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PREPARATION AND STUDY OF THE PROPERTIES OF TYPE X ZEOLITES IN THE AMMONIUM AND HYDROGEN ION-EXCHANGE FORMS

In the preparation of zeolites there arises a question concerning the formation and properties of the hydrogen ion-exchange form of a zeolite. In addition, a hydrogen zeolite may be of independent interest as a specific form and as an initial form for obtaining cation-substituted zeolites. Here are meant processes in which ion exchange with the sodium form is difficult or leads to destruction of the zeolite lattice.

As is known, most zeolites are rather readily decomposed by acids, i.e., are unstable in an acidic medium, and it is natural that it is impossible to obtain a zeolite in the hydrogen form by ion exchange in an acidic medium. It is not excluded, however, that during prolonged washing with water of the sodium form of a zeolite, partial replacement of sodium ions by hydrogen ions (or hydroxonium ions) occurs and a mixed sodium-hydrogen zeolite is formed. M. M. Dubinin drew attention to this possibility ([1]). Barrer proposed obtaining a hydrogen zeolite starting from the silver form of a zeolite ([2]) and by oxidation of an ammonium zeolite ([3]). A possible route to obtaining the hydrogen form may also be decomposition, with liberation of ammonia, of the ammonium form of a zeolite. Indeed, during evacuation and heating of an unstable ammonium zeolite, the reaction is not excluded:

$$NH_4X = NX + NH_3,$$

where X denotes the anionic part of the aluminosilicate framework of the zeolite. As a result of this reaction, a hydrogen form may be produced*. In this connection, we obtained the ammonium form of type X zeolite and studied, by adsorption and spectroscopic methods, the products of its thermal decomposition.

The ammonium form of type X zeolite was obtained by the method of cation exchange of the sodium ions of the NaX form for ammonium ions. The zeolites

obtained were examined for ammonia content, and their Debyegrams were taken to check preservation of the zeolite structure**. To study the influence of the nature of the anion on the degree of substitution of ammonium ions, ammonium fluoride, chloride, bromide, and iodide were taken. Cation exchange was carried out with normal solutions of the indicated ammonium salts at the same exchange time (shaking 1 g of zeolite and 6 ml of a 1 N salt solution for one hour). The results of the exchange study are:

Salt	NH_4F	NH_4Cl	NH_4Br	NH_4J
NH_4 content after a single treatment of the zeolite, wt. %	3.28	4.74	4.35	4.06

On the basis of the data obtained, ammonium chloride was selected for the exchange, and the influence of the solution concentration was studied. For this

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* This route for obtaining the hydrogen form was used in work ([4]) and described in the patent literature ([5]). We became acquainted with the latter source after the results of our work had already been obtained.

** The Debyegrams of the zeolites were obtained by Ts. A. Gedzhadze.

0.1, 1, and 5 N ammonium chloride solutions were taken. We present the results of the study:

Normality of the NH_4Cl solution	0.1	1.0	5.0
Degree of ion exchange (wt. % ammonia after a single treatment)	1.34	4.74	4.72

As can be seen from the data obtained, 1 and 5 N ammonium chloride solutions give approximately the same degree of substitution of the ammonium ion; therefore, fearing destruction of the zeolite structure, we settled on a 1 N solution.

In developing the procedure for obtaining the ammonium form of the zeolite, the influence of temperature on the completeness of exchange was also studied.

The experiments were carried out at room temperature and at a temperature of about 90°. The results of chemical analysis showed that such a temperature, in comparison with room temperature, has practically no effect on the exchange.

In order to increase the ammonia content in the zeolite, multiple exchange was carried out. The results of the experiments are given in Table 1.

Table 1

Exchange	Degree of ion exchange, wt. % ammonia	Degree of sodium substitution by ammonium*, %
Single	4.74	55.4
Double	5.41	63.2
Triple	6.04	70.5
Quadruple	6.35	74.2
Quintuple	6.28	73.4

* The initial NaX form contained 10.94 wt. % sodium.

The data presented made it possible to choose a procedure for obtaining the ammonium form of zeolite type X. For the experiments, crystalline NaX zeolite was used, obtained on a pilot-plant installation by B. A. Lipkind (series Ts-202-98). Before the ion-exchange reaction, the zeolite was thoroughly washed with distilled water in order to remove excess alkali. After this, the aqueous zeolite suspension was settled, decanted, filtered, and dried. The finally dried zeolite was ground to a fine powder. The zeolite thus treated in the sodium form, in an amount of 1 g, was stirred for one hour with 6 ml of a 1 N ammonium chloride solution at room temperature. The zeolite was then filtered off on a Büchner funnel, washed with distilled water, and dried in air. The exchange was carried out three times. The ammonia content in the zeolite after triple exchange was 6.05 wt. %, as against the Na content in the original sample of 10.94%. Thus, the maximum degree of substitution of sodium ions by ammonium under our conditions was about 70%. Debyegram recording for the obtained zeolite NH_4X (actually $(NH_4)_nNa_mX$) showed the presence of a structure characteristic of type X zeolites.

Fig. 1. Adsorption isotherms of water vapor (upper curves) and benzene (lower curves) on NaX zeolite and ammonium zeolites NH_4-1, NH_4-5 (single and fivefold treatment with a 1 N NH_4Cl solution) and NH_4-5N (single treatment with a 5 N NH_4Cl solution) at 20°.

