

On the H-form of natrolite

ANNA YU. LIKHACHEVA^{1,*}, SERGEY A. VENIAMINOV², EVENIY A. PAUKSHTIS² and IGOR A. BELITSKY¹

¹Institute of Mineralogy and Petrography, pr. ak. Koptuyuga 3, 630090 Novosibirsk 90, Russia

*Corresponding author, e-mail: alih@uiggm.nsc.ru

²Boreskov Institute of catalysis, pr. ak. Lavrentieva 5, 630090 Novosibirsk 90, Russia

Abstract: To resolve the problem of existence of the H-form of natrolite, the thermal decomposition of NH₄-exchanged natrolite (as a precursor of the H-form) was studied by gas chromatography, IR spectroscopy and X-ray diffraction. Throughout the decomposition, the de-ammoniation is immediately followed by dehydroxylation, which is evidence for the instability of the H-natrolite formed after the removal of NH₃, and leads to a negligibly small concentration of the OH-groups. The natrolite structure can not persist after the removal of NH₃.

In the final step of decomposition, the adsorption of NH₃ onto Lewis centres accumulated in the amorphosed framework hinders the de-ammoniation. This seems to be one of the major factors which influence the observed increase in the activation energy for NH₃ desorption from 117 (±13) kJ/mol in the initial step to 270 (±20) kJ/mol.

Smooth vacuum degassing of NH₄-natrolite at 550 K leads to partial de-ammoniation, rather than formation of H-natrolite.

Key-words: natrolite, H-natrolite, ammonium natrolite, de-ammoniation, dehydroxylation, amorphisation, gas chromatography, IR spectroscopy.

Introduction

Natrolite, Na₁₆[Al₁₆Si₂₄O₈₀]·16H₂O, is a widespread fibrous zeolite with an ordered Si,Al distribution in the framework. The interest to the H-form of natrolite is related to the problem of the existence of fully protonated aluminosilicate frameworks, and to the way the framework and protons interact. The stability of the protonated framework has been widely studied for the large-pore zeolites, due to numerous applications of their H-forms in catalysis (Kuhl & Schweizer, 1975; Corma, 1995). H-zeolites are commonly obtained by vacuum calcination of their ammonium forms, when thermal dissociation of NH₄⁺ ion results in the removal of NH₃, leaving a proton linked to the framework oxygen as OH-group:



(Z – zeolite aluminosilicate framework, after Breck, 1974).

It has been shown experimentally and by quantum-chemical calculations (Barthomeuf, 1987), that the energy of the bond between the proton and the bridging oxygen is proportional to the aluminium content in the nearest framework environment. The stronger the interaction between the proton and the framework oxygen, the weaker the bridging Si-O-Al bond. This is why the H-forms of Al-rich zeolites are known to be unstable (Rabo & Gajda, 1989–90).

However, there are contradictory data on the stability of the H-form of natrolite. The structure of H₃O-natrolite (hydrated H-natrolite) obtained through the thermal degassing of NH₄-

natrolite at 523 K, has been reported by Stuckenschmidt *et al.* (1996). These authors emphasize that a spectroscopic study is needed to confirm the formation of H₃O-natrolite. On the other hand, the adsorption-energy study has revealed an irreversible loss of the rehydration capacity upon heating the NH₄-natrolite above 470 K, which suggests the collapse of the structure (Mirzai *et al.*, 1998). Gas chromatography and IR spectroscopy are convenient methods to monitor the removal of NH₃ (de-ammoniation) and OH-groups as H₂O (dehydroxylation), as well as the appearance of OH-groups during thermal decomposition of ammonium zeolites. In the present work, these methods are applied to study the thermal decomposition of NH₄-natrolite, which allows us to elucidate the mechanism of its degassing, and the appearance and stability of the H-form of natrolite.

Experimental

The starting material was a well-crystallized natural natrolite from pegmatite veins (Khibiny), with the chemical formula Na_{16.0}Mn_{0.05}Ca_{0.02}K_{0.01}[Al_{16.2}Si_{23.8}O₈₀]·16.25H₂O determined by X-ray fluorescence. The water content of 9.53 wt. % was determined by the thermogravimetry analysis. The crystals were crushed and 1 g of the fraction 0.05–0.2 mm, pre-treated at 470 K for 2 days, was placed in a quartz tube together with 8 g of NH₄Cl, and exchanged in a vapour of sublimated NH₄Cl at 620 K during 3 days. After

