LITERATURE CITED

1. I. Kh. Raskina, Zhur. Vses. Khim. Boshch., 15, 257 (1970).
2. P. I. Petrovich, Khim. Prom., 1974, No. 11, 9.
3. K. Venkataraman, Chemistry of Synthetic Dyes, Vol. 6, Academic Press (1970-72).
4. Swiss Patent 559194 (1975); Ref. Zh. Khim., 19N235 (1975).
5. I. L. Kotlyarevskii, M. P. Terpugova, and É. K. Andrievskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1964, 1854.
6. M. P. Schmidt and A. Hagenböcker, Chem. Ber., 54, 2191 (1921).
7. F. Kajimoto, H. Takahashi, and J. Tsuji, J. Org. Chem., 41, 1389 (1976).
8. F. H. Witt, Chem. Ber., 45, 2381 (1912).
9. H. Foster, J. Am. Chem. Soc., 82, 3780 (1960).
10. Beilstein, Vol. 26, Verlag von Julius Springer, Berlin (1937), p. 72.

COMPARATIVE STUDY OF ACTIVITY OF H^+ FORM OF TYPE Y, MORDENITE, AND ZSM-5 ZEOLITES IN TOLUENE DISPROPORTIONATION REACTION

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The catalytic properties in the toluene disproportionation reaction have been studied predominantly on the type Y and mordenite zeolites [1]. The activity is markedly affected by the structure of the zeolite, the SiO_2/Al_2O_3 ratio, the nature of the acid centers, the presence of a transition metal, etc. Special attention has been given recently to ultrahigh silica zeolites of the ZSM type, which are promising catalysts for a whole series of processes [2, 3]. According to the data in [4-6], these catalysts can also be used as efficient catalysts in the toluene disproportionation reaction. At the same time, the information in the scientific literature on this problem is scanty [7]. In the present paper a comparative study was made of the catalytic activity of the H form of the type Y, mordenite, and ZSM zeolites in the toluene disproportionation reaction.

A comparison of the data on the conversion of toluene at 420°C reveals that on the studied catalysts the reaction proceeds almost completely toward disproportionation (selectivity 80-90%). Under these conditions (Fig. 1) zeolite HY exhibits the highest catalytic activity, which decreases quite rapidly with time.

The HZSM and HM specimens are less active than HY, and they show a close initial degree of conversion (~ 5%). It should be mentioned that zeolite HM is gradually deactivated, while HZSM retains the original activity.

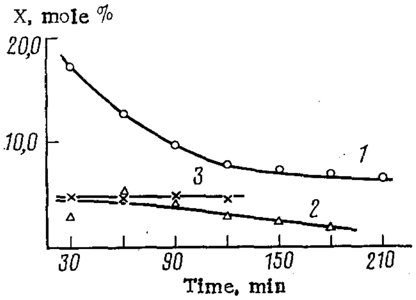

Fig. 1. Catalytic activity as a function of the experiment time at 420°C: 1) HY; 2) HM; 3) HZSM.

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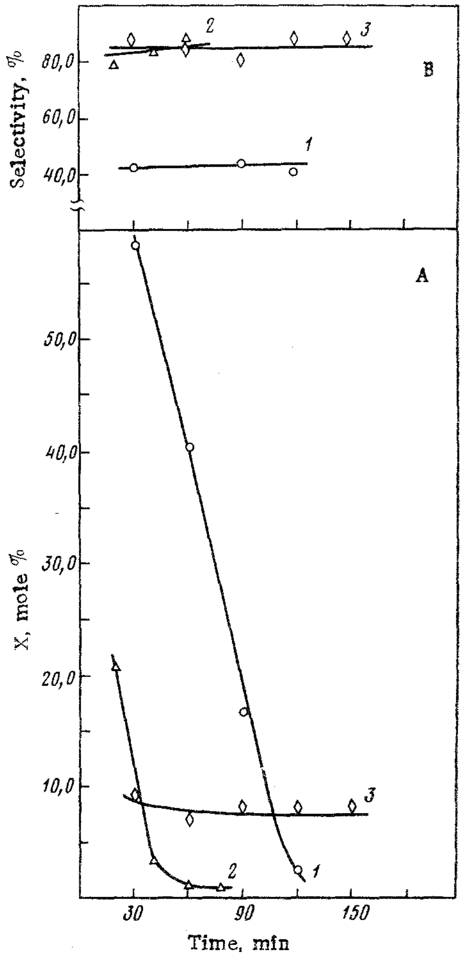

Fig. 2. Catalytic activity (A) and selectivity (B) as functions of experiment time at 450°: 1) HY; 2) HM; 3) HZSM.

