INFLUENCE OF HEAT TREATMENT ON THE ADSORPTION, STRUCTURAL, AND CATALYTIC PROPERTIES OF DECATIONIZED L ZEOLITES

I. V. Mishin, A. L. Klyachko, T. Matkhé,
G. A. Ashavskaya, and G. M. Kutateladze

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The specific features of the catalytic action of zeolites are associated with the presence in them of a regular crystal structure. The maintenance of the skeleton upon heat treatment is of great importance for the creation of zeolite catalysts. However, a comparison of the catalytic activity with the degree of crystallinity of zeolites which have undergone heat treatment has heretofore scarcely been utilized in catalytic investigations.

The purpose of the present work was to study the structural changes in decationized L zeolites treated at various temperatures and to compare the results of the adsorption and x-ray diffraction measurements with the catalytic activity of these zeolites in the conversions of o-xylene.

EXPERIMENTAL

The original sample of KNaL with the composition $K_{9.96}Na_{0.11}[Al_{20}Si_{26}O_{72}]$ with an SiO_2/Al_2O_3 mole ratio equal to 5.2 was synthesized at the All-Union Scientific-Research Institute of the Petroleum Industry. Zeolites with different degrees of exchange of K^+ for NH_4^+ (17-90) were prepared by treating the original sample with NH_4NO_3 solutions.

The x-ray diffraction analysis of the zeolites was conducted on a Dron-2 diffractometer with the use of Cu K_α radiation with an Ni filter and a rate of rotation of the goniometer equal to 2 deg/min. The total intensities of the reflections from the 100, 001, 220, 221, 212, and 222 planes were used for the calculation of the crystallinity; the sum of these reflections for the original zeolite KL after heating at 100°C was taken as 100% crystallinity.

The adsorption and desorption isotherms of benzene vapor were measured at 20°C on a weighing instrument quartz coils. Before the measurements, tablets of the zeolites, which were molded without a binder, were subjected to a vacuum (10^{-5} torr) at 350°C. The porosity was evaluated from the adsorption and desorption isotherms of benzene.

The catalytic activity in the conversion of o-xylene was measured in a microbatch system at 300°C. The carrier gas was He, which was supplied at the rate of 2.1 liters/h. The weight of the catalyst in all the experiments was 0.2 g, and the batch volume was 4 µl. The gas-chromatographic separation of the products was conducted in a column containing Porolite with 5% Bentone-34 and 5% dioctyl phthalate. After the batch was fed into a column thermostated at 40°C, its temperature was increased to 110°C under programmed conditions at the rate of 12 deg/min. Preliminary calibration established that areas of the chromatographic peaks vary proportionally to the concentration of the reaction products: xylenes, trimethylbenzenes, and toluene.

DISCUSSION

Variation of Crystallinity. Zeolite L with a low degree of exchange (30%) was found to be completely stable during heating at from 300 to 650°C (Fig. 1). In the case of the zeolites with α = 56 and 82%, structural irregularities begin to be manifested already at comparatively low temperatures (>300°C), at which the process of dehydration is completed [1], and after heating at 500°C, their crystallinity does not exceed 15-30%, according to the x-ray diffraction data.

According to the x-ray diffraction measurements in zeolite L ~30% of the K^+ are found in the large channels and are easily replaced by NH_4^+ ions [2]. When L zeolites with α = 30% are subjected to dehydration followed by the decomposition of the NH_4^+ ions, the zeolite skeleton is not destroyed, since the principal secondary structural elements, i.e., the can-