For an adsorption characterization of the ammonium form of type X zeolite obtained, the adsorption of water and benzene vapors on NaX, on several NH_4X samples, and on products of their thermal decomposition was studied on a microbalance apparatus[(6)]. At the first stage of the adsorption study, adsorbent samples were evacuated at room temperature (20°) to a pressure of 10^{-5} mm.

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Fig. 2

Figure 2: Fig. 2

mm Hg. As will be shown below, under this treatment regime water and ammonia are partially removed from the zeolite. On the basis of the measurements, adsorption isotherms of water and benzene vapors were constructed (Figs. 1 and 2).

After carrying out the adsorption–desorption cycle at 20°, the temperature of the zeolite sample was gradually raised and brought to 300°. Evacuation was continued until a pressure of 10^{-5} mm Hg was established and the weight of the samples under study became constant. After this, the sorption tube of the apparatus was cooled to 20°, and at this temperature the adsorption of water and benzene vapors was studied.

Fig. 2. Adsorption isotherms of water vapor (upper curves) and benzene (lower curves) at 20° on NaX, H-1, H-5, and H-1; 5 N zeolites heated in a vacuum apparatus to 300°.

On the basis of the isotherms obtained, Table 2 was compiled, which gives the limiting adsorption amounts of vapors (a_0) and the limiting adsorbed volumes (v_0) of the adsorbents studied for water and benzene vapors. The calculation of a_0 and v_0 was carried out by the method of M. M. Dubinin ([1]). In calculating the limiting adsorption volumes, the densities for the corresponding bulk liquid phases were used. The data obtained (see Table 2) show that the products of thermal decomposition of ammonium zeolite differ little from sodium zeolite in their adsorption of water vapors, while for benzene vapors they surpass it.

Fig. 3. IR spectra of zeolite NH_4X at room temperature (dashed curve) and heated in vacuum (solid curve) at 300° for 4 h.

Fig. 4. IR spectra of zeolite HX saturated with water vapor at room temperature (1), and of the same sample after dehydration at a temperature of 330°

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

(2).

We investigated the infrared spectra of synthesized ammonium zeolite of type X at room temperature and of the products of its thermal decomposition at 300°. The spectra were recorded on an IKS-12 infrared spectrometer with LiF prisms in the region 2.5—5 μ and NaCl in the region 5.5—7.7 μ. A thin layer of zeolite was applied by sedimentation from isobutyl alcohol onto a plane-parallel fluorite plate transparent in the IR region ([7]). The alcohol was evaporated by heating the plate with an IR lamp. The thickness of the adsorbent was 0.6—1.2 mg/cm^2. In the IR spectrum of zeolite NH_4X at room temperature, bands are observed at 1390, 1430, 1480, 1670, 3190, and 3300 cm^{-1} (Fig. 3). As is known from the literature data ([8]), the ammonium group is characterized by two bands in the regions 1390—1430 and 3100—3200 cm^{-1}.

Thus, the bands at 1390 and 3190 cm^{-1}, appearing in the IR spectrum of zeolite NH_4X, must belong to the ammonium group. The band at 1670 cm^{-1} is due to deformation vibrations of water, while the band at 3300 cm^{-1} characterizes the hydroxyl groups of water and isobutyl alcohol. The remaining bands are due to aliphatic CH bonds. When the sample is evacuated in vacuum at room temperature, all bands weaken, including those of the ammonium group. The weakening of the intensities of the ammonium-group bands can be explained by the transition of the ammonium form of the zeolite into the hydrogen form. The release of ammonia upon evacuation of the ammonium form of the zeolite without heating was also detected by us by chemical means.

Table 2

Zeolite	H_2O ($p/p_s = 0.40$) a_0, mmol/g	H_2O ($p/p_s = 0.40$) v_0, cm^3/g	C_6H_6 ($p/p_s = 0.18$) a_0, mmol/g	C_6H_6 ($p/p_s = 0.18$) v_0, cm^3/g
NaX	17.35	0.312	2.68	0.239
NX-1	15.00	0.270	2.94	0.261
HX-5	17.30	0.311	2.94	0.261
HX-1 (5N)	16.00	0.288	3.03	0.269

Heating the zeolite during evacuation to a temperature of 120° intensifies the disappearance of all bands and, finally, in the spectrum of a sample heated at 300° for 4 hours, in the region 1300–4000 cm^{-1}, continuous absorption is observed without any characteristic bands (Fig. 4). It should be noted that the sharp band at 3550 cm^{-1}, which, according to Shimansky et al. ([4]), remains in the spectrum after thermal treatment (in the temperature range 288–600°)

and is assigned to surface OH groups of the zeolite, was not detected under the conditions of our experiments.

Upon adsorption of water vapor on the dehydrated zeolite (Fig. 4), the usual water bands appear at 1670 and 3300 cm^{-1}, disappearing when the sample is heated to 330°, after which continuous absorption, characteristic of the zeolite in the spectral regions studied by us, is still observed.

As a result of the investigation carried out, the conditions for obtaining the ammonium form of type-X zeolite were established; spectral and adsorption methods showed that upon its thermal decomposition a hydrogen form is formed, which in its adsorption properties is close to NaX zeolite.

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Note: Figure translations are in progress. See original paper for figures.