STUDIES OF ADSORPTION MECHANISM ON ZEOLITES
OF THE FAUJASITE TYPE BY INFRARED SPECTROSCOPY. I.
ADSORPTION OF METHANOL
ON DECATIONATED X-TYPE ZEOLITES

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Sorption of methanol on a decationated X-type zeolite has been studied by means of infrared spectroscopy. Interaction of the hydrogen bond type has been established between methanol molecules and the structural —OH groups. Some of the —OH groups enter a chemical reaction with methanol, forming firmly bound methoxyl groups.

Knowledge of the adsorption mechanism of adsorbate molecules is a condition for setting up the statistical molecular theory of adsorption on sorbent surface and often it is even a condition for the explanation of catalytic processes, taking place in the catalysts surface. Zeolites — molecular sieves — display excellent sorption and catalytic properties and therefore a great deal of attention is being given to the studies of sorption mechanism of molecules[1−4].

Zeolites are crystalline aluminosilicates possessing the characteristic of ionexes. In the surface of their skeleton there is a number of adsorption centers which manifest themselves in the sorption of molecules, depending both on their chemical composition and on the nature of the functional groups. Molecules which are adsorbed due to not much specific adsorption forces of the van der Waals type are not sensitive towards different adsorption centers of the zeolite surface and consequently the course of their heats of adsorption is nearly linear, resembling adsorption on sorbents with homogeneous surface[4,5]. On the other hand, molecules with electrostatic moments as well as those with functional groups that allow a hydrogen-bond like interaction or formation of complex coordination bonds with a definite kind of adsorption center, display a rather high variability of adsorption heat in dependence on the adsorbed amount[6−9], as a result of both specific and non-specific interactions with different adsorption centers of the lattice. Whereas the adsorption equilibrium of molecules of the former type can formally be described by any of the theories of adsorption on homogeneous surface, taking into account intermolecular interaction, description of the adsorption behaviour of specifically sorbed molecules faces difficulties, even if the theory of sorption on heterogeneous surfaces is applied.

Important function of cations and their role as adsorption centers has been demonstrated several times[6−12]. Study of sorption of molecules reacting specifically with cations has proved that different sites of cations in the lattice of the X-type zeolite have different functions which is connected with different accessibility of the given site of cation to the adsorbed molecule[13−15]. The lattice of zeolite was found to contain also structurally bound —OH groups which led to

extensive studies of their effect on the sorption of different molecules[16−29]. The aim of these studies was to elucidate their function as acid centers. Especially decationated zeolite is suitable for investigating structurally bound —OH groups, since in its lattice Na^+ ions are replaced by NH_4^+ cations which on thermal decomposition yield protons forming —OH groups with oxygen of the lattice. It is well known that —OH groups present in the surfaces of SiO_2 and Al_2O_3 enter specific interactions with molecules of alcohols, including both weak interactions and strong bondings under the formation of surface bonded alkoxyls[30].

Despite of these facts no formation of surface bonded methoxy groups was found to exist on decationated X-type zeolites, not even after a long-lasting interaction with methanol at 400°C (see ref.[31]).

For this reason we have studied in the present work the formation and thermal stability of surface compounds of methanol by means of infrared spectroscopy.

EXPERIMENTAL

Apparatus and Technique

A high-vacuum all-glass apparatus was built up for the measurement of infrared spectra of adsorbed molecules. The measuring cell of the dimensions $40 \times 28 \times 12$ mm was provided with CaF_2 windows, which were cemented to its ground edges with piceine. The oven for heating the samples was placed in a quartz tube over the cell. Connection to the glass cell as well as to the rest of the apparatus was provided by intermediate glass seal. Gas pressure in the apparatus was measured
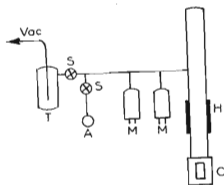

Fig. 1

Schematic Drawing of the Apparatus

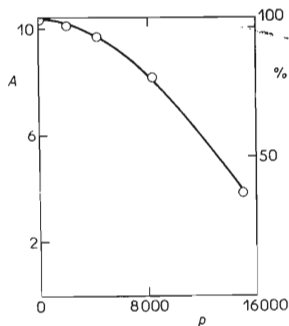 C CaF_2 cell, H oven, M manometers, S cocks, T freezing trap, A ampoule containing adsorbate.