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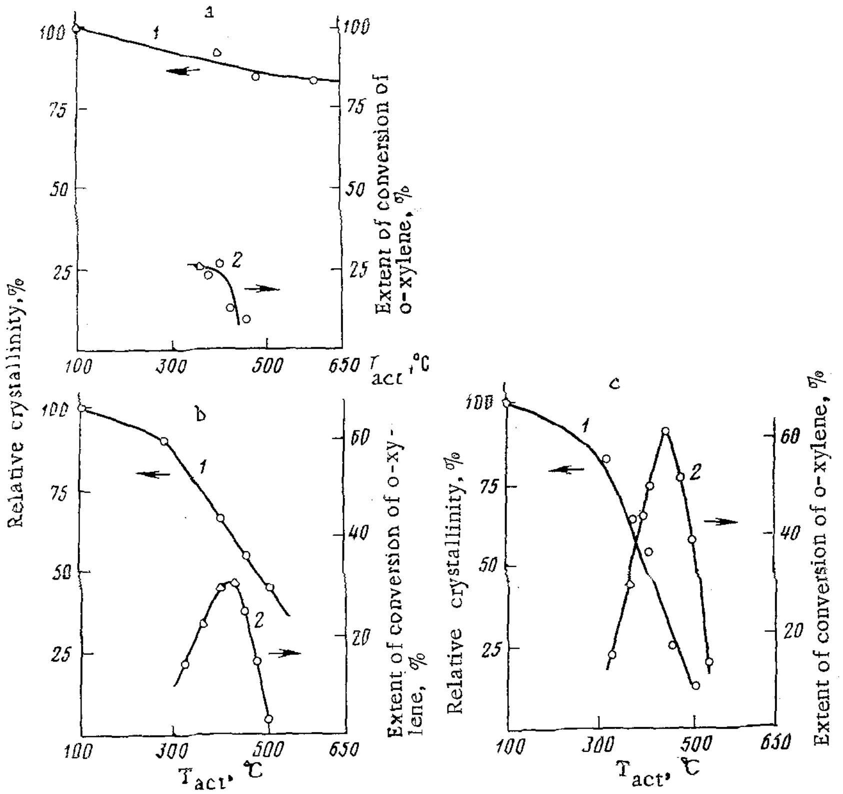

Fig. 1. Dependence of the relative crystallinity (1) and catalytic activity in the conversion of o-xylene (2) on the activation temperature for zeolites NH_4KL-30% (a), NH_4KL-56% (b), and NH_4KL-82% (c).

crinite cells and the hexagonal prisms, are stabilized by the large K^+ cations. After the K^+ ions have been expelled by NH_4^+ ions from sites located between neighboring cancrinite cells and in the centers of these cells, the thermostability drops sharply. The thermal decomposition of the NH_4^+ cations results in the formation of proton centers, which cannot remain at the centers of the ε cells or in the distorted eight-membered channels after dehydration and move toward one of the O atoms. This creates an unfavorable distribution of the charges and weakens the skeleton.

Alteration of Porous Structure. Measurement of the adsorption of benzene vapor makes it possible to determine the changes in the volume of the micropores and the secondary porosity of L zeolites during heat treatment. At low relative pressures (below $p/p_s = 0.1$) the isotherms (Fig. 2) show a sharp increase in the adsorption of benzene, which is associated with the filling of the micropores and the formation of a monolayer on the surface of the secondary pores. In this case, the zeolite micropores formed by 12-membered channels are filled. A comparison of the values of the adsorption at $p/p_s = 0.1$ for the NH_4KL zeolites showed that the higher the degree of exchange, the more strongly is the zeolite destroyed as the temperature of the heat treatment is increased. According to the data in Table 1 and the results of the x-ray diffraction measurements (see Fig. 1), the decrease in the micropore volume is significantly smaller than the drop in the relative crystallinity. Such a phenomenon must be encountered in evaluating the stability of the structure of zeolites on the basis of x-ray diffraction and adsorption data [3]. Heating probably, first of all, destroys the regular arrangement of the skeletal fragments, although complete destruction of the channels does not yet occur.

If the adsorption at $p/p_s = 0.1$ is taken as the volume of the micropores, it turns out that the original zeolite KL adsorbs 0.098 cm^3/g benzene, although the volume of the large channels calculated from the x-ray diffraction data is 0.16 cm^3/g. The difference between these values may be attributed to the incomplete crystallization of the zeolite. Adsorption occurs in nonzeolite pores at relative pressures greater than 0.1. In the samples investigated there are nonzeolite pores of two types: narrow pores with a radius 10-15 Å, which are filled at $p/p_s = 0.1$-0.3, and wide pores with radii > 300 Å, in which benzene is adsorbed at

