

INFLUENCE OF ZEOLITE STRUCTURES ON THEIR DEHYDRATION CATALYTIC PROPERTIES

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The present study deals with the investigation of relationship of crystalline structure of zeolites to their catalytic activity.

Study of the character of dehydration reaction of *isopropyl* alcohol over synthetic type faujasite, L, erionite zeolites and on the natural clinoptilolites and their hydrogen forms, high-temperature adsorption of compounds of the base character, and application of isotopic heterogeneous exchange and microcalorimetric methods enabled the authors to find a relation between a structure and catalytic activity of zeolites.

Study of the catalytic activity and selectivity, the nature of the active sites and the influence of zeolite structure on the given properties deserves thorough consideration of investigators.

In papers [1—6] dehydration of *isopropyl* alcohol was investigated over synthetic zeolites. The role of cation nature and the degree of exchange of a monovalent cation by a polyvalent one on the catalytic activity of zeolites were studied. Notwithstanding the fact that the overwhelming majority of the authors relate catalytic activity of zeolites to the acidic nature of active sites, in certain cases direct relationship between the activity and the degree of acidity of zeolites is not clearly established [7].

In the present study catalytic activity of highly siliceous zeolites of different structure (NaY, KL, NaKE and natural clinoptilolites and their hydrogen forms) was investigated using the decomposition of *isopropyl* alcohol as a model reaction.

Experimental

The catalytic activity of zeolites was studied by the flow method. Experiments were carried out in a quartz reactor at atmospheric pressure. The analysis of the gaseous reaction products was made by GC.

Initial zeolites were washed to pH=9. X-ray diffraction studies of the treated samples, as well as of the zeolites used testify the preservation of crystalline lattice. The amount of the zeolite loaded into the reactor was 25 cm³. Experimental points were taken when constant activity of the catalyst has been reached. Ammonium zeolites were obtained by the treatment of initial zeolites with 0.25—0.50 and 1.0 N solutions of ammonium chloride with an addition of small amount of NH₄OH.

Hydrogen forms of zeolites were obtained by calcinating the ammonium forms up to 300—350 °C in nitrogen flow. All samples were preheated in a reactor under the flow of pure nitrogen, for 5 hr. High-temperature-adsorption of the compounds of basic character was carried out at 210 °C. After each experiment careful regeneration of catalyst was conducted, returning the sample to its initial activity.

Investigation of the possibilities of isotopic heterogeneous exchange of oxygen atoms in order to study oxidic catalysts, conducted by G. K. BORESKOV, was developed further in the studies of K. H. M. MINACHEV, where a novel approach of determination of absolute concentration and mobility of hydrogen of heterogeneous catalysts was applied for the reaction of heteroexchange of deuterium. We have used one of the versions of the method [8] described in a series of papers. Differential heats of adsorption were determined at 25 °C by using a microcalorimeter type Calve of the French firm "Cetaram".

Results and Discussion

Synthetic faujasite type NaY zeolite is not characterized by high dehydration capacity. Substitution of Na cations by ammonium ions and subsequent decomposition of the latter according to a conventional scheme leads to the formation of hydrogen (decaionized) forms of zeolite. The experimental data obtained show that a rise in the degree of exchange causes sharp increase of catalytic activity of faujasite type zeolite (Fig. 1). Decationization of Y type zeolites up to 30% decreases temperature values corresponding to the minimal and maximal values of conversion by more than 100°. Exchange of Na ions by NH_4^+ ions up to 47% with the subsequent

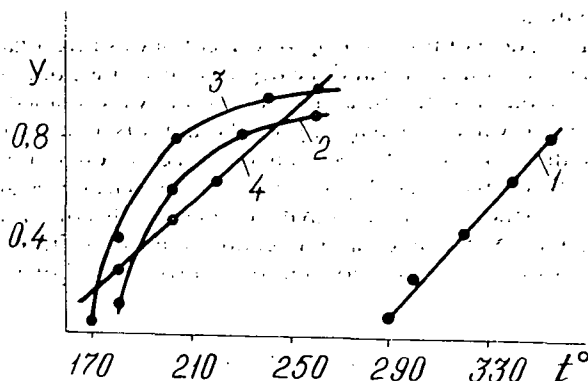


Fig. 1. Dehydration of isopropyl alcohol over faujasites: 1. NaY, 2. 0.30 HNaY, 3. 0.47 HNaY, 4. 0.69 HNaY.

decaionization, significantly enhances the catalytic properties of zeolites. Further decaionization causes no appreciable change in dehydration activity.

Synthetic type L zeolite exhibits low catalytic activity (Fig. 2). Decationization of initial zeolite NH_4KL causes considerable increase of catalytic activity.

