# PHYSICAL CHEMISTRY

S. P. ZHDANOV, A. V. KISELEV, V. I. LYGIN, T. I. TITOVA

1963

SovietRxiv

## Abstract

## Full Text

## PHYSICAL CHEMISTRY

**S. P. ZHDANOV, A. V. KISELEV, V. I. LYGIN, T. I. TITOVA**

# CHANGE IN THE INFRARED SPECTRUM OF ZEOLITES X DURING THERMAL TREATMENT IN VACUUM

*(Presented by Academician A. N. Frumkin, December 28, 1962)*

The method of infrared spectroscopy has been used little in adsorption for zeolites (see the reviews ($^1$)). In ($^2$) it was established that NaA zeolite treated at 400° contains no adsorbed water molecules or hydroxyl groups, and the conclusion was drawn that during dehydration of zeolites NaX and $NH_4X$ the formation of structural hydroxyl groups is possible. Infrared spectra have also been obtained for water ($^{2,3}$) and benzene ($^4$) adsorbed in the channels of a zeolite. In the present work we investigated changes in the spectrum of the sodium and ammonium forms of zeolites X during thermal treatment in vacuum. The initial zeolite crystals have the composition $1.02Na_2O \cdot Al_2O_3 \cdot 3SiO_2$, and the ammonium form $(0.68NH_4 \cdot 0.32Na)_2O \cdot Al_2O_3 \cdot 3.06SiO_2$. To eliminate scattering, zeolites, like silica gels ($^5$), were pressed under a pressure of 50 kg/mm$^2$ into tablets of \$ $10 mg/cm^{2}$.Heattreatmentofthesampleandrecordingofthespectrumwerecarriedoutinavacuumcuvetteanalogoustothatdescribedin
The spectra were recorded with a Zeiss UR-10 spectrometer.

Figures 1 and 2 show the spectra of zeolites treated in vacuum at different temperatures. The continuous absorption in the region 900–1150 cm$^{-1}$ is due to stretching vibrations of the silicon-oxygen framework ($^7$). In the spectrum of zeolite NaX (Fig. 1a) there also appear a broad band with two maxima at 762 and 685 cm$^{-1}$ and bands at 620, 572, and 465 cm$^{-1}$, belonging to vibrations of the aluminosilicate framework of the zeolites, since quartz and aluminosilicates ($^{7,8}$) have absorption bands in this region. In the spectrum of zeolite $NH_4X$ (Fig. 1b), the bands at 760 cm$^{-1}$ and 680 cm$^{-1}$ are more diffuse. Absorption

**Table 1**

Frequencies of the absorption bands of stretching vibrations of hydroxyl groups OH and OD in the spectrum of zeolites X under various regimes of thermal treatment in vacuum

Fig. 1. Change in the infrared spectrum of zeolite NaX (a) and ammonium zeolite (b) during thermal treatment in vacuum. At each temperature indicated at the curves, the sample was evacuated for 4 hours.

Figure 1: Fig. 1. Change in the infrared spectrum of zeolite NaX (a) and ammonium zeolite (b) during thermal treatment in vacuum. At each temperature indicated at the curves, the sample was evacuated for 4 hours.

| Treatment temperature, °C | Sodium zeolite $\nu_{OH}$ | Sodium zeolite $\nu_{OD}$ | Ammonium zeolite* $\nu_{OH}$ | Ammonium zeolite $\nu_{OD}$ |
|---|---|---|---|---|
| Initial 25 | 3600-3200 (v. str.)3695 (med.)3420 (str.) | 2650 (str.)2725 (wk.)2500 (med.) | 3600-3200 | 2600-2300 (v. str.)2697 (wk.) |
| 100 | 3690 (wk.)3400 (wk.) | 2725 (v. wk.)2500 (v. wk.) | | 2693 (med.) |
| 200 | 3690 (v. wk.)3400 (v. wk.) | 2725 (v. wk.)2500 (v. wk.) | 3655 (str.) | 2693 (str.) |
| 300 | 3690 (v. wk.) | 2725 (v. wk.) | 3655 (str.) | 2695 (med.) |
| 400 | 3690 (v. wk.) | 2725 (v. wk.) | 3655 (str.) | 2695 (med.) |

* The positions of the absorption bands of stretching vibrations of OH and OD associated with one another by a hydrogen bond cannot be determined because of overlap with the bands of absorption of stretching vibrations of NH and ND. V. str., str., med., wk., v. wk. denote, respectively, very strong, strong, medium, weak, and very weak intensities of the absorption band.

in this region is associated with the presence of isomorphous substitution of $Si^{4+}$ by $Al^{3+}$ ([8]). The increase in transmission in this region after evacuation at 25° (see Fig. 1) is due to the removal from the zeolite channels of water molecules having a broad librational vibration band at about 650 $cm^{-1}$ ([9]).

