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Catalytic isomerization of dihalobenzenes $C_6H_3X_2R$ in the presence of high-silica zeolites

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Catalytic isomerization of dichloro- and difluorobenzenes was carried out under conditions of a gas-phase reaction occurring in the presence of metallosilicates with the pentasil-type zeolite structure, in which several silicon atoms are isomorphically replaced by Al, Ga, or Fe atoms. A correlation between the acid properties of these zeolites and their ability to induce dihalobenzene isomerization was found.

Key words: isomerization, difluorobenzenes, dichlorobenzenes, zeolites.

At present, dihalobenzenes (DHB) of general formula $C_6H_3X_2R$ (where X = Cl or F, and R = H or CH_3) are the base for synthesizing plant protective agents with directed action, drugs, dyes, thermostable polymers, *etc.*

The present communication reports on a study of the catalytic properties of zeolites in the isomerization of dichloro- and difluorobenzenes (DCB and DFB).

Experimental

High-silica pentasil-type zeolites were synthesized under hydrothermal conditions from metallosilica gels without addition of organic compounds or in the presence of tetrabutyl- or tetraethylammonium ions. It was established by X-ray diffractometry and IR spectroscopy that the zeolites have the structure of pentasils of the types ZSM-5, ZSM-8, and ZSM-11. The high degree of crystallinity of the samples (at least 95 %) and the absence of admixed foreign phases were confirmed using adsorption of water vapor and *n*-heptane. The amount of out-of-frame aluminum, gallium, and iron was determined from chemical analyses of the samples and by analyzing the zeolites after ion exchange in solutions of cesium salts at pH 11. Although the overall Si/M ratio of all the samples was within 19—21, the true Si/M ratios in frame positions were found to be 20—25 (except for the Fe-containing silicate, in which the true Si/Fe ratio amounted to 100). Pentasils (5 cm^3) compacted without a binder (particle size 0.2—0.5 μm) were placed in an isothermal flow reactor. Isomerization was carried out at 673—923 K, a pressure of 0.1—3.5 MPa, and a volume rate of the liquid of 0.1—2 h^{-1}. The starting compounds and the products of their transformation were analyzed by GLC using a glass capillary column with an OV-101 phase. The selectivity of formation of each dihalobenzene isomer was calculated according to the formula

$$S_i = \frac{C_i}{C_0 - C'}$$

where C_0 is the concentration of the starting isomer, C' is the concentration of the reacted starting isomer, and C_i are the concentrations of the isomers obtained.

Results and Discussion

The results obtained upon isomerization of 1,2-DCB in the presence of the pentasils studied are shown in Fig. 1. The activity of the catalysts forms the series

Al-silicates > Fe-silicate > Ga-silicate

(the isomer ratio in the equilibrium mixture at 673 K is[1] 1,2-DCB : 1,3-DCB : 1,4-DCB = 0.18 : 0.44 : 0.38). For all types of the catalysts tested, the selectivity of 1,3-DCB formation increases with increasing conversion of the 1,2-isomer (Fig. 2) along the series

Fe-silicate > ZSM-8 > Ga-silicate > ZSM-5 > ZSM-11

at 10 % degree of conversion and along the series

Fe-silicate > Ga-silicate > ZSM-11 > ZSM-8 > ZSM-5

at 30 % degree of conversion.

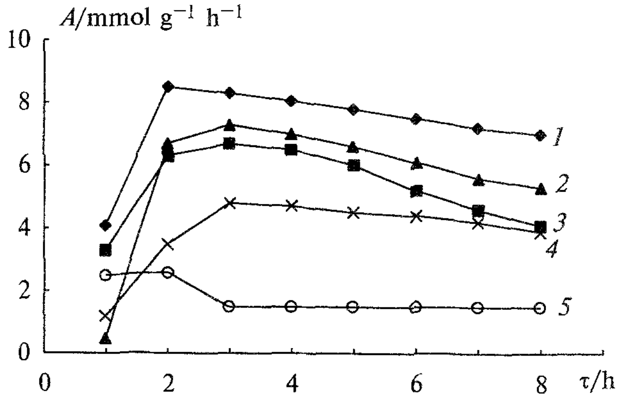

Fig. 1. Activity (A) of various zeolite catalysts in the isomerization of 1,2-DCB: *1*, ZSM-11; *2*, ZSM-8; *3*, ZSM-5; *4*, Fe-silicate; *5*, Ga-silicate.

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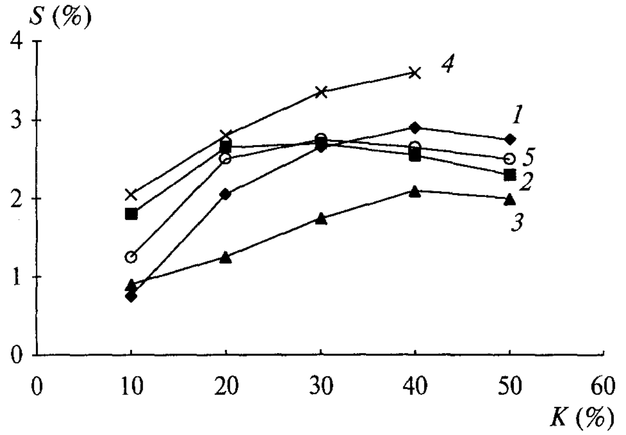


Fig. 2. Dependence of the selectivity (*S*) of 1,3- and 1,4-DCB formation on the degree of 1,2-DCB conversion (*K*). For designations, see Fig. 1.

