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Academician of the Academy of Sciences of the Georgian SSR G. V. Tsitsishvili, Sh. I. Sidamonidze,

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## Abstract

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## PHYSICAL CHEMISTRY

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# CATALYTIC ACTIVITY OF ZEOLITES NaX, CaA, AND HX IN CRACKING AND DEHYDRATION REACTIONS

Recently, increased interest has been shown in synthetic zeolites. In the dehydrated state, these crystalline aluminosilicates are finely porous bodies with cavities, entrances into these cavities, and channels that are strictly fixed in size. The structure and composition of zeolites determine their properties and selectivity and influence catalytic activity. The catalytic properties of zeolites are largely determined by the cations that compensate the negative charge of the anionic crystalline framework. In work ([1]) it was shown that, in the dehydrogenation of alkanes (up to $C_6$) on compressed CaA zeolite, the reaction pattern observed on amorphous aluminosilicates is reproduced. In the dehydrogenation of *n*-dodecane on CaA, benzene—so characteristic of alkane dehydrogenation processes occurring on amorphous aluminosilicates—was not found in the catalyst. On the basis of a careful analysis of the coking products it was established that, in the course of the reaction in the pores of the zeolite, benzene is formed, and only steric hindrance (the strict definiteness of the sizes of the entrance windows) prevents its removal from the pores of the zeolite. In work ([2]) it was established that at low temperatures, in the cracking reaction of *n*-decane, amorphous aluminosilicate and magnesium silicate are much inferior in catalytic activity to H-mordenite. Study of the dealkylation reaction on NaX ([3]) showed that this zeolite does not catalyze the cracking of cumene and that only by replacing $Na^+$ with $Ca^{2+}$ can a significant reaction yield be achieved. In works ([3,4]) it is proposed that the catalytically active centers of dehydrated crystals are localized inside the cavities of zeolites.

After completion of the present study, an interesting paper ([5]) appeared, in which the distinctive character of adsorption and of the kinetics of catalysis of cumene cracking on zeolite 10X was established and, in particular, the discrepancy of the experimental data with the equation of A. B. Frost.

We set ourselves the task of studying the catalytic activity of the synthetic zeo-

Fig. 1. Dehydration of isopropyl alcohol on HX zeolite (A), on NaX zeolite (B), and on CaA zeolite (V); $V_0$ is the feed rate, $y$ is the degree of conversion.

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lites NaX, CaA, and HX in the cracking reactions of cumene and the dehydration of isopropyl alcohol.

The study of catalytic activity was carried out in a flow apparatus with a temperature-control accuracy of ±1.5°. During the experiments, all conditions were created to eliminate possible systematic errors ($^6$). Analysis of the reaction products was carried out on a VTI-2 gas analyzer. Catalyst grains were obtained by pressing powdered zeolites at the same pressure and were diluted in the reactor with an inert substance (quartz). For the study we used NaX (series Ts-202–98) and CaA (series Ts-202–29), prepared by B. A. Lipkind, and HX zeolite, obtained at the P. G. Melikishvili Institute of Chemistry of the Academy of Sciences of the Georgian SSR by method ($^8$).

As a result of the study, we established that cracking of cumene on CaA, NaX, and HX zeolites does not occur below 400°; study of the course of the reaction becomes possible only at 425—435°. Constancy of the catalytic activity of zeolites is difficult to achieve because they are readily poisoned. Thus, a 30-minute passage of iso-$C_3H_7OH$ over the catalysts

deprives them of their cracking ability, and only after cumene has been passed for 4 hours is the initial activity restored. This observation is probably due to the greater affinity of zeolites for unsaturated hydrocarbons (propylene) and for polar substances (water). The lower catalytic activity of synthetic zeolites in the cracking reaction

**Fig. 1.** Dehydration of isopropyl alcohol on HX zeolite (**A**), on NaX zeolite (**B**), and on CaA zeolite (**V**); $V_0$ is the feed rate, $y$ is the degree of conversion.