the exchange, the natrolite was washed in distilled water and dried. According to the flame photometry analysis of residual metal cations, the degree of exchange achieved was greater than 97% (15.5 wt. % and 0.15 wt. % of Na_2O before and after the exchange). This allows the composition of the final material to be approximated to $(\text{NH}_4)_{16.2}[\text{Al}_{16.2}\text{Si}_{23.8}\text{O}_{80}]$. The X-ray powder diffraction (XRD) analysis confirmed the transition from the orthorhombic ($Fdd2$) unit cell ($a = 18.29(2) \text{ \AA}$, $b = 18.64(1) \text{ \AA}$, $c = 6.59(1) \text{ \AA}$) of the natural natrolite to the monoclinic unit cell ($C112_1$) ($a = 17.92(1) \text{ \AA}$, $b = 18.46(2) \text{ \AA}$, $c = 6.53(2) \text{ \AA}$) of the NH_4 -natrolite, which is in accordance with the data of Stuckenschmidt *et al.* (1992). The initial and calcined NH_4 -natrolite were characterized by thermogravimetry (TG) analysis using a Mettler TA-3000 thermobalance, with a heating rate of 3 K/min at 298–1043 K in air, and the sample weight of 30 mg.

Before performing the gas chromatography measurement, the sample of NH_4 -natrolite (20 mg) was kept in a flow of dry He at 373 K until the physically adsorbed water was removed. Then the sample was heated with a dry He flow at a rate of 3 K/min up to 1040 K in a quartz micro-reactor connected to a chromatograph. The experimental detection limit for NH_3 and H_2O was determined to be 10^{-4} mg. Calibration for NH_3 was done using a dosed reference mixture of NH_3 and He. Calibration for H_2O was done using a dosed probe of He saturated with water vapor under a fixed ambient temperature. Simultaneous detection of NH_3 and H_2O allowed to obtain the T-dependence for the rate of NH_3 and H_2O removal during the decomposition of the NH_4 -natrolite. This makes possible to compare the gas chromatography and the TG data.

IR measurements were conducted on a sample cyclically heated in the spectrometer cell (FTIR-8300, Shimadzu) to follow the changes in the N-H and O-H vibrations in 1200–4000 cm^{-1} region up to 870 K. A detailed description of gas chromatography and IR spectroscopy measurements is given in Likhacheva *et al.* (2004).

To compare the intensity of the ammonium IR band with the sample crystallinity at different steps of heating, another portion of the sample was cyclically heated in an evacuated quartz tube under the same conditions as for IR measurements, with registration of XRD patterns at each temperature step. For a comparison with the data on H_3O -natrolite of Stuckenschmidt *et al.* (1996), a sample of NH_4 -natrolite was heated in vacuum at about 550 K for 14 days, and then characterized by IR spectroscopy, XRD and TG analyses.

Results and discussion

Thermogravimetry

The DTG curve of NH_4 -natrolite is presented in Fig. 1 (1). This curve contains one broad peak in the range 650–950 K, corresponding to the weight loss of 15.6 wt. %, the total weight loss being 15.9 wt. %. For comparison, a complete de-ammoniation and dehydroxylation of NH_4 -natrolite with an ideal composition $(\text{NH}_4)_{16.2}[\text{Al}_{16.2}\text{Si}_{23.8}\text{O}_{80}]$ implies the removal of 10.29 wt. % of NH_3 and 5.45 wt. % of H_2O . So we may conclude that the weight loss due to the decomposition

of NH_4 -natrolite is almost complete, though the last points of the curve lie slightly above the baseline. The form of this curve differs significantly from the DTG curves of zeolites with more open structure, for example, that of ammonium chabazite, that has two distinct peaks, corresponding to de-ammoniation and dehydroxylation (Beyer *et al.*, 1977).

Gas chromatography

Heating the NH_4 -natrolite to 1040 K results in 10.66 wt. % loss of NH_3 and 5.53 wt. % loss of H_2O . These quantities are in reasonable agreement with the TG data, as well as with calculated amounts of NH_3 and H_2O corresponding to the complete decomposition of NH_4 -natrolite.