Fig. 2

Dependence of the Adsorption Capacity, A, of Zeolite NaX (in mmol/g argon, or in % at −183°C) on the Pressing Pressure p (kg cm^2)

in the region 10^{-3} to 10^{-7} Torr by an ionization manometer and in the region $10^0 - 10^{-3}$ Torr by a thermocouple manometer, type VIT. Adsorbates were kept in the liquid state in ampoules, connected with the apparatus by vacuum-tight metal stopcocks (fa Hoke). Vacuum was obtained first by means of an adsorption pump, filled with activated charcoal at $-190°C$ and further by a two-step diffusion pump, filled with high-vacuum oil Convalex 10. On evacuation of the sample a vacuum of $5 . 10^{-7}$ Torr could currently be obtained. The cell into which the sample was dropped on a quartz holder was then placed into the focus of the measuring beam from the infrared spectrometer. The prism spectrometer Zeiss UR-10 with NaCl and LiF prism was employed for measuring in the region $1000-4000$ cm^{-1}. The reference beam was then screened suitably to obtain optimum resolution of the absorption bands. Current spectrograms were recorded at the speed 50 cm^{-1}/min, using slit of the program No 8 of the mentioned spectrometer.

Samples of zeolite were pressed into thin plates of the average thickness $3-5$ mg/cm^2. Since we have found that zeolite may be mechanically affected during pressing of pellets, we studied the influence of the pressing pressure on the adsorption capacity of A- and X-type zeolites (see[32]). As can be seen from Fig. 2, sorption capacity (measured with argon at $-183°C$) diminished with increasing pressing pressure and simultaneously a decrease in the intensity with blurring of the difraction bands on the Debyegram of crystalline zeolite is observed. An electrone microscopic picture revealed that the crystals of zeolite partly dilapidate on pressing into smaller particles. The decrease in sorption capacity cannot, however, be explained only by this disintegration of larger crystals into smaller ones under simultaneous disappearance of cavities on the crystalline fracture, since a more profound destruction of the structure evidently takes place. In order to preserve high sorption capacity and also to avoid pollution of zeolite samples by further possible types of adsorption centers, i.e. by lattice defects, we used pressing pressures of about 1000 kg/cm^2 as in this case the decrease in sorption capacity did not exceed 3%.

Methanol used for adsorption measurements was of the highest purity and was dried on molecular sieve 4A. It was freed from the remnants of dissolved gases by repeated freezing out and evacuating the gaseous phase.

Zeolite NaX used for the preparation of NH$_4$ form had the composition Na$_2$O.Al$_2$O$_3$.2·6SiO$_6$ and was converted into the ammonia cycle by repeated ion exchange from NH$_4$Cl solution. Samples to be measured were after pelletation placed in a holder and were evacuated at a suitable temperature till the pressure within the apparatus fell down to the value of the order of 10^{-7} Torr. The spectrum was always recorded at room temperature, after evacuating the gaseous phase.

RESULTS AND DISCUSSION

—OH Groups Structurally Bound in Zeolites

Decationated zeolite X was prepared by thermal degradation of the NH$_4$ form of zeolite X analogously to the procedure described in a number of papers[16,17,23−25,28]. The overall picture of the preparation course can be seen from the spectra in Fig. 3. The spectra were measured in the regions $3400-3900$ cm^{-1} (Fig. 3a) and 1300 to 1900 cm^{-1} (Fig. 3b). Original hydrated zeolite which was only evacuated at 20°C is represented by a curve, showing a split band with two maxima at 1440 and 1500 cm^{-1}, corresponding to deformation vibrations in NH$_4^+$ cation of the zeolite lattice and further a band at 1690 cm^{-1}. On increasing the temperature of the sample to 100°, 250° and 350°C in vacuo (curves $2-4$) the NH$_4^+$ ion is decomposed and the inten-

