TO THE PROBLEM OF THE STATE OF WATER ADSORBED ON X-TYPE ZEOLITES

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Sorption of water on X-type zeolites was studied by means of infrared spectroscopy. It was found that the spectra of hydrazined zeolites show in the region of deformation vibrations a band at $1650 \, cm^{-1}$, assigned to adsorbed water. The band found at $1590 \, cm^{-1}$ is markedly more thermally stable and it is suggested that it might be attributed to the vibration of bivalent carbonate. The results obtained are discussed.

The state of water adsorbed in zeolites has continuously been the subject of investigation, since the development of modern, particularly spectral methods, allows to obtain further experimental data, complementing the scope of material obtained by classical methods, *e.g.* DTA, thermogravimetry *etc.*[1]. Infrared spectroscopy was employed for studying sorbed water in the A-and X-type zeolites and it was established that water molecules bonded in different ways are represented in the infrared spectrum both in the region of valence and deformation vibrations of —OH groups. The spectrum of hydrazined zeolites of the type A was found to display not only the $1650 \, cm^{-1}$ absorption band, assigned to adsorbed water that can be desorbed to 300°C, but also a band at $1590 \, cm^{-1}$ that, according to Juchněvič[3] and Schirmer[5] can be assigned to firmly bonded water. The intensity of the $1590 \, cm^{-1}$ band is constant even after desorption of water at 300°C and does not change even after deuteriation[3]. Similarly, Lygin, Kiselev and coworkers[4] found with NaX zeolite bands at 1660 and $1590 \, cm^{-1}$ which they assume to belong to two different forms of water of which the $1590 \, cm^{-1}$ band is assigned to the more stable and more firmly bonded H_2O form. The frequency of the $1660 \, cm^{-1}$ band depends on the electrostatic field of cation as was demonstrated by Ward[2] in the case of X zeolites containing various univalent and bivalent cations.

In spite of all these studies the problem of sorbed water has still not been satisfactorily elucidated. Calorimetric measurements of water sorption are charged with the strong dependence of ΔH value on the degree of sorption capacity saturation (ΔH decreases from 19 to 12 kcal/mol), as was shown in several papers[1,6−8], which supports the existence of active centers of different activity. It was established, however, by means of NMR measurements that water molecules display signals in the form of doublets, characteristic of crystallinic hydrates with firmly bonded molecules only at lower temperatures ($T < 250$ K). At higher temperatures the molecules become mobile and more than one species of molecules with the same degree of freedom[9−11] cannot be distinguished from the spectrum.

The present communication is devoted to the problem of differentiation of the absorbed states of H_2O molecules on NaX and HX zeolites. Our attention was

focused particularly on the estimation of band 1590 cm^{-1} assignment which was described by other authors as deformation vibration of firmly bonded water molecules.

EXPERIMENTAL

The following zeolites were used: Zeolite NaX, composition $Na_2O.Al_2O_3.2\cdot6\ SiO_2$ and zeolite NaX Linde, Lot No 1100262, composition $Na_2O.Al_2O_3.2\cdot3\ SiO_2$. Zeolites were transferred into the ammonia cycle by repeated ion exchange from NH_4Cl solution. Preparation of samples, experimental conditions, as well as the procedure of spectra recording on a UR-10 spectrophotometer were the same as described in the preceding paper[12].

RESULTS AND DISCUSSION

To verify the existence of the 1590 cm^{-1} absorption band in NaX zeolites, we have recorded the spectrum of hydrated zeolite, evacuated only at 20°C for 2−3 hours. Fig. 1a, b (curves 1, 2) gives the spectra of the NaX Linde and NaX-207 samples,
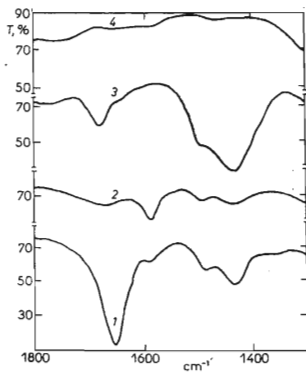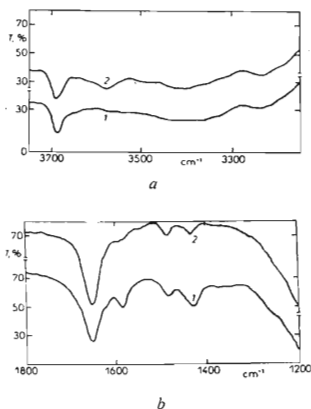

FIG. 1a, b

Infrared Spectra

 1 NaX Linde evacuated for 3 h at 25°C,
 2 NaX-207 evacuated for 3 h at 25°C.

FIG. 2

Infrared Spectra

 1 NaX Linde evacuated for 3 h at 25°C,
 2 NaX Linde evacuated for 3 h at 350°C,
 3 NH$_4$X evacuated at 25°C for 10 h, 4 NH$_4$X
 evacuated for 3 h at 350°C.

showing in both cases the bands at 1650 and 1590 cm^{-1} as a weak shoulder and broad bands at 3240, 3410 and 3685 cm^{-1} in the 3800—3100 cm^{-1} region.

Fig. 2 (curves 1, 2) demonstrates that during 3 hours' evacuation at 350°C the band of deformation vibration at 1650 cm^{-1} of the physically adsorbed water disappears. Simultaneously the bands of valence vibration of the bonded —OH groups, lying in the region 3600—3200 cm^{-1} become less intense.