The T-dependence of the NH_3 and H_2O removal rate upon heating the NH_4 -natrolite is presented in Fig. 2. As it is seen from Fig. 1 and 2, the total ($\text{NH}_3 + \text{H}_2\text{O}$) gas chromatography curve approximates well the DTG curve. It is seen that de-ammoniation and dehydroxylation start at about 570 K and proceed almost in parallel. This means that the OH-groups, formed after the removal of NH_3 , are unstable and immediately decompose. To get a more detailed picture of the interval between the removal of NH_3 and the decom-

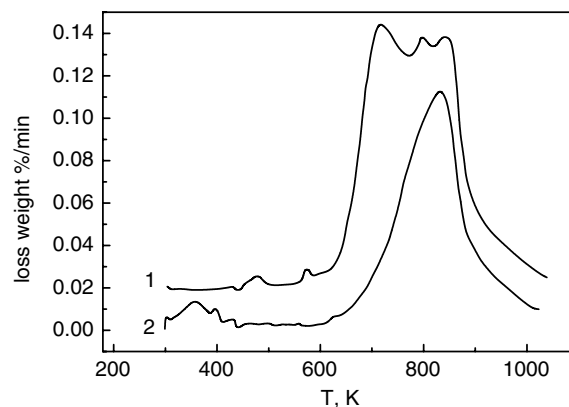


Fig. 1. DTG curves of NH_4 -natrolite: 1 – initial sample, 2 – after vacuum treatment at 550 K during 15 days.

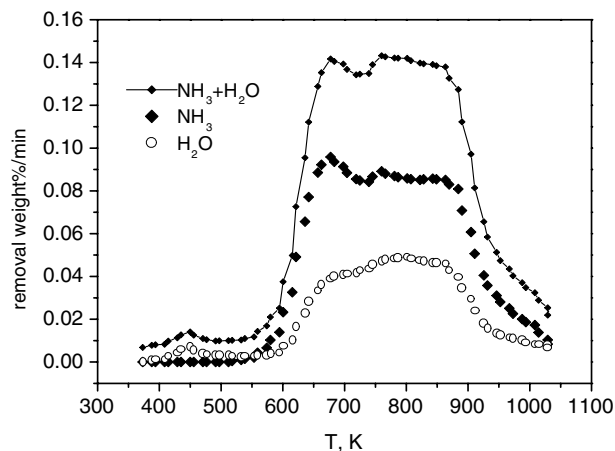


Fig. 2. Temperature dependence for the rate of NH_3 , H_2O , and $\text{NH}_3 + \text{H}_2\text{O}$ removal during linear heating of NH_4 -natrolite, derived from the gas chromatography data. The ($\text{NH}_3 + \text{H}_2\text{O}$) curve is shifted along the y axis. Heating rate: 3 °/min.

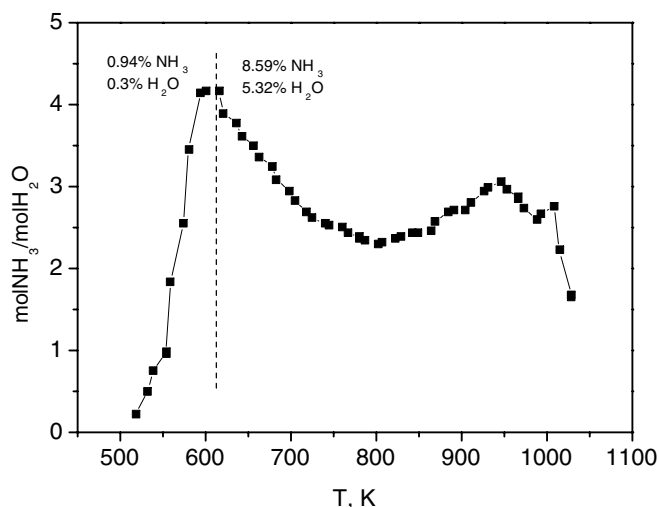
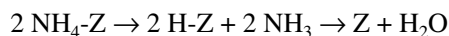


Fig. 3. Molar ratio $\text{NH}_3/\text{H}_2\text{O}$ in the gas mixture removed during thermal decomposition of NH_4 -natrolite. The total loss of NH_3 and H_2O at the initial and the next steps of decomposition (separated by vertical dashed line) is indicated.

position of OH-groups, the molar ratio $\text{NH}_3/\text{H}_2\text{O}$ in the gas mixture released from NH_4 -natrolite is plotted against temperature in Fig. 3. This ratio should equal 2, provided that, for two NH_3 molecules, one H_2O molecule is formed and immediately removed, in accordance with the decomposition scheme of ammonium zeolite:



(Z – zeolite aluminosilicate framework, after Breck, 1974).

At the early stage of degassing, the ratio $\text{NH}_3/\text{H}_2\text{O}$ is much higher than 2, indicating a maximum delay between the de-ammoniation and the dehydroxylation. After this short period of accumulation of the OH-groups, these begin to decompose, as shown by the decrease of the $\text{NH}_3/\text{H}_2\text{O}$ ratio closer to the stoichiometric value 2. This suggests again that, upon heating the NH_4 -natrolite, the de-ammoniation is shortly followed by dehydroxylation. Thus, the thermal behaviour of NH_4 -natrolite sharply differs from that of the Al-poor, large-pore zeolites, where de-ammoniation and dehydroxylation do not overlap, and the H-form can be obtained (Beyer *et al.*, 1977; Rabo & Gajda, 1989–90).