NaKL type zeolite is also characterized by a low catalytic activity. Very low conversion ($y=0.056$) of isopropyl alcohol occurs at 300 °C, and reaches its maxi-

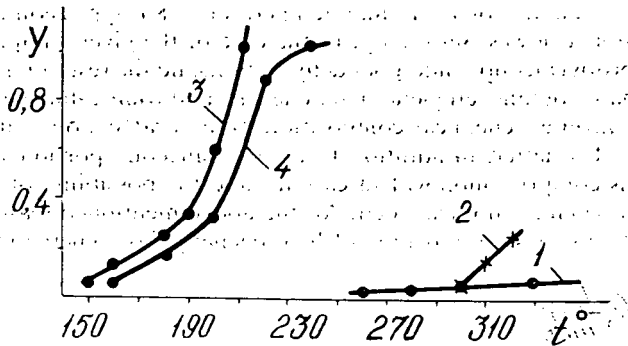


Fig. 2. Dehydration of isopropyl alcohol over zeolite L, erionite and their hydrogen forms: 1. KL, 2. NaKE, 3. HKL, 4. HNaKE

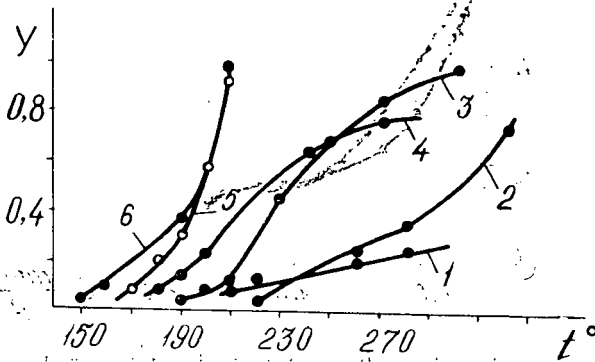


Fig. 3. Dehydration of isopropyl alcohol over natural clinoptilolites: 1. KI(2), 2. KI(3), 3. KI(1), 4. HKI(2), 5. HKI(3), 6. HKI(1)

mum at 320 °C ($y=0.21$). Conversion of the erionite type zeolite into its hydrogen form essentially increases its catalytic activity enabling complete conversion of *iso*-propyl alcohol — at a temperature as low as 240 °C.

Natural clinoptilolites of Boga (1), Dzegvi (2) and Khekordzula (3) origin (Georgian SSR) proved to be of special interest from catalytic point of view. As seen from Fig. 3 initial clinoptilolite of Boga origin provides complete conversion of *iso*propyl alcohol at 300 °C, that is, significantly exceeds in its catalytic activity synthetic monovalent cation forms of type faujasite, erionite and L zeolites. Conversion of the given clinoptilolite into its hydrogen form improves its catalytic properties (190 °C — $y=0.38$; 210 °C — $y=1.00$).

Natural clinoptilolites of Dzegvi and Khekordzula origin are also characterized by high activity. An advantage of clinoptilolites is expressed in their high selectivity; in all experiments water and propylene were the end products of the conversion of *iso*propyl alcohol. In the case of synthetic zeolites and their hydrogen forms selectivity of the process was not always achieved: samples of HNaKE and HNaY showed

traces of hydrogen and propane at high temperatures. KL type zeolite and its hydrogen forms exhibited lowest selectivity. In the case of the given samples more than a half of the *isopropyl* alcohol undergoes dehydration, and the rest of it forms hydrogen, propane, methane, butane, ethylene, 1-butene, *cis*- and *trans*-2-butenes. As compared with synthetic zeolites, chemical composition of natural clinoptilolites is far more heterogeneous. The latter, in addition to aluminosiliceous portion and the cations of alkali metals comprise monovalent cations, and the possibility of the presence of amorphous phase *etc.* is not excluded. All the above-mentioned reasons may be responsible for the increase of a degree of heterogeneity from energetic point of view.