When the temperature is increased from 200°, the framework-vibration spectrum of zeolite $NH_4X$ undergoes greater changes than the spectrum of zeolite NaX. In the spectrum (Fig. 1b) the band at about 680 $cm^{-1}$ almost disappears and a maximum at 725 $cm^{-1}$ begins to appear, which may indicate a rearrangement of the crystalline framework of zeolite $NH_4X$.

**Fig. 1.** Change in the infrared spectrum of zeolite NaX (a) and ammonium zeolite (b) during thermal treatment in vacuum. At each temperature indicated at the curves, the sample was evacuated for 4 hours.

Weak bands in the region 1300-1500 $cm^{-1}$ (Fig. 1a) are also observed in the

Fig. 2

Figure 2: Fig. 2

spectra of natural aluminosilicates (7,10). Calcination at 800° (see Fig. 1) leads to broadening of the framework-vibration bands, analogous to the change in the spectrum on transition from crystalline quartz to amorphous quartz (7), and characterizes the destruction of the crystalline structure of the zeolite.

In the spectra of both forms of zeolites (Fig. 1), before treatment there are broad bands at about 3400 and 1645 $cm^{-1}$ in the absorption region of liquid water (9). In the spectrum of zeolite NaX at an evacuation temperature of 25° and of ammonium zeolite at 200°, narrow bands appear respectively at 3690 and 3655 $cm^{-1}$; their intensity decreases upon subsequent thermal treatment (Fig. 1, Table 1), with the 3400 $cm^{-1}$ band disappearing from the spectrum earlier than these narrow bands. In the spectrum of the ammonium form of the zeolite, in addition to the absorption bands of stretching and deformation vibrations of the hydroxyl groups of water (Table 1), bands are observed at about 3250 and 3000 $cm^{-1}$, which may be assigned to stretching vibrations of NH groups of the $NH_4^+$ ion (11). The band at 1452 $cm^{-1}$

belongs to deformation vibrations of the $NH_4^+$ ion (11) and almost completely disappears after treatment at 200°. The broad band, shifted to 1700 $cm^{-1}$, in the spectrum of the ammonium zeolite treated at 100–200° (Fig. 1b), can be explained by superposition of the bands of adsorbed water molecules and the 1685 $cm^{-1}$ band of the $NH_4^+$ ion. The narrow absorption band at 800 $cm^{-1}$, especially clearly manifested in the spectra of the zeolite treated at 100 and 200°, may be assigned to pendulum vibrations of the NH bond (11).

**Fig. 2.** Change in the infrared spectrum of deuterated NaX zeolites (a) and ammonium zeolite (b) upon thermal treatment in vacuum. At each temperature indicated by the curves, the sample was evacuated for 4 hours.

The broad band near 2180 $cm^{-1}$ in the spectra of unevacuated zeolites is a combination band of deformation and librational vibrations of water molecules (10). The band near 2350 $cm^{-1}$ in the spectra of the initial zeolites apparently belongs to adsorbed $CO_2$ molecules. By repeated admissions of $D_2O$ vapor it is possible to exchange H for D in $H_2O$ molecules and in $NH_4^+$ (Fig. 2). Thermal treatment of deuterated NaX zeolite leads to a decrease in the intensity of the broad stretching-vibration band and to the appearance of a new narrow band at 725 $cm^{-1}$ (Fig. 2, Table 1). In the spectrum of the deuterated sample of the ammonium form (Fig. 2b) continuous absorption is observed in the region 2600–2300 $cm^{-1}$, of OD and ND groups (10–12). Evacuation at 25° leads to the almost complete removal of the stretching-vibration band of liquid $D_2O$ (Fig. 2b). After evacuation at 25°, a new narrow band of OD stretching vibrations at 2697 $cm^{-1}$ already appears in the spectrum; its maximum intensity is reached in the sample evacuated at 200° (Fig. 2b, Table 1). The broad band in the region of 2400 cm$^{-1}$ belongs to stretching vibrations of ND of the $ND_4^+$ ion ($^{11}$) and almost completely disappears after evacuation at 200°.

The change in the infrared spectra of zeolites shows that the main part of the associated water molecules is removed as a result of evacuation at 25°. The presence in the spectrum of zeolites evacuated at 100—200° of several bands of stretching and deformation vibrations of hydroxyl groups (Figs. 1 and 2) indicates the possibility of several types of bonding of water molecules with the surface of the zeolite channels. It is possible that the broad band of stretching vibrations of hydroxyl groups in the spectrum of samples (Figs. 1 and 2) evacuated at 100—200° belongs to water molecules forming a hydrogen bond with oxygen atoms of the zeolite ($^{2}$). It is also possible that some of the water molecules in NaX zeolite interact with $Na^+$ and give rise to the narrow band at 3690 cm$^{-1}$. The shift of this band relative to the band of mole-