To describe the mechanism of degassing of NH_4 -natrolite in more detail, the T-dependence of the rate constant of de-ammoniation (dehydroxylation) derived from the gas chromatography data is presented in Fig. 4. The rate constant is calculated assuming a first order relationship for the rate of NH_3 (H_2O) removal with respect to the NH_3 (H_2O) concentration in the sample:

$$k = W_t/A_t,$$

where W_t is the rate of NH_3 (H_2O) removal, and A_t is the current concentration of NH_3 (H_2O) in the sample. The observed slope variations of the NH_3 and H_2O curves indicate that the mechanism of degassing of NH_4 -natrolite changes throughout the thermal decomposition. The sharp bend of the H_2O curve at 1.7 ($10^3/\text{K}$) corresponds to the beginning of dehydroxylation. The linearity of the NH_3 curve in the range of 1.5 – 1.9 ($10^3/\text{K}$) implies a first-order relationship for the

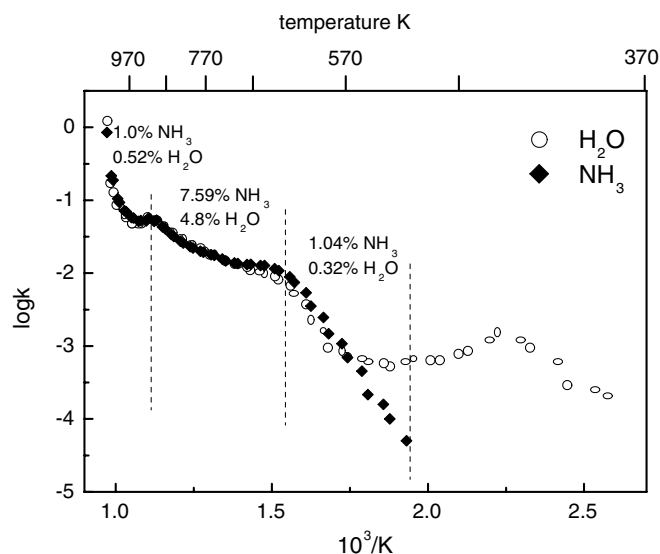


Fig. 4. Temperature dependence of the first-order rate constant (k) for desorption of NH_3 and H_2O during linear heating of NH_4 -natrolite. k was calculated by $k = W_t/A_t$, (W_t is the rate of NH_3 (H_2O) removal, A_t is the current concentration of NH_3 (H_2O) in the sample) The total loss of NH_3 and H_2O at the different steps of decomposition (separated by vertical dashed lines) is indicated.

removal of NH_3 from natrolite. A first-order relationship is typical for the rate of the NH_3 desorption from the acid proton centres in large-pore zeolites, the overall crystallinity of the large-pore zeolites being preserved during the NH_3 desorption (Karge & Dondur, 1990). By analogy, we may assume that, at the initial step, the mechanism of de-ammoniation of NH_4 -natrolite consists of thermal dissociation of the NH_4^+ ion into NH_3 and proton (framework OH-group), and the removal of NH_3 out of the structure.

Noticeable decrease of the slope of the NH_3 and H_2O curves at 1.5 ($10^3/\text{K}$) implies the increasing influence of diffusion limitation onto the rate of degassing. This is probably related to an abundant amount of gas species in the structural channels of natrolite: more than one half of the total ammonia and water content (5.6 wt. % NH_3 , 3.7 wt. % H_2O) is removed between 670–870 K (1.1 – 1.5 ($10^3/\text{K}$), Fig. 4).

Noticeable straightening of the NH_3 and H_2O curves in the closing stage of degassing at 1.0 ($10^3/\text{K}$) suggests that the reaction, leading to the removal of these compounds from natrolite, differs from that of the previous stages. Most probably, this is due to the defects accumulated in the framework at the breaking of bridging bonds during dehydroxylation. In the next section, the character of these defects and gradual decrease of crystallinity of NH_4 -natrolite will be described using IR spectroscopy and XRD data.

