Brief Communications

Adsorption-energetic and IR spectroscopic studies of NH_4 natrolite

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The ammonium form of natural zeolite, natrolite, obtained by vapor phase ion exchange is similar to calcium-containing zeolites of the natrolite group in its de- and rehydration characteristics and the heats of immersion in water. The adsorption capacity and the heat of immersion in water are maximum after evacuation of the zeolite at 200 °C. The irreversible sintering of NH_4 natrolite occurs above 200 °C (up to 45% at 500 °C), accompanied by the formation of hydroxyl groups.

Key words: zeolites, natrolite, NH_4 natrolite, H natrolite, water adsorption; IR spectra; heat of immersion, ion exchange.

Comprehensive studies of thermal stability of natural calcium-containing zeolites of the various structural groups, in particular, zeolites of the natrolite group, made it possible to determine the mechanism of their step-by-step dehydration.[1] According to this mechanism, after a certain stage of dehydration, the irreversible solid-phase hydrolysis of multivalent cations occurs to form structurally distorted hydroxyl-containing compounds. In the case of dehydration of Na-zeolites, for instance, natrolite, solid-phase hydrolysis does not take place, and as a consequence no irreversible structural changes occur. In connection with this, it was of interest to obtain and study the hydroxyl-containing natrolite form and to compare its thermal stability with that of the calcium-containing representatives of this group, scolecite, mesolite, and thomsonite. Since the Ca form of natrolite cannot be obtained by ion exchange,[2] first natrolite was converted to its NH_4 form then was transformed to the hydroxyl-containing form by calcination.

Experimental

Ion exchange $Na^+ \rightarrow NH_4^+$ of natrolite does not occur if it is treated in solutions.[2] For this reason, a vapor phase procedure for the preparation of NH_4 natrolite was used.[3,4] Relatively large crystals of ground natrolite (~1 mm), which were selected using a microscope, were mixed with NH_4Cl powder. The mixture was placed in a thick-wall glass tube and evacuated at 200 °C, then the tube was sealed off *in vacuo*. The sealed tube was stored for 160 h at 200 °C (NH_4Cl sublimation point). The prepared NH_4 natrolite was thoroughly washed with hot water until it gave a negative reaction for chloride ions.

The initial natrolite sample was of the following composition (wt. %): Na_2O — 15.8; Al_2O_3 — 28.3; SiO_2 — 46.3; CaO — 0.2; MgO — 0.11; P_2O_5 — 0.02; K_2O — 0.1; TiO_2 — 0.2; MnO — 0.06; Fe_2O_3 — 0.6; H_2O — 9.6; after ion exchange, Na_2O — 2.2, and the content of other oxides remained almost unchanged. Thus, 85% Na^+ was replaced by NH_4.

The ammonium form of NH_4 natrolite was characterized by chemical analysis, DTA, X-ray diffraction analysis, and IR spectroscopy data.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 359—361, February, 1998.

Adsorption-energetic properties of the calcined samples of the NH_4 natrolite were studied using a DAK-1-1 microcalorimeter and vacuum spring quartz balances. IR spectra were recorded on a UR-20 spectrophotometer equipped with an adsorption-vacuum setup with a cell for measuring IR spectra.[5]

An NH_4 natrolite sample was evacuated at 25—500 °C with intervals of 30—50 °C. After evacuation, the rehydration heats (the heats of immersion in water at 25 °C) and the values of adsorption (rehydration) at $p/p_s = 0.5$ and 25 °C (where p_s is the equilibrium pressure of saturated water vapors) were measured at each temperature.