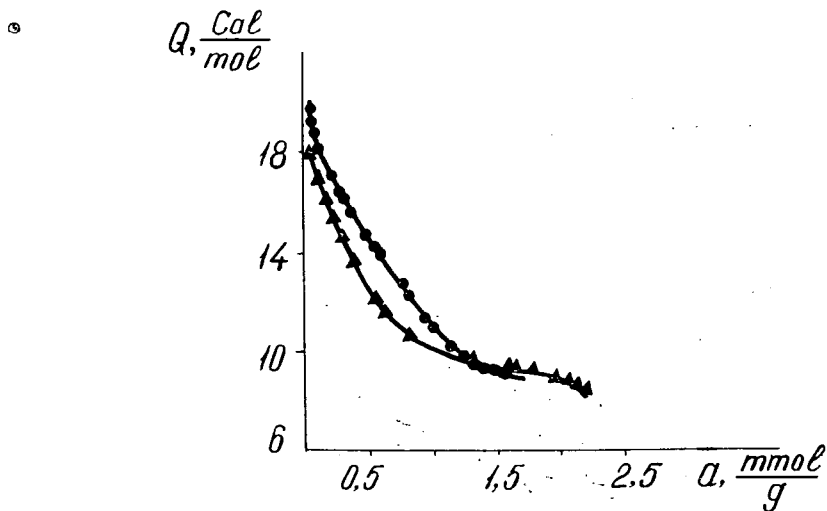


Fig. 4. Dependence of differential heats on adsorption values $Q_a=f(\bar{a})$ for the systems CO_2 — HKI(3) (●), CO_2 — K1(3) sample — 0.25N HCl (▲)

In order to elucidate the character of the above-mentioned degree of energetic heterogeneity, microcalorimetric method was used to determine the differential heats of adsorption of carbon dioxide over clinoptilolites of Khekordzula origin and their hydrogen forms. Consideration of the dependence of $Q_a=f(\bar{a})$ has shown that the zeolites under investigation manifest clearly expressed heterogeneity (Fig. 4). In contrast to the synthetic zeolites, curves of $Q_a=f(\bar{a})$ are not characterized by certain plateaus, they manifest specific sharp slopes. Similar results were obtained for clinoptilolites [9]. Choosing adsorption of ammonia as a model system, the authors [9] offer multi-stepped curve of $Q_a=f(\bar{a})$. Thus, the increased order of energetic heterogeneity of clinoptilolites is beyond doubt. In the case of the zeolites under study, several kinds of coordinatively unsaturated polyvalent cations and hydroxyl groups unequally polarized by them, $\text{Me}(\text{OH})^+$ complexes, imperfections of different nature, admixed amorphous phase *etc.* may serve as active sites. It must be taken into account that heterogeneity of the possible catalytic active sites does not affect the selectivity of clinoptilolites, it is always maximum and appreciably exceeds the selectivity of synthetic zeolites.

With the view to elucidate the nature of the active sites responsible for decomposition of *isopropyl* alcohol, we have conducted high-temperature (210 °C) adsorption of bases over zeolites. Experimental data have shown that the addition of ammonia causes complete deactivation of catalysts, and poisoning by pyridine suppresses the greater part of activity. Decrease of catalytic activity due to the addition of compounds of basic character enables us to suggest, that catalytic activity of the zeolites studied by us is conditioned by acid sites. High selectivity of clinoptilolites at an evident abundance of a variety of active sites increases the necessity of a further thorough examination of the views on the narrowness of the band of acidic spectrum, conditioning the process of dehydration. Deviation from selectivity, observed in the case of L type zeolite, may be ascribed to the specific nature of zeolite structure, but not to the variety of hydroxyl groups.

With the view to investigate kinetic properties of hydrogen atoms isotopic heterogeneous exchange method was used.

Studies of KL zeolites show that hydrogen atoms enter the isotopic heteroexchange only at high temperatures ($t > 250$ °C). KL zeolites consist only of one type of hydrogen atoms, mobility of which significantly increases with the rise of temperature (at 300 °C, $w_2 \cdot 10^3 = 4.2 \text{ min}^{-1}$; 400 °C—7.3; 500 °C—10.6). Neither the hydrogen atoms of 0.35 HKL decationized zeolites participate in the exchange of D_2 at 250 °C. Exchange of atoms of protium by deuterium is observed at high temperatures. Decationization of KL zeolites causes marked increase of a total concentration of hydrogen atoms — proportionate to decationization degree (for KL (H_s)=0.47 mmol/g; for 0.35 HKL (H_s)=1.24 mmol/g). At the given temperature all hydrogen atoms are characterized by similar kinetic properties.

Already at 250 °C hydrogen atoms of erionite show the ability of participating in isotopic exchange. Hydrogen atoms in the zeolite KNaE are represented into two H_A and H_B varieties. The amount of atoms of the type H_B exceeds that of H_A almost by an order of magnitude ($H_A=0.05 \text{ mmol/g}$, $H_B=0.45 \text{ mmol/g}$). Inversion of this ratio with increasing temperature is of special interest.

The results obtained by the method of heteroexchange of deuterium show that for the type L zeolites hydrogen atoms enter heteroexchange at temperatures significantly exceeding the temperature interval of dehydration process, for erionite the temperatures partly overlap. Hence, it may be supposed that hydrogen atoms are not dominating in the process of dehydration, but the possibility is not excluded that these atoms may play significant role in the other processes proceeding by carbonium-ion mechanism at high temperatures.

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