In the linear part of the NH_3 curve (1.5 – 1.9 ($10^3/\text{K}$)), an apparent activation energy of 117 (± 13) kJ/mol is estimated, to be compared with that for NH_3 desorption from the acidic proton centres in large-pore zeolites (mordenite, faujasite), lying between 80 and 150 kJ/mol (Shannon *et al.*, 1985; Karge & Dondur, 1990; Yin *et al.*, 1997). In the steep part of the NH_3 and H_2O curves (at 1.0 ($10^3/\text{K}$), Fig. 4), corresponding to the final stage of degassing, an apparent activation energy of 270 (± 20) kJ/mol is estimated. Thus, the

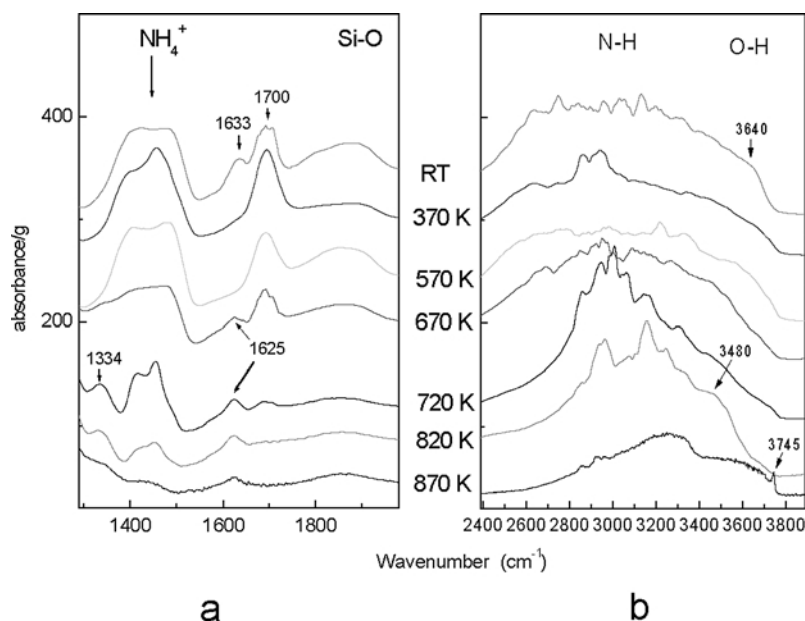


Fig. 5. IR spectra of NH_4 -natrolite in the region of (a) bending and (b) stretching N-H and O-H vibrations after vacuum heating to 870 K.

last portion of NH_3 and H_2O (about 1 % of the initial content) is much more strongly held in natrolite, as compared to the initial step of degassing.

IR spectroscopy

IR spectra for NH_4 -natrolite registered at different temperature steps are displayed in the region of N-H and O-H vibrations in Fig. 5. At room temperature, the IR spectrum contains intensive bands of bending (1450 cm^{-1} , 1700 cm^{-1} , Fig. 5a), overtones ($2500\text{--}3000\text{ cm}^{-1}$) and stretching vibrations ($3000\text{--}3400\text{ cm}^{-1}$, Fig. 5b) for the NH_4^+ molecule (Nakamoto, 1978). The intensity of the ammonium IR bands at the initial steps of heating (up to 670 K) is close to the upper response limit of the spectrometer, due to a high concentration of absorbing centers in the sample, which presents a self-supported pellet. The progressive de-ammoniation at 670 K leads to a decrease of the concentration of absorbing NH_4^+ molecules, and the intensity of the ammonium bands

becomes roughly proportional to the ammonium content in the sample. In the region of $1700\text{--}2200\text{ cm}^{-1}$, the framework Si-O overtone bands are observed. Weak shoulders at 3640 and 1633 cm^{-1} are due to residual water and disappear at 370 K.

The intensive de-ammoniation at 670–870 K is seen from the decrease of the integral intensity of the ammonium band at 1450 cm^{-1} . Note that the shape of this band changes sharply at 720 K. It may reflect the change of site symmetry due to the deformation of channels hosting NH_4^+ ions, as a result of progressive amorphisation. Despite this, the integral in-

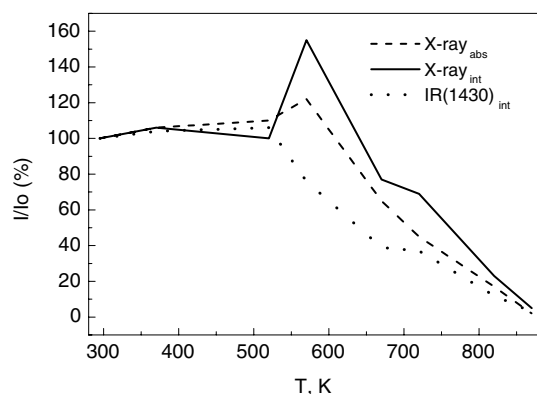


Fig. 6. Relative integral intensities of the ammonium IR band at 1450 cm^{-1} and the (220) X-ray peak of NH_4 -natrolite, after stepwise vacuum heating at 370–870 K.