Running the reaction at 450° (Fig. 2) leads to more important changes in the dependence of the activity on the time in the case of zeolites HY and HM when compared with zeolite HZSM; the HY and HM specimens are deactivated quickly, whereas HZSM retains a stable activity during the entire experiment. A practically selective conversion of toluene toward disproportionation is observed on the HM and HZSM catalysts. The HY zeolite is characterized by a low selectivity due to the progress of side reactions. Here various alkylaromatic hydrocarbons were detected in the catalyzate.

The mentioned differences in the three types of zeolites at 450° are manifested more distinctly at 470 and 500° (Fig. 3). Thus, the HY and HM zeolites are deactivated at 470° even more rapidly than at 450°. A similar effect was mentioned earlier [8] for the rare-earth modifications of zeolite Y when this reaction is run in the absence of a carrier gas.

In contrast, the high stability of zeolite HZSM is also retained under more drastic conditions. Thus, when the experiment temperature was raised from 470 to 500° an increase was observed in the catalytic activity of this catalyst in the conversion of toluene (see Fig. 3), which remained constant in our studied time interval. In analogous experiments the samples of the HY and HM zeolites (see Fig. 3) were completely deactivated even at 470°. The high stability of the HZSM zeolite when compared with HY and HM can be explained primarily by the characteristics of its structure, which, according to [9], does not permit the formation and accumulation of substantial amounts of condensation products, which are the "precursors" of coke. From the presented results (see Fig. 3) it can be seen that raising the temperature to 470° does not lead to important changes in the selectivity.

It is interesting to mention that on the HY and HM specimens, in the region where the degrees of conversion at 450-500° are below 3%, a change is observed in the equilibrium composition of the obtained xylenes. With decrease in the toluene conversion the amount of p-xylene increases up to 30-40% (its equilibrium amount

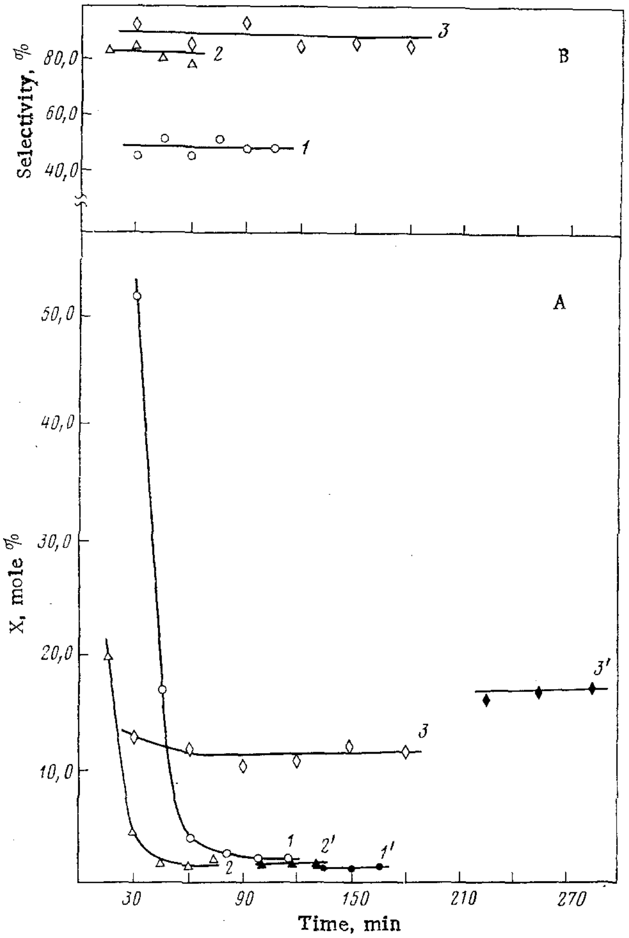

Fig. 3. Catalytic activity (A) and selectivity (B) as functions of the experiment time at 470° (light dots) and at 500° (dark dots): 1) HY; 2) HM; 3) HZSM.

for these temperatures is 23%). It may be assumed that the intense formation of coke on zeolites HY and HM shrinks the pores of the zeolites and favors obtaining the isomer with the smallest kinetic diameter, i.e., p-xylene. An analogous change in the equilibrium composition of the xylenes is also observed on different modifications of zeolite ZSM [4-6]. A similar effect on the HZSM specimens was not established under our adopted conditions.

EXPERIMENTAL

The ultrahigh silica zeolite ZSM-5 was synthesized as described in [10]. The zeolite samples as the H form were obtained by the thermal decomposition of the NH_4^+ modification in the air. The degree of decationization was 82% for HY and practically 100% for HM and HZSM-5. The SiO_2/Al_2O_3 mole ratio of the HY, HM, and HZSM-5 samples was respectively equal to 5.1, 10.0, and 70. Prior to experiment the catalysts were processed in a dry air stream at 500°. The experiments were run in an apparatus of the flow type at atmospheric pressure in the absence of a carrier gas. The toluene conversion (X, mole %) was studied in the range 420-500°. The selectivity of the reaction was calculated using the equation $(A + 2C)/B \cdot 100\%$, where A, B, and C are respectively the yields of xylenes, benzene, and trimethylbenzenes.