water molecules in the band at 3755 cm$^{-1}$ (12) may be explained by their interaction with the cation (13). The assignment made in (3) of this band to vibrations of structural hydroxyl groups of the zeolite is uncertain, since this band is shifted relative to the absorption band of "free" hydroxyl groups of silica gels (3749 cm$^{-1}$) (1,14), is of low intensity, and is more easily removed on evacuation (15). In (3) it is assumed that structural hydroxyl groups are formed upon rupture of siloxane bonds of the zeolite as a result of reaction with $H^+$ ions formed in the decomposition of $OH_3^+$ ions. However, the spectral criteria for detecting the $OH_3^+$ ion are not sufficiently evident because of overlap of the bands (16,17). The chemical composition of the zeolite studied by us gives no grounds to suppose the existence of an excess charge. Comparison of the spectrum of the zeolite with the bands of $OH_3^+$ (16,17) likewise does not make it possible to conclude that there is an appreciable quantity of $OH_3^+$ ions. Without rejecting the possibility of formation of new structural groups during heat treatment of zeolites, it should be noted that they can exist mainly as dislocations in the crystal framework, since the formation of a large number of hydroxyl groups will inevitably cause destruction of the crystal structure. In the cases studied by us, the most favorable possibilities for destruction of the crystal structure are observed in the decomposition of the $NH_4^+$ ion during heat treatment of the ammonium zeolite. As follows from the spectra (Figs. 1 and 2 ), the direct consequence of decomposition of $NH_4^+$ and $ND_4^+$ ions at 100—200° is an increase in the intensity of the newly appearing narrow bands at 3655 and 2695 cm$^{-1}$. The intensity of these bands is higher than in zeolite NaX (Figs. 1 and 2 ). In addition, the position of these narrow bands in zeolites NaX and in the ammonium form is different (Table 1). All this makes assignment of the narrow bands in the spectrum of the ammonium zeolite to vibrations of structural hydroxyl groups more probable than in the case of zeolite NaX.

The nature of the change in the framework spectrum indicates preservation of the crystal structure of zeolite NaX upon heating in vacuum to 400°, and a restructuring of the structure of the ammonium zeolite already at 200°. At this same temperature the $NH_4^+$ and $ND_4^+$ ions are destroyed. Water molecules associated with one another are for the most part removed already at 25°. The spectra indicate the existence of several types of bonding of water molecules with the surface of the zeolite channels. Formation of structural hydroxyl groups is most probable in the decomposition of the ammonium zeolite.

Moscow State University
named after M. V. Lomonosov

Institute of Chemistry of Silicates
Academy of Sciences of the USSR

Received
25 XII 1962

## CITED LITERATURE

1. A. N. Terenin, in: *Surface Chemical Compounds and Their Role in Adsorption Phenomena*, Moscow, 1957, p. 206; A. V. Kiselev, V. I. Lygin, *Russ. Chem. Rev.*, **31**, 351 (1962).
2. G. J. C. Frohnsdorff, G. L. Kington, Proc. Roy. Soc., **247**, 469 (1958); G. V. Tsitsishvili, G. D. Bagratishvili, *Synthetic Zeolites*, Publishing House of the Academy of Sciences of the USSR, 1962, p. 38.
3. H. A. Szumanski, D. N. Stamines, G. R. Lynch, J. Opt. Soc. Am., **50**, 1323 (1960).
4. V. N. Abramov, A. V. Kiselev, V. I. Lygin, *Zh. Fiz. Khim.*, **37**, No. 5 (1963).
5. V. I. Lygin, N. N. Kavtaradze, E. G. Boreskova, *Zh. Fiz. Khim.*, **35**, 932 (1961).
6. V. Ya. Davydov, A. V. Kiselev, V. I. Lygin, *Kolloidn. Zh.*, **25**, No. 2 (1963).
7. J. M. Hunt, M. P. Wischerd, L. C. Bonham, Anal. Chem., **23**, 1478 (1950).
8. V. A. Kolesova, *Optics and Spectroscopy*, **6**, 38 (1959).
9. P. A. Giguere, K. B. Harvey, Canad. J. Chem., **34**, 798 (1958).
10. V. T. Bykov, V. N. Sushin, *Kinetics and Catalysis*, **3**, 788 (1962).
11. G. Herzberg, *Vibrational and Rotational Spectra of Polyatomic Molecules*, IL, 1949.

12. D. E. Bethel, N. Sheppard, J. Chem. Phys., **21**, 1421 (1953).

13. I. E. Perel' gin, *Optics and Spectroscopy*, **16**, 353 (1962).

14. A. V. Kiselev, V. I. Lygin, *Kolloidn. Zh.*, **21**, 581 (1959).

15. R. S. McDonald, J. Phys. Chem., **62**, 1168 (1958).

16. C. C. Forrisso, D. F. Hornig, J. Chem. Phys., **23**, 1464 (1955).

17. M. Falk, P. A. Giguere, Canad. J. Chem., **35**, 1195 (1957).

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