sity of its vibration decreases. Analogously, the band $1690\ cm^{-1}$ diminishes very quickly and at 250°C it disappears entirely. In view of the fact that the intensity of this band is substantially decreased at 100°C, it can be assinged to deformation vibrations of adsorbed water, the most part of which is desorbed already at this temperature, as was assumed also by other authors[10,21]. As follows from Fig. 3a, a broad band of associated —OH groups appears after desorption at 20°C (curve *1*), ranging from $3000-3600\ cm^{-1}$ with a flat maximum at $3400\ cm^{-1}$ and a further intensive band of free —OH groups vibration at $3600\ cm^{-1}$ with a faint shoulder at $3750\ cm^{-1}$. The broad band of associated —OH groups looses its intensity very quickly with proceeding desorption of the adsorbed water molecules (curves *2* and *3* at 100° and 250°C, respectively) and at 350°C it is no more visible. On the other hand, the intensity of free —OH groups vibrations increases up to 350°C, with a structure of broad bands $3560\ cm^{-1}$ and $3650\ cm^{-1}$ appearing after desorption of the adsorbed water. Intensive bands of free —OH groups in the region $3500-3700\ cm^{-1}$ after evacuation of the sample at 350°C, together with the absence of the band of —OH groups deformation vibrations at $1680\ cm^{-1}$ prove that the —OH groups are the structural ones, being a part of the zeolite skeleton. From the list of adsorption bands found by other authors with X- and Y-type zeolites, as presented in Table I, it is evident that our results are in accordance with the data from the literature.

An unambiguous interpretation of the individual bands has not yet been reported. The bands of —OH groups valence vibrations are most frequently assigned to —OH groups bound in various ways in the zeolite skeleton. The band $3740\ cm^{-1}$ is usually assigned to Si—OH groups, bound similarly as it is in the silica gel surface, their intensity being almost identical[18]. The usual explanation of the low intensity of this
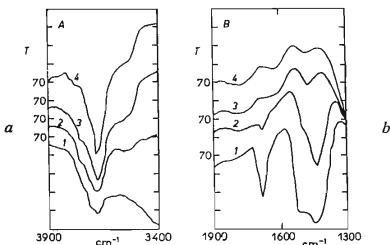

Fig. 3

Infrared Spectra of Zeolite NH_4X after Activation *in vacuo* at Different Temperatures

1 20°C, 4 h; *2* 100°C, 2 h; *3* 250°C, 4 h; *4* 350°C, 2 h.

band is that Si—OH groups are the terminal[19] groups of the zeolite crystal. These groups exist only in the geometric surface of crystals which amounts only a few per cent of the total sorption capacity of zeolite and therefore their relative contents is small. An alternative explanation of the existence of the 3740 cm^{-1} band can be the presence of a certain small amount of amorphous SiO$_2$ in zeolite[21].

Decationated zeolites of the HY type usually display further two bands 3650 cm^{-1} and 3545 cm^{-1} which have no analogy with other systems. On deuteration both these band are shifted by $\Delta\nu$ which corresponds to the expected isotopic shift and thus excludes the possibility of combination bands[26]. According to Angel and Schaffer[21] the 3650 cm^{-1} band can be assigned to Si—OH group, while the band at 3545 cm^{-1} should correspond to two adjacent —OH groups, mutually interacting through a weak hydrogen bond. Carter, Lucchesi and Yates[18] have found in the spectra of partially decationated X-type zeolite a band of the frequency 3700 cm^{-1} which, according to Angell and Schaffer[21], has also been found in a number of Y-type zeolites in the vicinity of 3690 cm^{-1}. By the latter authors it is assigned to Al—OH. It is probable that the band at 3695 cm^{-1}, described by Habgood and Ward[10,38], which appears in the spectrum of NaX only after addition of a small amount of water, interferes obviously only incidentally with the band of structurally bound —OH groups found by Carter, Lucchesi and Yates[18], occurring in partially decationated zeolites. Taking into account this interpretation it can be assumed that the band 3680 cm^{-1} described in the present publication can have some relation to the valence vibrations of —OH groups in Al—OH groups. The broad band at 3545 cm^{-1}