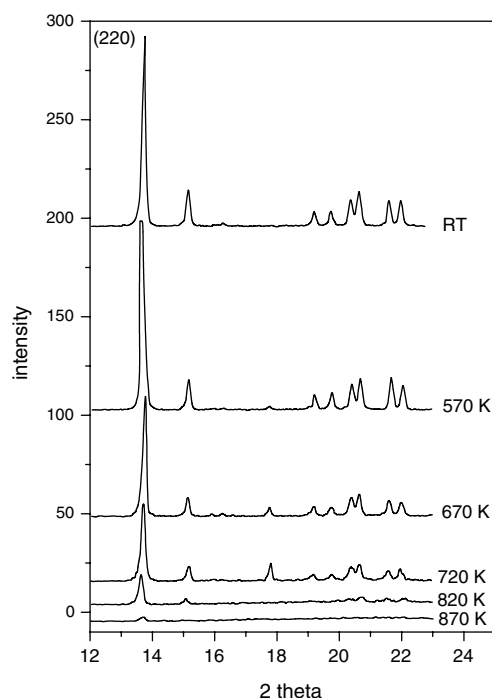


Fig. 7. XRD patterns of NH_4 -natrolite, after stepwise vacuum heating to 870 K. The (220) peak at 570 K is truncated, its intensity exceeding the dimension of the plotter tape.

tensities of the 1450 cm^{-1} bands at 670 K and 720 K are comparable (Fig. 6), probably due to a relatively small temperature interval. We should note that a similar narrowing of the ammonium band was observed in NH_4 -analcime at the progressive stage of de-ammoniation, in an essentially amorphous sample (Likhacheva *et al.*, 2004). As it is seen from Fig. 6 and 7, the decrease of the ammonium band, which is roughly proportional to the degree of de-ammoniation, is accompanied by a decrease of the XRD peaks of NH_4 -natrolite. An appreciable increase of the integral XRD intensity of (220) peak at 570 K (Fig. 6) is due to the removal of a part of the NH_4^+ ions, which occupy the H_2O positions in natrolite. It is known that the main X-ray reflection (220) of natrolite is suppressed by cations occupying the H_2O positions in the structure channels (Seryotkin, 1995). Upon further heating, when the natrolite structure is progressively destroyed due to the breaking of the framework bonds at dehydroxylation, the IR ammonium band and the XRD peak decrease in parallel (Fig. 6).

In the region of the O-H vibrations at $3500\text{--}3600\text{ cm}^{-1}$ (Fig. 5b), no appreciable bands appear during the de-ammoniation. A weak shoulder at 3480 cm^{-1} is observed in the spectrum at 820 K. This shoulder may be assigned to the OH stretching mode of H_2O molecules, its shift to lower values being due to hydrogen-bonding interaction with other water molecules or the framework (Jacobs *et al.*, 1993). This is most probably a sign of water formed at dehydroxylation, which is accumulated in the natrolite channels, when a high degree of amorphisation is achieved. Another weak band at 3745 cm^{-1} , observed at 870 K, belongs to isolated terminal Si-OH groups (Jacobs *et al.*, 1993); these may serve as an additional indirect evidence for highly destroyed framework. Thus, we do not observe any appreciable features in the IR spectrum, which might be assigned to the bridging framework OH-groups. This is in accordance with the gas chromatography data, which evidence for the instability of the OH-groups formed after the removal of ammonia.

As it is seen from Fig. 6, a high degree of amorphisation is achieved at 670–720 K when approximately 50 % of ammonium are lost. At this stage, two additional bands at about 1330 and 1625 cm^{-1} appear in the IR spectrum (Fig. 5a). These bands are typical of NH_3 bonded to Lewis acid sites (marked as $\equiv\text{Al}:\text{NH}_3$), the latter representing a coordinated unsaturated Al species, or a non-framework Al (Shannon *et al.*, 1985; Corma, 1995). The term “non-framework” is generally applied to Al atoms having one or more Al-O framework bonds broken as a result of dehydroxylation (Freude *et al.*, 1983; Alvarez *et al.*, 1997). The process leading to the formation of the non-framework Al is called “de-alumination” (Shannon *et al.*, 1985; Bodart *et al.*, 1986). For Al-rich framework aluminosilicates, like natrolite, the de-alumination is an essential part of the amorphisation process.