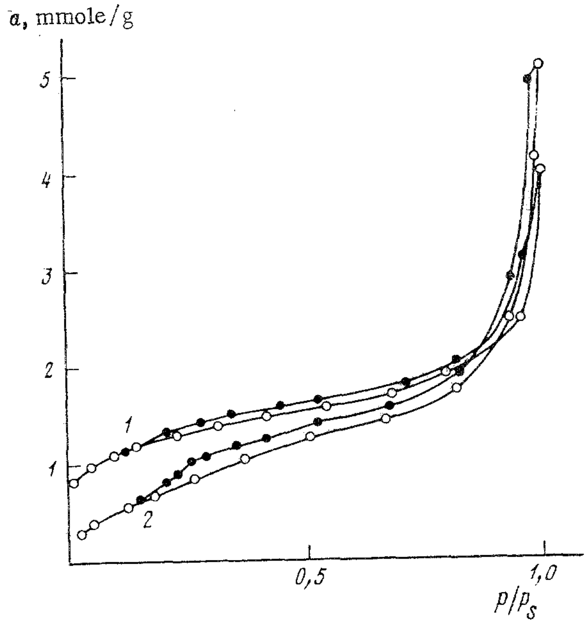

Fig. 2. Adsorption and desorption isotherms of benzene on zeolites: 1) original KL sample; 2) zeolite NH_4KL-82% heated in air at 500°C (the light points correspond to adsorption, and the dark to desorption).

TABLE 1. Adsorption of Benzene Vapor ($p/p_S = 0.1$) by Decationized L Zeolites

Zeolite	a, mmole/g after activation		
	in vacuum, 350°C	in air	
		400°	500°
KL	1,10	—	—
NH_4KL-65%	1,25	1,09	0,96
NH_4KL-82%	1,36	1,02	0,85
NH_4KL-90%	0,95	0,74	0,57

$p/p_S > 0.9$. At relative pressures from 0.3 to 0.9 the adsorption increases only slightly. Apparently, the samples of L zeolites do not contain pores with radii from 15 to 300 Å.

The presence in the samples of pores with radii from 10 to 15 Å is apparently due to an admixture of an amorphous phase, which appears as a result of the incomplete crystallization of the zeolite. The volume of these pores is 0.01 to 0.02 cm^3/g and does not change during the heat treatment of the zeolites. The amorphous phase formed under the action of elevated temperatures most likely does not contain open pores.

A sharp increase in adsorption at high relative pressures ($p/p_S > 0.9$) is observed on all the adsorption isotherms and is associated with the filling of the wide pores with $r > 300$ Å. The total volume of these pores cannot be determined from the adsorption of benzene; however, the part which is filled with benzene at saturation amounts to 0.3-0.4 cm^3/g and is practically not dependent on the chemical composition or the treatment conditions of the zeolites. The presence of a large number of wide pores indicates that in the L zeolites studied the crystallites have dimensions <1 μm and that at high relative pressures benzene fills the space between these crystallites.

Catalytic Activity. The conversion of o-xylene results in the formation of isomerization products, viz., m- and p-xylene, and disproportionation products, viz., toluene and trimethylbenzene. The total extent of conversion of o-xylene was taken as a measure of the ac-

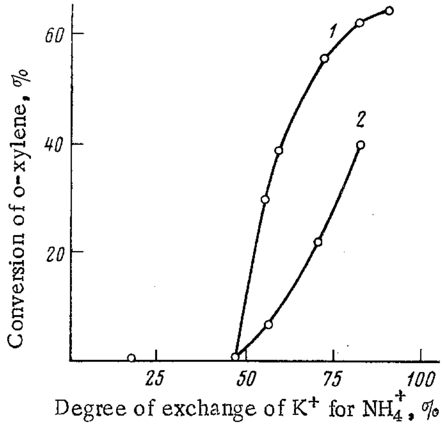

Fig. 3. Dependence of the catalytic activity of NH_4KL zeolites in the conversion of o-xylene on the degree of ion exchange for samples activated at 425°C (1) and 500°C (2).

tivity of the NH_4KL zeolites. As follows from the data on the catalytic activity (Fig. 3), the zeolites with a degree of decationization >50% display appreciable activity. The existence of a threshold concentration of K^+ cations, above which the conversion of xylene at 320°C is not observed, is associated with the fact that the formation of the strong acid centers occurs only after the removal of half of the K^+ cations [4]. The data in Fig. 3 also show that an increase in the heating temperature of the NH_4KL zeolites from 425 to 500°C sharply lowers the activity.