TABLE I

Absorption Bands of —OH Groups on Zeolites of the X and Y Type

Zeolite	(—OH), cm^{-1}				Ref.
NaX	3 750	3 700	3 650		18
NaX	3 750	3 695	3 655	—	20
NaY	3 748	—	3 652	—	21
NaY	3 735	3 690	3 690	3 380 3 280	38
HY	3 745	—	3 650	3 545	19
HY	3 744	—	3 636	3 544	21
HY	3 742	—	3 643	3 540	24
HY	—	—	3 650	3 550	27
HY	3 740	—	3 635	3 540	20
HY	3 745	—	3 650	3 545	22
SiO$_2$	3 750	—	—	—	33
HX	3 750	3 680	3 650	3 560	this work

assigned to adjacent —OH groups which mutually interact through a hydrogen bond, did not show according to Ward[25] the necessary distinct dependence of intensity on temperature and its interpretation remains therefore dubious. Nevertheless we have found this band to have a maximum at 3560 cm^{-1}, in good agreement with all literature data.

Adsorption and Chemisorption of Methanol

There are scarcely any data available on the sorption of methanol on X- and Y-type zeolites. While the mechanism of sorption of alcohols on SiO_2, Al_2O_3 and other oxides has been studied in detail[30], particularly as to the interaction with the surface —OH groups of these sorbents, in the case of zeolites the attention was focused to the interaction of methanolic —OH or —OD group with cations Na$^+$, Ca^{2+} and Sr^{2+} (ref.[39]). The only work, devoted to the mechanism of methanol sorption on de-cationated zeolites, was that of Geodakjan, Lygin and Kiselev[31] who did not find any methylation of zeolite —OH groups at 400°C. It was confirmed by our preliminary experiments that at temperatures over 200°C a chemical reaction takes place on decationated zeolite. However, as follows from the spectra in Fig. 4a,b,c metha-nol is adsorbed in the temperature range between 20°–150°C by a complicated mechanism including bonds of various strengths. Physically bound methanol can be removed by sufficiently long evacuation at the temperature of its boiling point. The weakly bound methanol evidently enters interactions in the form of hydrogen bond which is manifested, on curve 2 in Fig. 4a, by a considerable decrease in the intensity of free —OH groups bands under simultaneous increase of the broad band of associates in the vicinity of 3400 cm^{-1}. Methanol which is even at 100°C still rather firmly bound is represented in Fig. 4b, curve 2, by two broad bands of C—H valence vibrations, in Fig. 4c by deformation vibrations 1470 (antisym-metric) and by a weak band 1370 cm^{-1} corresponding probably to —OH bending-in-plane vibrations[40]. After evacuation of this form of methanol at 250°C the firmly bound stable form still remains, which gives a spectrum, invariant up to 400°C, as can be seen from Fig. 4a,c, curves 3–6. This form displays two narrow intensive bands of C—H valence vibrations 2870 cm^{-1} (symmetric) and 2980 cm^{-1} (anti-symmetric). In the vicinity of band 2980 cm^{-1} weak shoulders can be detected at 3030 cm^{-1} and 2940 cm^{-1}. Yates[41] who studied the formation of methoxy groups on Cabosil described the following bands appearing after interaction with methanol: 3000 cm^{-1}, 2962 cm^{-1}, a narrow band 2856 cm^{-1}, further shoulders 3040 cm^{-1} and 2935 cm^{-1} which he takes as characteristic of methoxyl groups. In contrast to me-thoxyl groups, methyl groups bound directly in —Si—(CH$_3$)$_3$ reveal only single bands 2970 cm^{-1} and 2915 cm^{-1} and methyl groups bound in Al—(CH$_3$)$_3$ show bands 2940 cm^{-1} and 2898 cm^{-1}. It is probable that the shoulders at 3030 cm^{-1} and 2940 cm^{-1} observed in the present work, support the possibility of the formation

