RESEARCH OF THE ACID PROPERTIES OF THE AMMONIUM FORM OF ZEOLITE (CLINOPTILOLITE) (NH4X)

BY

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Abstract

The work involved methods for assessing the acidity of the surface of oxide catalysts, since acid sites play a significant role in a number of catalytic reactions. To date, the most studied and widespread of natural centers is ammonium salts with an aqueous solution of 0.1 NNH$_4$ clinoptilolite. It is known that in a homogeneous liquid medium, Brønsted or Lewis acids and bases behave as rather nonspecific catalysts in relation to most of the reactions listed above. It has been established that preliminary thermal dehydroxylation of catalysts stabilizes their surface with respect to ammonia. The study showed that the decomposition of the ammonium form of zeolite begins at 373 K and ends almost at 573 K.

Keywords: catalyst, clinoptilolite, ammonium, zeolite, proton, alkaline earth.

INTRODUCTION

These days, the attention of many researchers has been drawn to methods for assessing the surface acidity of oxide catalysts, since acid sites play a significant role in a number of catalytic reactions.

Here it should be recalled that back in 1923 the concept of acid was expanded by Brønsted and, independently of him, Lowry began to classify substances with the ability to accept a proton as acids. However, Lewis meant an acid as a substance capable of donating an electron. Any center on the surface of the catalyst that donates a proton is, in Brønsted's terminology, called acidic: such centers cannot exist on a completely dehydrated surface. At the same time, the acid center, according to Lewis's definition, is capable of accepting electrons from molecules or ions, i.e. from the substance adsorbed during the catalytic reaction [1–3].

The ability of zeolites to exchange cations is one of their characteristic properties. Usually, these are cations of elements with a valence range from 1 to 5 Na, K, Mg, Ca, Fe, Cr, Mn, Cu, etc. Cations of alkali and alkaline earth metals are quite mobile and can, to one degree or another, be exchanged for other cations. The significant mobility of both cations and water molecules provides the possibility of ion exchange and reversible dehydration [4].

Thus, the characteristics of a zeolite include three components: framework topology, cations, compensating negative lattice charge due to the presence of aluminum and

zeolite water. In general, the chemical composition of zeolites is described by the formula:

$Me_{2n}O \cdot Al_2O_3 x SiO_2 \cdot y H_2O$
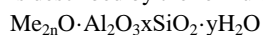
where n–is the valency of the alkali cation Me_1, x– is the molar ratio of SiO_2/Al_2O_3, and y– is the number of moles of water. To date, the most studied and widespread of natural zeolites is clinoptilolite, but the structure of the latter is still the subject of research. In natural clinoptilolite, the SiO_2/Al_2O_3 molar ratio reaches 9–10 or more [5]. The treatment of zeolites with ammonium salts with an aqueous solution of 0.1 N NH_4Cl can be represented by the following scheme:

$NH_4Cl + H_2O \rightarrow NH_4OH + HCl$
↓
$NH_4OH \rightleftarrows NH_3 + H_2O$
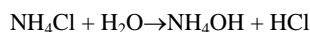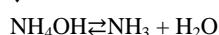
METHODS OF PROCESSING CLINOPTILOLITE

To study the ion exchange properties of CL (clinoptilolite) samples from various deposits, the following decationization technique was mainly used: rock grinding, fraction with granule size 0.5–0.25 mm.

Natural samples of CL were subjected to a preliminary 3-fold acid treatment with a 0.1N solution of salts Ca $^{2+}$, Na$^+$, K$^+$, NH_4 at a temperature of 353–363 K for 6 hours. The duration of each treatment, after which the zeolite was filtered and dried, was 1 hour, the zeolite: salt ratio was 1:10. At the end, the CL was washed with distilled water until the reaction for anions was negative; chlorine ion and dried at a temperature of 393–453 K. Final annealing at 973 K (6 hours). When the ammonium form is heat treated, the following form is formed [6]:

H—N— H— O—●—H with H below N and lone pairs shown on O
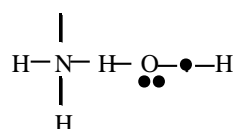
During thermal vacuum treatment of the ammonium form of zeolite, the dehydroxylation process begins at 473 K. From the same moment, the formation of L-centers begins, by the time the decomposition process of NH4+ is not yet completed, the dehydroxylation process has already begun [7-9].