of cumene, in comparison with amorphous aluminosilicates, can be explained by steric hindrance: because of their large size, cumene molecules are unable to penetrate into the primary pores of the zeolite. The small observed conversion of cumene at elevated temperatures ($t$ = 425—435°) is apparently due to the secondary porosity of the zeolite grains. M. M. Dubinin in his works ($^7$) showed that the secondary porosity of zeolites, in contrast to the primary porosity, is not characterized by specificity. The small fraction of secondary porosity in the total porosity of the zeolite accounts for the low catalytic activity of molecular sieves.

**Fig. 2.** Dehydration of isopropyl alcohol on HX, NaX, and CaA zeolites at 330°.

NaX, CaA, and HX zeolites are characterized by highly effective dehydrating

Fig. 2. Dehydration of isopropyl alcohol on HX, NaX, and CaA zeolites at 330°.

Figure 2: Fig. 2. Dehydration of isopropyl alcohol on HX, NaX, and CaA zeolites at 330°.

properties (HX > NaX > CaA). On the HX and NaX forms, dehydration of iso-$C_3H_7OH$ is observed at 210° and proceeds considerably more intensively than on active alumina. On HX zeolite the degree of conversion $y$ already at 240° approaches unity. For NaX and HX zeolites, beginning at 240°, a decrease in the degree of conversion is observed with an increase in the alcohol feed rate (Fig. 1). This dependence, observed up to $y = 0.4$, unambiguously indicates peculiar diffusion complications in the reaction occurring on zeolites. The points obtained for absolute iso-$C_3H_7OH$ and its aqueous solutions fall on a common line, which makes it possible to regard water vapor as non-toxic in the dehydration reaction.

NaX, CaX, and HX zeolites do not change the direction of the reactions of cumene cracking and isopropyl alcohol dehydration.

To determine the activation energy of the dehydration of isopropyl alcohol, we used the graphical method proposed in ($^9$). This method makes it possible to determine kinetic constants and to establish the region in which the process takes place without data on the reaction mechanism. The activation energy determined by this method for the dehydration of isopropyl alcohol on NaX zeolite in the temperature interval 240—270° reaches 7.4 kcal/mol, and for the HX form, 27 kcal/mol. Such a strongly perceptible difference in the activation energies on NaX and HX crystalline aluminosilicates suggests that the temperature intervals of the regions in which the dehydration reaction proceeds on these zeolites are different.

In conclusion, it should be noted that the different catalytic activity exhibited by NaX, HX, and CaA zeolites cannot be due solely to macrofactors (steric hindrance, transport of alcohol molecules and reaction products into the pores of the zeolite). Here, apparently, the individual properties of the cations also play a considerable role (see Fig. 2).

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## REFERENCES

1. P. N. Galich, A. A. Gutyria et al., DAN, **144**, No. 1, 147 (1962).
2. A. U. Kough, J. B. Sand, J. Am. Chem. Soc., **83**, No. 6, 3536 (1961).

3. V. J. Frillete, P. B. Weisz, R. L. Golden, J. Catalysis, No. 4 (1962).

4. V. J. Frillete, P. B. Weisz, R. L. Golden, J. Catalysis, No. 4 (1962).

5. K. V. Topchieva, B. V. Romanovskii, Khon T Khoang, DAN, **149**, No. 3, 644 (1963).

6. K. V. Topchieva, B. V. Romanovskii, S. A. Veniaminov, Vestn. Moskovsk. Univ., No. 1, 5 (1960).

7. M. M. Dubinin, Izv. AN SSSR, OKhN, 1961, No. 7, 8.

8. G. V. Tsitsishvili, G. D. Bagratishvili et al., DAN, **152**, No. 5 (1963).

9. G. M. Panchenkov, Yu. M. Zhorov, DAN, **130**, No. 6, 1280 (1960); DAN, **135**, No. 5, 1172 (1960).

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