CONCLUSIONS

Important differences were established in the selectivity and stability of three types of zeolites (HY, HM, and HZSM) in the toluene disproportionation reaction at 450-500°. The high stability of the ultrahigh silica zeolite ZSM-5 specimen is explained by the characteristics of its structure.

LITERATURE CITED

1. Kh. M. Minachev and Ya. I. Isakov, Adv. Chem. Ser., 121, 451 (1973).
2. L. I. Piguzova, New Ultrahigh Silica Zeolites and Their Application in Petroleum Refinery [in Russian], TsNIITENeftekhim., Moscow (1977).
3. P. B. Weisz, Proc. Seventh Int. Congr. Catal., Tokyo, 1980, p. 1.
4. R. A. Morrison, US Patent 4052476 (1977).
5. W. W. Kaeding, US Patent 4016219 (1977).
6. W. O. Haag and D. H. Olson, US Patent 4097543 (1978).
7. N. Y. Chen, F. J. Kaeding, and F. G. Dwyer, J. Am. Chem. Soc., 101, 6783 (1979).
8. B. M. Kozlov, S. M. Lakiza, Kh. M. Minachev, E. S. Mortikov, A. S. Leontiev, and N. F. Kononov, Neftekhimiya, 2, 252 (1975).
9. N. Y. Chen and W. E. Gorwood, J. Catal., 52, 453 (1978).
10. R. I. Argauer and G. R. Landoldt, US Patent 3702886 (1972).

REACTION OF ANIONIC Pt(IV) σ-ARYL COMPLEXES WITH ELECTROPHILES AND NUCLEOPHILES

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The reaction of H_2PtCl_6 with aromatic compounds in either acetic acid or aqueous trifluoroacetic acid as the medium leads to the formation of anionic Pt(IV) σ-aryl complexes [1-4]. According to [5-7], the reaction proceeds on the type of electrophilic aromatic substitution. The reaction of anionic σ-aryl complexes with some electrophilic and nucleophilic reagents was studied in the present paper. CF_3COOH and Cl_2 were used as the electrophiles; the reaction of the complexes with such nucleophiles as arenes and olefins was studied.

The behavior of the complexes toward long heating was studied in aqueous CF_3COOH. The anionic σ-aryl complex accumulates first when a solution of H_2PtCl_6 and excess toluene in $CF_3COOH-H_2O$ is heated at 94.5°C. The kinetic curve for the accumulation section (Fig. 1) gives a linear semilogarithmic anamorphosis [7]. The concentration of the complex reaches a maximum in 1 h, after which the complex begins to decompose rapidly, accompanied by the formation of chlorotoluene, ditolyl, and Pt(II) derivatives. The complex undergoes almost complete decomposition during the next 2.5 h. The decomposition of the complex is slowed up considerably if, after reaching its maximum concentration, the excess toluene is removed by extraction with hexane (in Fig. 1 this point is indicated by an arrow). A green complex (ν_{max} 15,600 cm^{-1}) accumulates at the same time, which can be extracted with chloroform. The concentration of this complex in the extract was determined spectrophotometrically. The indicated absorption band gradually disappears if a small amount of ethanol or water is added to the $CHCl_3$ solution and the solution assumes a yellow color. The PMR spectrum (in $CDCl_3$) of this complex has a multiplet at δ 7.00-7.67, and the CH_3 group appears as singlets with δ 2.18, 2.29, and 2.38. The nature of this derivative is not entirely clear. A possible structure is the structure of an aryl derivative that is protonated in the aromatic ring.

As can be seen from Fig. 1, extraction of the toluene by hexane and its replacement by anisole causes the σ-tolyl complex to decompose at approximately the same rate as in the presence of toluene. As a result, the diaryls are formed mainly by the reaction of the Pt(IV) σ-aryl complex and the free arene.

When one arene is replaced by another more nucleophilic arene, i.e., by one that contains a more electron-donor substituent, the decomposition of the complex precedes the transmetalation.

$$\mathrm{ArPt(IV)} + \mathrm{Ar'{-}H} \overset{(H+)}{\rightleftarrows} \mathrm{Ar'Pt(IV)} + \mathrm{Ar{-}H}$$

Thus, when the σ-tolyl complex is heated with an excess of either anisole or ethylbenzene in $CF_3COOH-H_2O$ a mixture of the starting complex with either the Pt(IV) σ-anisyl or σ-ethylbenzene derivative is formed. On longer heating

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