The drop in catalytic activity when the activation temperature is increased might have been attributed to the destruction of the structure of the zeolites. However, a study of the dependence of the total extent of conversion of o-xylene on the activation temperature T_{act} for NH_4KL zeolites with degrees of exchange equal to 30, 56, and 82% led to the conslusion that no direct correlation between the activity and the stability of the skeleton is observed (see Fig. 1). The NH_4KL-30% sample is relatively inactive, and an influence of T_{act} on the extent of conversion of o-xylene can be traced only above 360°C. The activity of this zeolite remains practically unchanged when it is heated from 360 to 400°C and it drops at a higher T_{act}, although the total crystallinity varies only slightly up to 600°C.

In the case of the NH_4KL-50% and NH_4KL-82% zeolites, the extent of conversion increases sharply when T_{act} is increased from 320 to 425°C and then drops sharply, while the decrease in the crystallinity of these samples becomes appreciable already at T_{act} > 300°C and occurs continuously over the entire range of temperatures indicated.

Such a nature of the curves indicates that the increase and the decrease in the catalytic activity should be associated with the formation and deactivation of catalytically active sites. The main role in the conversion of hydrocarbons on zeolites is played by proton centers. They form during the activation of NH_4 forms of zeolites as a result of the decomposition of the ammonium ions. The data from IR spectroscopy and DTA show that the destruction of NH_4^+ ions in L zeolites begins at once after dehydration and is completed near 450°C [1, 5]. The increase in catalytic activity when T_{act} is increased from 320 to 425°C is due, in most likelihood, to the formation of hydroxyl coating.

A further increase in T_{act} is accompanied by a decrease in activity, and the zeolites heated at T > 500°C are practically incapable of converting o-xylene. According to the DTA data obtained with the same samples, the bulk of the hydroxyl groups are removed below 500°C [6]. The dehydroxylation process apparently occurs at once after deammoniation and perhaps partially overlaps it. As a result, there is a sharp drop in activity in comparatively narrow ranges of variation of the heat-treatment temperature. The study of the heats of adsorption of NH_3 on these samples [4] revealed the existence of acid centers of three types in the decationized zeolites. It was shown that the total number of acid centers decreased to half when the temperature of the heat—vacuum treatment was increased from 300 to 480°C, the centers with q_{NH_3} = 120 and 100 kJ/mole vanishing. The catalytic activity in the conversion of o-xylene is probably attributed to such centers.

The tendency of the H forms of L zeolites to undergo dehydroxylation may be attributed to the high concentration of OH groups in the limited volume of the intracrystalline space. Thus, simple division of the volume of the unit cell of zeolite L (2205 Å^3) among the eight OH groups in the NH_4KL-82% sample gives a value of 276 Å^3. This is significantly smaller than the volumes of the unit cells of mordenite and zeolite Y per OH group (400 and 388 Å^3, respectively).

Thus, a comparison of the data on the changes in the crystallinity and catalytic activity leads to a conclusion that the structural changes in the skeleton do not have a direct influence on the activity. The zeolite with a degree of decationization equal to 82%, for example, displays a maximum activity when T_{act} = 425°C, at which no more than 40% crystallinity is maintained. Pichat et al. [5] also believe that the decrease in crystallinity is not the reason for the decrease in the acidity and catalytic activity of decationized zeolites. They attribute the decrease in the activity of the samples with high degrees of exchange to migration of the proton centers into portions of the crystal structure which are inaccessible to the reactants. However, the good agreement between the temperature ranges for the loss of weight in the high-temperature region and the change in catalytic activity [6] still leads to the conclusion that the sharp decrease in activity in the NH_4KL zeolites is caused by the removal of the OH groups.

CONCLUSIONS

1. The changes in the catalytic activity of decationized L zeolites during heat treatment are associated with the formation and removal of proton centers and are not directly related to the decrease in crystallinity.

2. The x-ray diffraction measurement of the decrease in crystllinity during heat treatment reflects the destruction of structural elements but does not permit evaluation of the degree of amorphization of zeolites.

3. The destruction of the skeleton of decationized L zeolites is accompanied by a decrease in the volume of the micropores, but it does not influence the content of open pores and macropores.

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