial and decationized forms and in the presence of decationized and dealuminated mordenite at 150-550°C, atmospheric pressure, and a space velocity of 180 h<sup>-1</sup>.

2. The Na- and H-forms of the ultrahigh-silica zeolite lead mainly to the isomerization of xylenes, while the isomerization and disproportionation of xylenes take place on the mordenites.

3. In the presence of the Na- and H-forms of the ultrahigh-silica zeolite, which possesses a high stability in comparison with the decationized mordenite, the isomerization of m- and o-xylenes is characterized by an enhanced selectivity with respect to the formation of pxylene.

## LITERATURE CITED

- Kh. M. Minachev, D. A. Kondrat'ev, A. A. Dergachev, B. K. Nefedov, T. N. Bondarenko, T. V. Alekseeva, and T. B. Borovinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1304 (1981).
- Kh. M. Minachev, D. A. Kondrat'ev, A. A. Dergachev, T. B. Borovinskaya, T. N. Bondarenko, B. K. Nefedov, and T. V. Alekseeva, Izv. Akad. Nauk SSSR, Ser. Khim., 1833 (1981).
- Kh. M. Minachev, D. A. Kondrat'ev, B. K. Nefedov, T. N. Bondarenko, A. A. Dergachev, and T. V. Alekseeva, Izv. Akad. Nauk SSSR, Ser. Khim., 2646 (1979).
- 4. Kh. M. Minachev, D. A. Kondrat'ev, B. K. Nefedov, A. A. Dergachev, T. N. Bondarenko,
- T. V. Alekseeva, and T. B. Borovinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 2509 (1980).
- I. V. Mishin, A. L. Klyachko-Gurvich, and A. M. Rubinshtein, Izv. Akad. Nauk SSSR, Ser. Khim., 445 (1973).
- 6. A. Cortes and A. Corma, J. Catal., <u>51</u>, 338 (1978).
- 7. M. A. Lanewala and A. P. Bolton, J. Org. Chem., 34, 3107 (1969).
- 8. S. L. Kiperman, Introduction to the Kinetics of Heterogeneous Catalytic Reactions [in Russian], Nauka, Moscow (1964), p. 417.
- 9. C. N. Satterfield, Mass Transfer in Heterogeneous Catalysis, M. I. T. Press, Cambridge, Mass. (1969).
- P. B. Weisz, The Seventh International Congress on Catalysis, Tokyo (1980), Preprint of Plenary Lectures, P1-1.
- 11. J. R. Anderson, K. Foger, T. Mole, R. A. Rajadhyaksha, and J. V. Sanders, J. Catal., 58, 114 (1979).
- 12. H. S. Bierenbaum, S. Chiramongkol. A. H. Weiss, J. Catal., 23, 61 (1971).
- 13. Kh. M. Minachev, D. A. Kondrat'ev, T. N. Bondarenko, A. A. Dergachev, B. K. Nefedov, and T. V. Alekseeva, Izv. Akad. Nauk SSSR, Ser. Khim., 1300 (1981).
- 14. S. M. Csicsery, J. Catal., 23, 124 (1971).

ELECTROPHILIC ADDITION TO BICYCLO[1.1.0]BUTANE

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The electronic structure of bicyclo[1.1.0]butane (I) [1], in particular the C(1)-C(3) bond, accounts for its capacity to react similar to unsaturated systems with some electrophilic reagents, in particular, with Hg(OAc)<sub>2</sub> [2-4].

We studied the reaction of (I) with a series of mercury compounds, HgCl<sub>2</sub>, HgBr<sub>2</sub>, HgI<sub>2</sub>, MeHgCl (IIa-d), and Me<sub>2</sub>Hg. Compounds (IIa-c) are capable of adding to cyclopropanes, olefins, and acetylenes [5].

Under mild conditions at 20°C in  $CH_2CH_2$ , (I) reacts vigorously with (IIa-c) giving  $\sim 70\%$  yields of organomercury salts which are insolube in organic solvents. The structure of these salts was determined by demercuration of the products formed in alkali medium by the action of NaBH<sub>4</sub> [6] with conversion to the corresponding halides; this method was used for determining the products of the addition of Hg(OAc)<sub>2</sub> to bicyclobutanes [2-4, 7].

The reduction of the products of the addition of (IIa) to (I) gave a 1:3 mixture of chlorocyclobutane (VIIIa) and chloromethylcyclopropane (IXa). Demercuration of the products of the reaction of (I) with (IIb) and (IIc) gave, in addition to (VIII) and (IX), open-ring compounds, 4-bromo-l-butene (Xb) and 4-iodo-l-butene (Xc)

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