At 573–673 K, the decomposition of weak B-centers continues with the formation and accumulation of L-centers, and the decomposition of B-centers begins with the formation of L-centers. Already at 873–923 K, only L-centers are present in the zeolite. When such a zeolite is treated with water vapor, some of the B-centers are restored. Dehydroxylation of weakly acidic OH groups occur first. The nature of the carbonium ion formation step has been the subject of much debate. If B-centers act as acidic sites, then the carbonium ion is formed by the addition of a proton to any unsaturated part of the hydrocarbon molecule: if L-centers initiate the formation, then the carbonium ion is formed by the transfer of a hydride ion from the hydrocarbon molecule. In principle, the formation of carbonium ions is possible on both

those and other centers, which greatly complicates the analysis of the mechanism of formation of these ions. Since both centers exist on the surface of most acid catalysts, which centers can be given preference in the first stage of carbonium ion formation [10].

It is known that in a homogeneous liquid medium, Brønsted or Lewis acids and bases behave as rather nonspecific catalysts in relation to most of the reactions listed above. As was shown in the previous sections, the surface of zeolite catalysts, when exposed to ammonia, undergoes both irreversible and reversible changes. In the first case, dehydroxylation, dealumination, and amorphization take place. As a result, the concentration, strength, and type of acid sites change. In the second case, the zeolite surface is stabilized; during ammonia adsorption, it is possible to vary mainly the concentration and strength of acid sites. All changes that catalysts undergo must naturally affect their catalytic activity.

It should also be noted that the Kerr mechanism can be considered dissociative and therefore requires higher temperatures. From the literature it is known that with hydroxyl groups according to the Kerr mechanism amidozeolite is formed at 773 K.

(1)
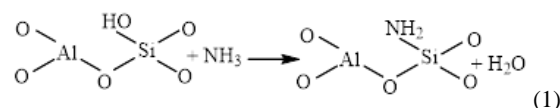
The latter decomposes at high temperatures of 873–1073 K and, according to Kerr, ammonia is released and a dehydroxylated zeolite is formed according to the following scheme:


(2)
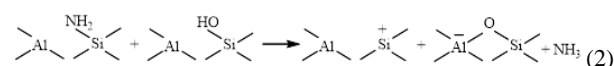
We confirmed the irreversibility of these reactions as follows: a sample of NH_4X zeolite was decomposed in a flow of dry He to 573 K, then subjected to ammonia treatment in the presence of water vapor at the same temperature, then cooled to 373 K and adsorption was carried out with a mixture of ammonia and water vapor. Addition of vapor water into the system during high-temperature (573 K and above) treatment with ammonia does not suppress dehydroxylation.

Since zeolites have a spectrum of acidity, the Si-OH bonds are not equal in strength, so the interaction of H$^+$ with the OH group occurs predominantly with weak acidic centers [11].

The remaining more mobile protons react with NH_2 groups to form NH_3 and dehydroxylated centers only at higher temperatures.

Proton delocalization occurs according to the following scheme:

(3)

(I)   (II)

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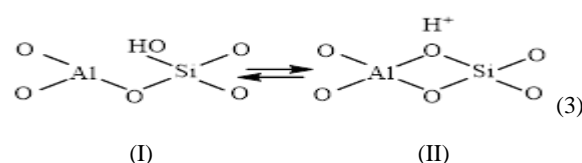
Form II is a classic Brønsted acid, which does not appear in ICS. At low temperatures (below 300^0C) form I exists, which is visible in the IR spectrum (Fig. 1) [8].