The extinction coefficient for the $\equiv\text{Al}:\text{NH}_3$ band at 1625 cm^{-1} is known to be lower than that for the NH_4^+ ion band at 1450 cm^{-1} by an order of magnitude (Yin *et al.*, 1997). This means that, at 720 K, the amount of NH_3 molecules bonded to Lewis sites is comparable to that of the residual NH_4^+ molecules. Note that the 1625 cm^{-1} band remains stable whereas the ammonium band at 1450 cm^{-1} diminishes at higher temperatures (Fig. 5a). It follows that the adsorption of NH_3 on

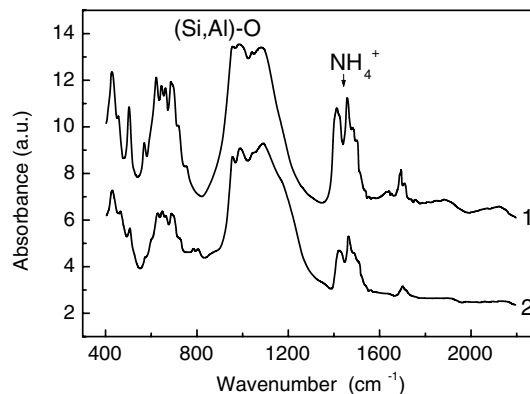


Fig. 8. IR spectra of NH_4 -natrolite (1) before and (2) after vacuum treatment at 550 K during 15 days.

Lewis sites represents the intermediate step for NH_3 removal at the final stage of de-ammoniation of NH_4 -natrolite. The Lewis sites are known to easily adsorb NH_3 molecules to form stable complexes (Corma, 1995; Yin *et al.*, 1997), which seems to be the main reason for the increase of the activation energy observed by gas chromatography. The adsorption of NH_3 onto the Lewis sites is probably facilitated by a high degree of disarrangement of the structure, thus preventing fast diffusion of NH_3 through the sample.

Finally, we present on Fig. 8 and 1 the IR spectra and DTG curves of NH_4 -natrolite before and after vacuum treatment at 550 K during 14 days. We should remind that this was done to examine the possibility of obtaining H-natrolite by smooth temperature treatment. The persistence of the peak at 1450 cm^{-1} typical of the NH_4^+ group shows that the degassing of NH_4 -natrolite at 550 K does not lead to an appreciable de-ammoniation. As it is seen from the comparison of the gas chromatography and the DTG curves (Fig. 1, 2), the main peak in the DTG curve corresponds to simultaneous removal of ammonia and water. Heating the NH_4 -natrolite at 550 K for 14 days results in a decrease of the main peak (Fig. 1). We may conclude that the corresponding part of ammonia (about 30–35 % of the total NH_3 content) is lost during the heating, that is, a partial de-ammoniation occurs. We should notice that the overall crystallinity of the NH_4 -natrolite is retained, the intensity of the XRD peaks being lower as compared to the initial sample. This allows us to suppose that the crystalline phase obtained under similar conditions by Stuckenschmidt *et al.* (1996) is most probably a partially de-ammoniated NH_4 -natrolite. Slight changes in the unit-cell parameters, observed in our sample by XRD analysis (initial NH_4 -natrolite: $a = 17.92(1)$, $b = 18.46(2)$, $c = 6.53(1)\text{ \AA}$; heated NH_4 -natrolite: $a = 17.91(1)$, $b = 18.479(1)$, $c = 6.53(1)\text{ \AA}$, $C112_1$), do not contradict much the data reported by Stuckenschmidt *et al.* (1996), taking into account the difference between single-crystal and powder XRD analyses.

Conclusions

During the thermal decomposition of the NH_4 -natrolite, the de-ammoniation is immediately followed by dehydroxylation. This is evidence for the instability of the H-natrolite

formed after the removal of NH_3 , and leads to a negligibly small concentration of the OH-groups. The natrolite structure can not persist after the removal of NH_3 . In this respect, the thermal behaviour of the NH_4 -natrolite is similar with that of the NH_4 -analcime (Likhacheva *et al.*, 2004). These two zeolites present an interesting example of the Al-rich and dense frameworks, which can not exist in fully protonated form because of too high concentration of the proton centres, that is shown to be unattainable for a number of zeolites (Barthomeuf, 1987).

The mechanism of de-ammoniation changes throughout the thermal decomposition of NH_4 -natrolite. In the initial step, the apparent activation energy for NH_3 desorption is estimated to be 117 (± 13) kJ/mol. The removal of NH_3 is immediately followed by dehydroxylation, which leads to a progressive loss of crystallinity. In the final step, the adsorption of NH_3 onto the defect centres accumulated in the amorphous framework hinders the de-ammoniation. The chemical character of bonding in the $\equiv\text{Al}:\text{NH}_3$ complexes makes them more stable as compared to the H-bonded NH_4^+ ions. This seems to be most reasonable explanation for the observed increase in the activation energy for NH_3 desorption to 270 (± 20) kJ/mol.