The selectivity depends on the activity of the catalysts (see Figs. 1, 2). The highest activity provides the maximum selectivity. An increase in activity brings about a decrease in selectivity with respect to 1,3-DCB for all the samples except the Fe-silicate. This probably results from the fact that isomerization of 1,2-DCB involves protic acid centers located both in zeolite channels and on the outer surfaces of the crystals. Unlike alumosilicates, strong acid centers on the outer surface of Fe-silicates are blocked by iron oxide clusters and do not participate in acid-base transformations.[2]

We also made an attempt to carry out isomerization of DFB. According to literature data, the electronic state of the fluorine atoms in DFB, their low polarizability, and the high strength of the C—F bond determine the high inertness of DFB under catalytic isomerization conditions.[3] Insignificant isomerization under these conditions is accompanied by side processes such as disproportionation and dehydrofluorination. Catalytic isomerization of DFB is possible in the presence of "magic acids".[4] Because zeolites of the pentasil family possess a set of strongly acidic active sites, it was reasonable to expect that catalytic isomerization of DFB would be feasible on heterogeneous catalysts. This assumption was confirmed experimentally.

Table 1 presents results obtained on isomerization of individual DFB isomers in the presence of ZSM-5 type zeolites. It follows from the data obtained that 1,4-DFB virtually does not undergo isomerization under the reaction conditions, while 1,3-DFB isomerizes more readily than the 1,2-isomer.

Experiments showed that Ga- and Fe-silicates are quite inactive in DFB isomerization, while ZSM-5, ZSM-8, and ZSM-11 display the same series of activity as in the case of DCB. On the other hand, the catalysts favor the formation of the 1,3-isomer from 1,2-DCB, but the 1,4-isomer is predominantly formed from 1,2-DFB.

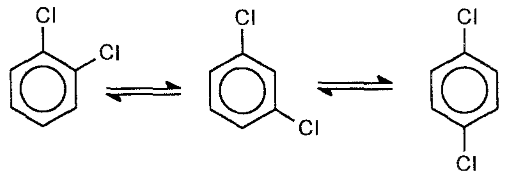
Table 1. Catalytic isomerization of individual difluorobenzene isomers (3.5 MPa, volume rate of feed of the liquid 1 h^{-1})

T/ K	Starting isomer	Content of DFB isomers in the catalysate (mass. %)		
		1,2-	1,3-	1,4-
673	1,2-DFB	100.0	—	—
723		98.3	0.7	1.0
923		95.1	1.8	3.1
673	1,3-DFB	—	96.4	3.6
723		—	96.3	3.7
923		3.1	91.5	5.4
673	1,4-DFB	—	—	100.0
723		—	—	100.0
923		—	—	100.0

Table 2. Catalytic isomerization of individual dichlorobenzene isomers (3.5 MPa, volume rate of feed of the liquid 1 h^{-1})

T/ K	Starting isomer	Content of DCB isomers in the catalysate (mass. %)		
		1,2-	1,3-	1,4-
573	1,2-DCB	89.5	6.4	4.1
673		28.2	48.1	23.7
573	1,3-DCB	6.0	85.5	8.5
673		21.4	53.2	25.3
573	1,4-DCB	5.6	5.7	88.7
673		10.6	42.2	47.2

In our opinion, this effect results from some features of DFB rather than from differences in the mechanisms of DCB and DFB isomerization. In analogy to the isomerization of DCB in the presence of HCl,[5] this mechanism probably involves stepwise migration of chlorine atoms, *i.e.*, 1,2-DCB is first transformed into the 1,3-isomer and then into the 1,4-isomer:



Isomerization of DFB probably also occurs by 1,2-shifts.[6] Due to the low ability to undergo protonation and the strong polar effect of the fluorine atoms, 1,4-DFB is inert to isomerization.

Thus, the present study showed that zeolites possessing the pentasil structure can catalyze the isomerization of DFB and DCB. The activity and selectivity of pentasils in the isomerization depend on their chemical composition.

References

1. D. Stall, E. Westram, and G. Zinke, *The Chemical Thermodynamics of Organic Compounds*, John Wiley and Sons, New York, 1969.
2. G. K. Ione and V. N. Romannikov, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauki,* 1990, 131 (in Russian).
3. G. A. Olah, W. S. Tolguesi, and R. E. A. Dear, *J. Org. Chem.*, 1962, 27, 16, 3449.
4. *Carbonium Ions*, Vol. III, Wiley-Interscience, New York, 1972.
5. V. A. Koptyug, *Izomerizatsiya aromaticheskikh soedinenii* [*Isomerization of Aromatic Compounds*], Novosibirsk, 1963, 523 (in Russian).
6. L. T. Scott and J. R. Highsmith, *Tetrahedron Lett.*, 1980, **21**, 4703.

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