Also, the study of the infrared spectra of zeolites after their heat treatment in a wide temperature range allows us to obtain new important data regarding their dehydration and rehydration, the state of water, the existence of hydroxyl groups and hydronium ions (H_3O^+).

The study of the infrared spectra of clinoptilolites and their ion-exchange forms showed that, depending on the radius of the atomic weight and charge of the exchange cations, there is a change in the position of the maxima and intensities of high-frequency bands in the region of 3100–3700 cm^{-1}, as well as in the content of water molecules. Cations have little effect on the nature of the spectrum of clinoptilolite in the region of natural vibrations of the framework (400–800 cm^{-1}) and Al, Si–O bonds (900–1200 cm^{-1}). An interesting feature of the clinoptilolite spectra is the presence of a band at 1690 cm^{-1}, which is due to bending vibrations of the hydroxanium ion (H_3O^+).

On a sample of NH_4X using IR at 723 K, a decrease in the intensity of the bands of hydroxyl groups by 29% from the original was detected (at 393 K). However, when the temperature was lowered to 393 K, the intensity of the bands was completely restored [9].
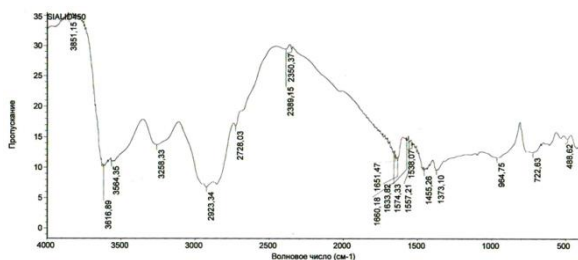

Fig.1. IR spectroscopy of natural clinoptilolite.

If strong bases are adsorbed on the surface of a zeolite even at room temperature, a noticeable shift of the equilibrium to the right occurs due to the formation of a protonated form of the adsorbed base. And the proton relaxation time of the decationized zeolite on which pyridine (C_5P_5N) was adsorbed, the proton mobility is 4 times lower. Adsorption of the weak base toluene increases proton mobility very slightly. With the complete transfer of protons to ammonia molecules from Brønsted centers, as one might expect, the adsorbed compound is an ammonium ion and the spectrum will characterize this compound. It follows that low-temperature dehydroxylation is carried out by a sharp increase in proton mobility during the adsorption of basic molecules according to the following mechanism [10]:

(4)
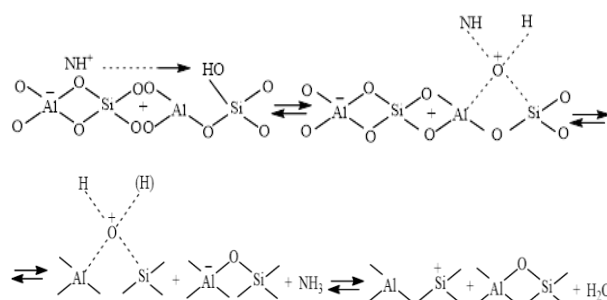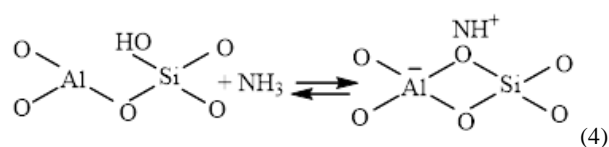
The reversibility of these reactions was confirmed experimentally. The experiment consisted of the following: a sample of NH_4X was decomposed in a flow of dry helium to 573 K (until the release of ammonia completely ceased). Then it was cooled to 373K and adsorption was carried out from a mixture of ammonia and water vapor. As a result, the original form of NH_4X was completely restored [12].