of methoxy groups. The question remains which center in the zeolite lattice effects chemisorption of methanol under the formation of surface-bound methoxyl. From Fig. 4a it is evident that methanol sorbed at 100°C (curve 2) attacks structural —OH groups. A part of molecules which are weakly bound through a hydrogen bond is desorbed at 250°C. This is manifested in the spectrum of free —OH groups (Fig. 4a, curve 3) by reappearing of the absorption bands $3680 \, cm^{-1}$, $3635 \, cm^{-1}$ and $3560 \, cm^{-1}$ which, however, do not attain the same intensity as before adsorption on the same sample of zeolite (Fig. 4a, curve 1). This finding can be explained in the way that a part of structural —OH groups enter a very strong interaction with methanol molecule. Most probably a methoxy group is formed under simultaneous desorption of water molecule, analogously as it is formed on porous glass, silica gel or Al_2O_3 (see[30]). This phenomenon does not of course exclude the possibility of existence of a further type of adsorption center for the formation of surface bound methyl.
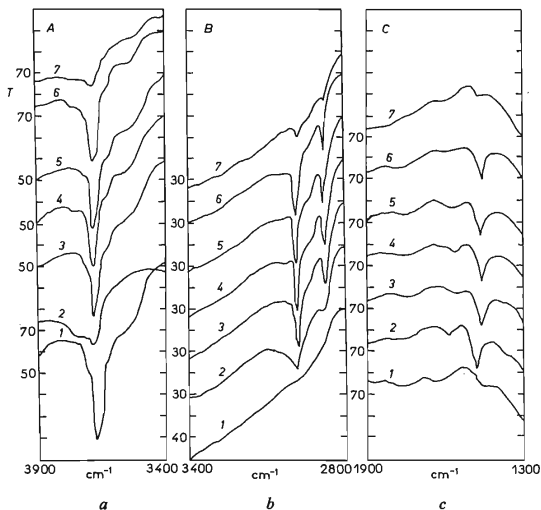

FIG. 4

Dependence of the Spectrum of Adsorbed Methanol on HX Zeolite on the Desorption Temperature

1 Spectrum prior to methanol adsorption, *2* after adsorption of methanol at 100°C (4h) and after evacuation at 100°C (4 h). Spectra after further desorption: *3* 250°C, 3 h; *4* 300°C,3 h; *5* 350°C, 3 h; *6* 400°C, 4 h; *7* 500°C, 5 h.

The position of the bands of C—H stretching vibration in methoxy groups is strongly dependent on the electronegativity of the atom to which the methoxy group is attached, as it is illustrated on the example of methylates (Fig. 5), whose spectra were published in a number of papers[34−37]. The found position of the C—H stretching vibrations corresponds probably rather to the covalent character of the bond between methoxyl and the zeolite skeleton. Surface bound methoxyls are according to the spectra in Fig. 4b considerably thermally stable, since the intensity of their bands diminishes only at 500°C when the dehydroxylation of the surface already takes place (Fig. 4a − c, curve 7).
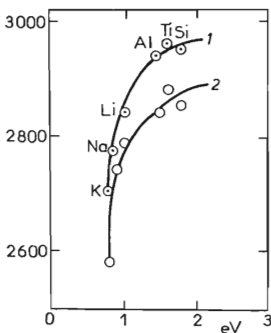

Fig. 5

Dependence of Wave Number of C—H Valence Vibrations (cm^{-1}) in Methylates on the Electronegativity of the Given Elements
1 Antisymmetric C—H, 2 symmetric C—H.

CONCLUSIONS

Two forms of rather firmly bound methanol were identified on decationated zeolite prepared by decomposition of the NH$_4$ form of X-type zeolite; a weakly bound form interacting with the structural —OH groups a hydrogen bond and a more firmly bound one forming surface methoxy groups. Structural —OH groups of zeolite were established as one of the possible centers of formation of surface bound methoxy groups.

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