Results and Discussion

The ammonium natrolite form has been studied previously;[3,6] however, its dehydration has not been investigated in detail. X-ray diffraction analysis data show that the parameters of a natrolite elementary cell are changed to a considerable extent after exchange of Na^+ for NH_4^+ (by 85%): $a = 17.90$, $b = 18.40$, $c = 6.60$ Å (for the original nitrolite $a = 18.30$, $b = 18.63$, $c = 6.60$ Å). These results are consistent with the literature data.[7] In the X-ray diffractogram, reflections 080 completely dissappeared and the intensities of reflections 10, 60, 660, and 440, which characterize positions of Na^+ ions and H_2O molecules, noticeably changed. These facts indicate that water molecules were removed and Na^+ ions were exchanged for ammonium ions. Disappearance of reflections 153 and 311 indicates that the skeleton is strongly distorded. The presence of absorption bands at 1420—1480 cm^{-1} (Fig. 1) in the IR spectra points to the insertion of NH_4^+ ions into the natrolite structure after the thermal vacuum treatment. As the temperature of the treatment increases, the intensity of the absorption bands of ammonium ions decreases to the point of its complete disappearance at 450—500 °C. In the region of 3000 to 3700 cm^{-1}, not presented in Fig. 1, there is an intense broadened band of the OH groups formed as a result of removal of molecular ammonia; a significant decrease in the water vapor adsorption was observed for the same samples at $p/p_s = 0.5$. Therefore, the appearance of the OH groups in natrolite leads to irreversible structural changes and decreases the adsorption capacity.

The decrease in the thermal stability of natrolite, when converted to the hydroxyl-containing (hydrogen) form, is more clearly seen in its adsorption-energy characteristics (Fig. 2). When the temperature of treatment is increased to 100—150 °C the, amount of the removed water increases, and the heat of immersion in water (Q_i) increases to 290 J g^{-1}, respectively, whereas the Q_i maximum value is 185 J g^{-1} for the initial natrolite within this temperature range.[8] When the treatment

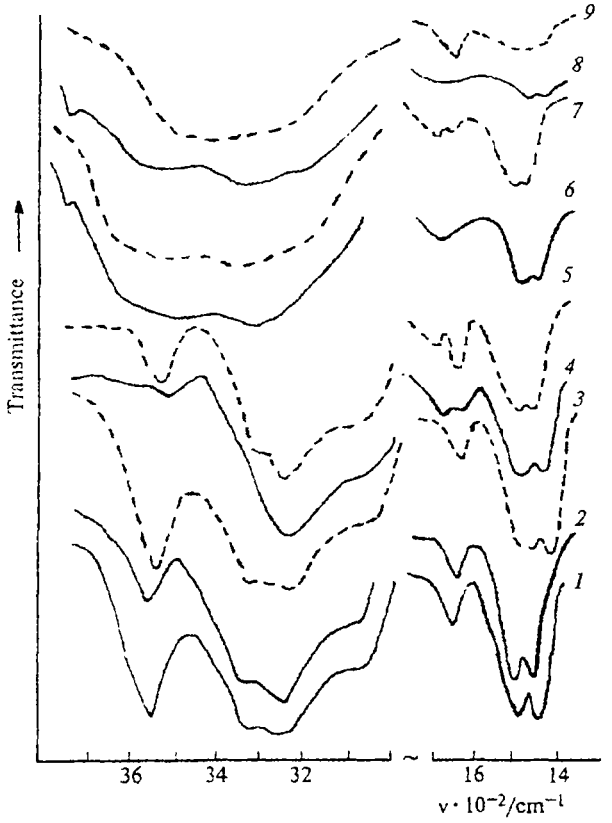

Fig. 1. IR absorption spectra of the dehydrated (*2*, *4*, *6*, *8*) and rehydrated (*3*, *5*, *7*, *9*) NH_4 natrolite: *1*, original natrolite dehydrated by evacuation at T/°C = 200 (2), 250 (*4*), 300 (*6*), 400 (*8*); rehydrated after evacuation T/°C = 200 (*3*), 250 (*5*), 300 (*7*), 400 (*9*).