The installation diagram is shown in Fig. 2. Helium from a cylinder (1) through a reducer (2) and valve fine adjustment (3) enters the cleaning system (4, 14). Then it passes through the comparative chamber of the katharometer (5), the reactor (6) with a catalyst sample, the Pregl apparatus (7) with crushed KOH (to absorb water), and then through series-connected traps (8) and (9.) After this, the gas flow is directed into the working chamber of the katharometer, and from it into the rheometer (10). To calibrate the detector, there is a device at the top of the trap (9) for injecting ammonia using a gas syringe. The katharometer signal was recorded using a standard circuit on a KSP-4 recorder (12).
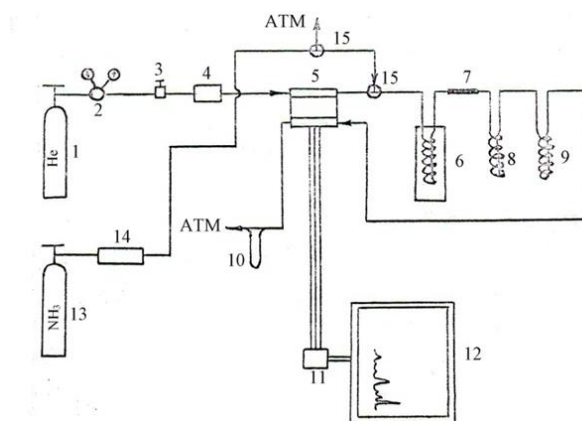

Fig.2. Experimental setup for studying the acid properties of catalysts. 1,13 – cylinders with helium and ammonia, 2 – reducer, 3 – fine adjustment valve, 4, 14 – cleaning system, 5 – catharometer detector, 6 – reactor, 7 – apparatus with crushed KOH (for water absorption), 8,9 – traps, 10 – rheometer, 11 – bridge power supply, 12 – chromatograph, 15 – three-way valves.

The method for studying the acidic properties of NH_4X is as follows: a sample of air-dry zeolite (0.2 g) was loaded into the reactor, gas communications were connected to it, and helium began to flow at room temperature at a constant rate (30 ml/min). Then, placing it under trap (9) Dewar vessel with liquid nitrogen, the temperature of the sample was raised to 373 K. The catalyst was kept at this temperature for 2 hours.

After this, the Dewar flask with liquid nitrogen was moved to trap (8), and trap (9) was defrosted [13].

Using three-way valves (15), a "helium + ammonia" mixture with a constant concentration of NH_3 was fed into the system until the zeolite was completely saturated. Saturation time was 2 hours. Experiments showed that the onset of decomposition of this sample corresponds to 373 K. In this case, a small amount of ammonia released was determined using a katharometer, as described above. Before the experiment, all catalysts were subjected to preliminary heat treatment [11, 14].

The activity and selectivity of the process were determined from the chromatogram of the mixture leaving the reactor with the catalyst; in this case, the sampler is connected after the reactor using taps I and II.

The study showed that the decomposition of the ammonium form of zeolite begins at 373 K and ends almost at 573 K, which is in good agreement with literature data [15–19].

The behavior of the ammonium form of zeolite when pierced in an air atmosphere was also studied. There is a standard preliminary heat treatment of catalysts. Before each experiment, they are calcined in a flow of moist (or dry) air at temperatures of 803-823 K for an hour, then the system temperature is reduced to operating temperature and the reaction is carried out. It has been established that preliminary thermal dehydroxylation of catalysts stabilizes their surface with respect to ammonia. A mechanism for the "chemical" dehydroxylation of zeolites has been proposed. It has been found that on decatonated zeolites, the total number of acid sites, as well as the ratio of protic and aprotic centers, significantly depend on the pretreatment conditions - temperature, heating mode, nature, atmosphere (inert or oxidizing).

CONCLUSION

The study showed that the decomposition of the ammonium form of zeolite occurs in the temperature range 373 K -573 K. At 873–923 K, only L-centers are present in the zeolite, but treatment of such a zeolite with water vapor restores some of the B-centers. It has been established that the total number of acid sites in decatonated zeolites depends on the conditions of their pretreatment.

ACKNOWLEDGMENT

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