Smooth vacuum degassing of NH_4 -natrolite at 550 K leads to partial de-ammoniation, rather than formation of H-natrolite.

Acknowledgements: We are grateful to Dr. S. Quartieri and Dr. W.H. Baur for their helpful comments. This work was supported by RFBR grants # 04-05-64351, 05-05-64657.

References

- Alvarez, L.J., Ramirez-Solis, A., Giral, P.B. (1997): Mechanisms of formation of extraframework Al_2O_3 in zeolites. *Zeolites*, **18**, 54-62.
- Barthomeuf, D. (1987): Zeolite acidity dependence on structure and chemical environment. *Mat. Chem. Phys.*, **17**, 49-71.
- Beyer, H.K., Jacobs, P.A., Uytterhoeven, J.B., Till, F. (1977): Thermal stability of NH_4 -chabazite. *J.C.S. Faraday Trans. 1*, **73**, 1111-1118.
- Bodart, P., Nagy, J.B., Debras, G., Gabelica, Z., Jacobs, P.A. (1986): Aluminum siting in mordenite and dealumination mechanism. *J. Phys. Chem.*, **90**, 5183-5190.
- Breck, D.W. (1974): Zeolite molecular sieves. J.Wiley, New York, 815 p.
- Corma, A. (1995): Inorganic solid acids and their use in acid-catalyzed hydrocarbon reactions. *Chem. Rev.*, **95**, 559-614.
- Freude, D., Frochlich, T., Pfeifer, H., Sheler, G. (1983): NMR studies of aluminium in zeolites. *Zeolites*, **3**, 171-177.
- Jacobs, W.P.J.H., van Wolput, J.H.M.C., van Santen, R.A. (1993): An in-situ Fourier transform infrared study of zeolitic vibrations: dehydration, deammoniation, and reammoniation of ion-exchanged Y zeolites. *Zeolites*, **13**, 170-182.
- Karge, H.G. & Dondur, V. (1990): Investigation of the distribution of acidity in zeolites by temperature-programmed desorption of probe molecules. 1. Dealuminated mordenites. *J. Phys. Chem.*, **94**, 765-772.
- Kuhl, G.H. & Schweizer, A.E. (1975): Structural stability of sodium ammonium zeolite X. *J. Catal.*, **38**, 469-476.
- Likhacheva, A. Yu., Veniaminov, S.A., Paukshtis E.A. (2004): Thermal decomposition of NH_4 -analcime. *Phys. Chem. Minerals*, **31**, 306-312.
- Mirzai, J.I., Guliev, T.M., Akhmedov, V.N., Isirikyan, A.A. (1998): Adsorption-energy and IR spectroscopic studies of NH_4 -natrolite. *Russ. Chem. Bull.*, **47**, 352-354.
- Nakamoto, K. (1978): Infrared and Raman spectra of inorganic and coordination compounds. Wiley, New York, 395 p.
- Rabo, J.A. & Gajda, G.J. (1989-90): Acid function in zeolites. *Catal. Rev. - Sci. Eng.*, **31**, N4, 385-430.
- Seryotkin, Yu.V. (1995): X-ray diffraction study of natural and modified zeolites. Ph.D. Thesis, Novosibirsk, 138 p.
- Shannon, R.D., Gardner, K.H., Staley, R.N., Bergeret, G., Gallezot, P., Auroux, A. (1985): The nature of the nonframework aluminum species formed during the dehydroxylation of H-Y. *J. Phys. Chem.*, **89**, 4778-4788.
- Stuckenschmidt, E., Kassner, D., Joswig, W., Baur, W.H. (1992): Flexibility and distortion of the collapsible framework of NAT topology: the crystal structure of NH_4 -exchanged natrolite. *Eur. J. Mineral.*, **4**, 1229-1240.
- Stuckenschmidt, E., Joswig, W., Baur, W.H. (1996): Flexibility and distortion of the collapsible framework of NAT topology: the crystal structure of H_3O -natrolite. *Eur. J. Mineral.*, **8**, 85-92.
- Yin, F., Blumenfeld, A.L., Gruver, V., Fripiat, J.J. (1997): NH_3 as probe molecule for NMR and IR study of zeolite catalyst acidity. *J. Phys. Chem.*, **101**, 1824-1830.

Received 29 November 2004

Modified version received 15 July 2005

Accepted 15 December 2005