The band of valence vibration of free —OH groups at 3685 cm^{-1} also looses intensity upon evacuation. However, in the spectrum remain the bands at 1590, 1485 and 1430 cm^{-1} which are stable even upon evacuation of the sample at 350°C, as follows from the spectrum in Fig. 2 (curve 2). This supports the finding of Lygin, Kiselev and coworkers[4] who have established that the band 1600—1590 cm^{-1} is more stable during desorption than the 1650 cm^{-1} band. Similarly, in agreement with the cited work, the band at 1590 cm^{-1} was not found with the original zeolite NH_4X after its thermal decomposition to the hydroxylated form HX (Fig. 2, curves 3, 4). This band also appears in the spectrum of the NaA type zeolite[3] which according to Juchněvič does not undergo any changes upon deuteriation at 20°C. Juchněvič tried to explain this phenomenon by assuming that water to which he assigned the 1590 cm^{-1} band is bonded in a form of a stable structure that does not allow deuteriation owing to high activation energy of the exchange process. For this reason we attempted the effect of D_2O vapours ($p \approx 10$ Torr) for 10 hours at 300°C where the D_2O molecules attain a considerable amount of thermal energy that should make the deuteriation possible. Fig. 3 shows the spectra prior to deuteriation (curve 1) and after deuteriation for 10 hours (curve 2) at 300°C. After deuteriation there appear bands at 1220, 1430, 1485 and 1590 cm^{-1}. The band at 1220 cm^{-1} is assigned to deformation vibration of the adsorbed heavy water D_2O, the band at 1430 cm^{-1} is strengthened by superposition with the band of the HDO deformation vibration lying in this region[16]. The bands 1590—1485 cm^{-1} are not affected by deuteriation, whereas the band at 1650 cm^{-1} completely disappears. This can arise suspicion that the band at 1590 cm^{-1} does not correspond at all to any deformation vibration of water but that it is caused by another effect. This assumption is also supported by the fact that the deformation vibration v_2 of free water molecules in the gaseous state lies at 1595 cm^{-1}, whereas with molecules bonded by intermolecular hydrogen bridges, as it is the case in liquid or adsorbed water, it is shifted towards higher frequencies. It seem improbable that the deformation vibration of firmly bonded molecules might not be affected by this bond and that its frequency would not be shifted towards higher values.

Further experiments revealed that the band at 1590 cm^{-1} along with the bands at 1485—1430 cm^{-1} disappear completely only after heating the zeolite to 500°C in vacuum (Fig. 4, curve 1). Upon rehydratation the 1590 cm^{-1} band was not found when the water used as sorbent was carefully freed from CO_2 both by degassing and by adding crystalline $Ba(OH)_2$. However, in sorption of dry CO_2 it was found

that the intensity of the bands $1485-1430 \text{ cm}^{-1}$ increases in the first place, as can be seen in Fig. 4, curve 2. In accordance with the literature[13,14], we have also found the bands at 1715 and 1380 cm^{-1} that appear in the Raman spectra of gaseous CO_2. Similarly to Habgood and Bertsch[13] we have ascertained that the 1590 cm^{-1} band is pronounced especially in sorption of CO_2 on a zeolite containing a certain amount of H_2O. Therefore we suppose that the existence of the 1590 cm^{-1} band must be assigned to the formation of a certain form of carbonate in the zeolite surface rather than to a form of firmly bonded and unaccessible water molecules. According to Nakamoto[17] v_1 vibrations of bivalent carbonate which are active in the IR spectrum of molecules of the point group C_{2v} can be expected in the region $1580-1620 \text{ cm}^{-1}$. This carbonate is probably present in the zeolite (in addition to monodentate which can be assigned the vibrations $v_5 = 1485 \text{ cm}^{-1}$ and $v_1 = 1430 \text{ cm}^{-1}$) already during its preparation and especially in the drying procedure when the wet zeolite is in contact with atmospheric CO_2 at a higher temperature. The fact that the 1590 cm^{-1} band has been observed neither with the genuine NH_4X nor with the decationized form of zeolite X formed by thermal decomposition of the ammonia form supports our hypothesis that it is a form of carbonate since ammonium carbonate is less stable than alkali metal and alkali earths carbonates.

CONCLUSIONS

1. The adsorbed water displays in the region of bending vibrations of the IR-spectrum only one absorption band with the maximum at 1650 cm^{-1} for NaX and at 1680 cm^{-1} for NH_4X zeolite. *2*. The absorption band with the maximum at 1590 cm^{-1} assigned in the literature to firmly bonded water is caused probably by surface carbonates.
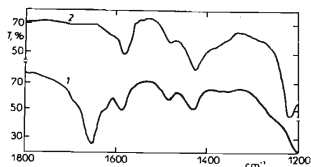
Fig. 3

Infrared Spectra

1 NaX Linde prior to deuteriation (the sample was evacuated for 3 h at 25°C), *2* NaX Linde after adsorption of D_2O for 10 h at 300°C and evacuation for 1 h at 25°C.
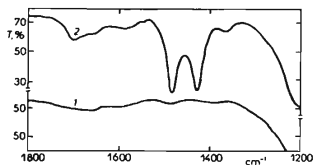
Fig. 4

Infrared Spectra

1 NaX Linde evacuated for 10 h at 500°C, *2* NaX Linde after sorption of CO_2 for 2 h at 25°C and evacuation for 1 h at 25°C.

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Note added in proof: We consider that the exchange process includes also the transport phenomena of water molecules, the decomposition of the firmly bonded complex, *etc.* Some of these steps may be activated.