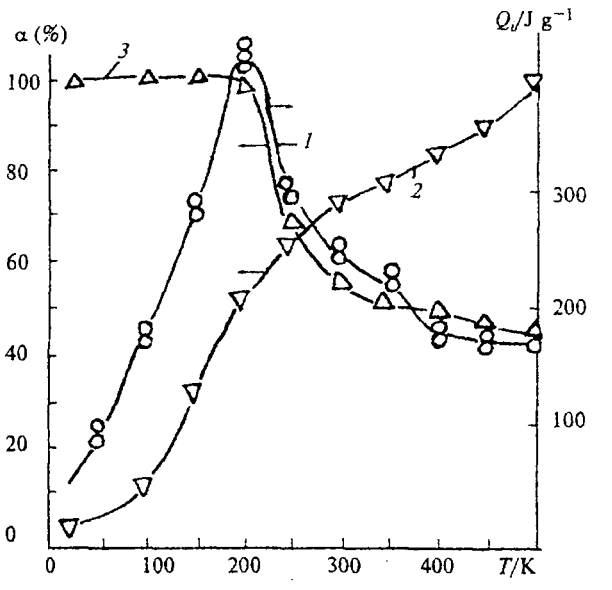

Fig. 2. Heats of immersion of NH_4 natrolite in water (at 25 °C) depending on the evacuation temperature: *1*, for 4 h; *2*, relative dehydration values (%); *3*, relative rehydration values (%) at $p/p_s = 0.5$ and $T = 25$ °C (*a*, relative adsorption values in dehydration and rehydration, *i.e.*, the portion of residual water in the zeolite compared to its maximum content).

temperature increases to 200 °C, the weight loss of NH_4 nitrolite reaches its limit value, at which the reversible water adsorption is maximum (100%). As seen in Fig. 2, at temperatures above 200 °C, NH_4 natrolite begins to lose its adsorption (rehydration) ability, and the initial natrolite remains thermally stable up to 650 °C.[8]

The values of heats of immersion of NH_4 and Na natrolite[8] evacuated at 200 °C are maximum and equal to 415 and 330 J g^{-1}, respectively. However, over the temperature range from 200 to 400 °C, the Q_i value for the initial natrolite remains constant,[8] and the Q_i *vs.* T curve for the NH_4 natrolite has a maximum as in the case of calcium-containing zeolites, *i.e.*, scolecite, mesolite, and thomsonite.[9] The $Q_i = f(T)$ curve over the temperature range from 200 to 500 °C can be arbitrarily divided in two portions: 200—350 °C and 350—500 °C. In the first portion, the heat of immersion sharply decreases, and in the second portion, it remains almost constant. The curve of the relative amount of absorbed water changes with the temperature in parallel with the Q_i *vs.* T curve.

Thus, in the course of formation of the hydroxyl groups in natrolite, the irreversible deformation of its structure occurs, *i.e.*, the ammonium form of natrolite is thermally unstable.

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Received April 9, 1997;
in revised form June 26, 1997

Condensation of nitriles of polyhalogenated carboxylic acids and benzonitrile with 2-hydroxy-4,6-dimethylacetophenone

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Condensation of 2-hydroxy-4,6-dimethylacetophenone with trifluoro- and trichloroacetonitriles gives 2-amino-5,7-dimethyl-2-trifluoro(trichloro)methyl-4-chromanones. The condensation with 2,2,3,3-tetrafluoropropionitrile, perfluorovaleronitrile, and benzonitrile stops at the stage of formation of the corresponding enamines.

Key words: condensation, nitriles of polyhalogenated carboxylic acids, 2-hydroxy-4,6-dimethylacetophenone, ring-chain isomerism; enaminones, chromanones, chromones.

We have previously shown[1] that 2-hydroxyacetophenone reacts with trifluoro- and trichloroacetonitriles in the presence of *N*-ethylanilinomagnesium bromide to form enaminones in the form of *Z*-isomers with coplanar *s-cis*-conformation stabilized by intramolecular hydrogen bonds. 2-Acetyl-1-naphthol reacts similarly, and in this case, the reaction is accompanied by partial cyclization of the resulting enaminone to 2-amino-2-trifluoro(trichloro)methyl-5,6-benzo-4-chromanones.[2]

We found a new example of ring-chain isomerism in the aromatic β-hydroxyenaminone series, when we studied the reaction of nitriles of halogenated carboxylic acids with 2-hydroxy-4,6-dimethylacetophenone. Condensation of this ketone with trifluoroacetonitrile gave a mixture (approximately 1 : 1) of ring-chain isomers, 3-amino-1-(2-hydroxy-4,6-dimethylphenyl)-4,4,4-trifluorobut-2-en-1-one (**1a**) and 2-amino-5,7-dimethyl-2-trifluoromethyl-4-chromanone (**2a**), in a total yield of

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 362—363, February, 1998.

1066-5285/98/4702-0354 $20.00