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Thermochimica Acta 269/270 (1995) 599–611

thermochimica
acta

Adsorption of water on ZSM-5 zeolites [☆]

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Received 23 December 1993; accepted 29 November 1994

Abstract

The non-isothermal desorption of water adsorbed on ZSM-5 zeolites at room temperature shows, depending on the cation type (H^+, Na^+), differently structured desorption curves. A kinetic analysis based on various methods shows that the course of desorption is well described by a first order rate equation considering a distribution function for the desorption energy. In addition, adsorption isotherms were measured at room temperature. The adsorption energy distribution functions calculated with a regularization method can be correlated with the desorption energy distributions. FTIR investigations of water-loaded zeolites enables the assignment of desorption steps to different adsorbate complexes.

Keywords: Adsorption of water; Adsorption isotherms; Adsorption energy distribution functions; Desorption curves; FTIR; Temperature-programmed desorption; Thermal analysis; ZSM-5 zeolites

1. Introduction

Both adsorption and catalytic properties of zeolites are strongly determined by their water content. Therefore investigations of the adsorption behaviour of water are of great importance with respect to practical application of zeolites as adsorbents and catalysts.

Thermoanalytical methods are frequently used to characterize the adsorption properties of zeolites and their dependence on the exchange of cations or other

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[☆] Presented at the 6th European Symposium on Thermal Analysis and Calorimetry, Grado, Italy, 11–16 September 1994.

SSDI 0040-6031(95)02541-3

modifications [1–8]. A detailed "microscopic" interpretation of these "macroscopic" experiments is in most cases only possible in correlation with other experimental techniques. This problem has been addressed in the current paper, which represents an attempt to combine thermoanalytical investigations with other experimental methods in order to study in more detail the adsorption behaviour of water in zeolites NaZSM-5 and HZSM-5.

2. Experimental

2.1. Zeolites

The NaZSM-5 zeolite was a commercial material "HS30" ($Na_6(AlO_2)_6(SiO_2)_{90}$) supplied by Chemiewerk Bad Koestritz GmbH, Germany. The H-form, HZSM-5, was prepared by a threefold ion exchange with 0.1 N HNO_3 at room temperature. The Si/Al ratio was determined by chemical analysis and by ^{27}Al-MAS-NMR to be 15.

2.2. TPD simultaneous thermal analysis

The temperature-programmed desorption (TPD) was carried out in a conventional flow device with helium as carrier gas ($3\,l\,h^{-1}$). A heat conductivity detector was used for evolved gas detection. The zeolites were equilibrated with water vapour over a saturated $Ca(NO_3)_2$ solution in a desiccator. For each experiment 100 mg zeolite were used in a mixture with 1 g quartz of the same grain size (0.2–0.4 mm). The probe was placed in a quartz glass tube and flushed with helium ($3\,l\,h^{-1}$) at room temperature for 30 min. For TPD a linear heating program with different heating rates (2–20 $K\,min^{-1}$) was applied. In some experiments the adsorption was performed by means of a water vapour pulse and isothermal desorption of the water surplus.

Furthermore some measurements with a simultaneous thermal analysis apparatus (TG–DTG–DTA–EGA–QMS, Netzsch, Model STA-QMS 409/429-403) were carried out. For all of these experiments the sample weight was about 40 mg. A heating rate of $10\,K\,min^{-1}$ and a helium flow of $4.5\,l\,h^{-1}$ were used. The desorbed water was recorded by means of the mass peak at 18 AMU. In addition, the mass peaks of CO_2 (44 AMU), N_2 (28 AMU) and O_2 (32 AMU) were registered.

2.3. Adsorption measurements

The adsorption isotherms of water vapour were determined gravimetrically on a McBain balance fitted to a high-vacuum system (< 1 Pa) at 298 K. The pressure was measured with a mercury pressure gauge ($\pm$ 10 Pa) at 298 K. The pretreatment consisted in heating the zeolites at 673 K for 12 h. The temperature of the sample could be kept constant with a variation of $\pm$ 0.5 K. Blank runs were employed to allow for buoyancy effects. The data points are reproducible to within $\pm$ 6%.

2.4. FTIR investigations

The diffuse reflectance FTIR investigations were performed on a Bruker IFS 113v spectrometer equipped with a commercial diffuse reflectance unit ("praying mantis"). The spectra were recorded at a resolution of 4 cm^{-1} with 200 scans being averaged, in the range between 3000 cm^{-1} and 8000 cm^{-1}. Only the fundamental vibration region of the OH groups is shown in the present paper. Strong IR absorption of the quartz glass ampoules in which the samples were contained, prevented us from observing vibrations with wavenumbers less than about 3000 cm^{-1}.

The preparation of samples with different water loadings was carried out in the flow apparatus described above, starting from the completely hydrated zeolites. The probe was heated to different temperatures (5 K min^{-1}) and held at this temperature for a period of 10–30 min. After that the probe was cooled to room temperature and the sample transferred to quartz glass ampoules under a helium gas stream. For comparison, activated HZSM-5 and NaZSM-5 samples were prepared by performing a shallow-bed treatment at 673 K as described earlier in Ref. [9].

3. Results and discussion

The desorption curves (TPD) of water from NaZSM-5 and HZSM-5 are shown in Fig. 1. If the first desorption of water is carried out only up to 700 K, renewed desorption after re-adsorption of water at room temperature will produce the same desorption profiles. Apart from the desorption peak at about (360 ± 5) K both profiles

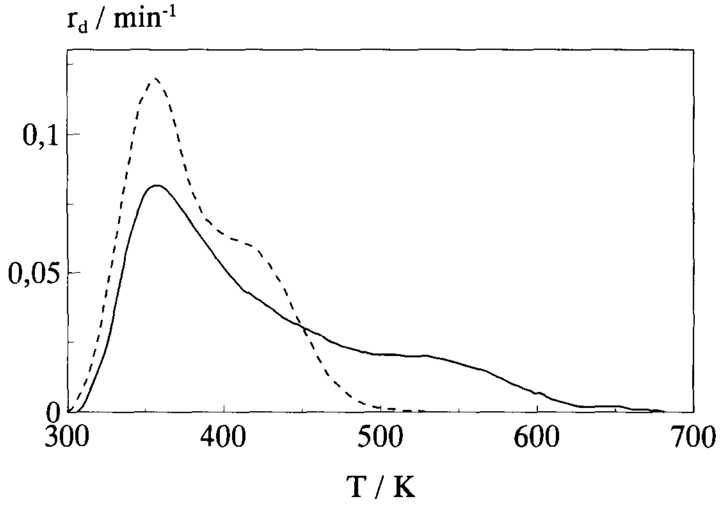

Fig. 1. Desorption curves (TPD) for zeolites NaZSM-5 (—) and HZSM-5 (- - - -) (10 K min^{-1}).

show different structures at higher temperatures. The desorbed amount of water was (50 ± 7) mg g^{-1} for both HZSM-5 and NaZSM-5 corresponding to about 16–17 water molecules per unit cell (u.c.).

Fig. 2 presents the results of the simultaneous TG–EGA investigations. Except for very small amounts of CO_2 in the temperature range 650–750 K, the loss of mass up to 1470 K was caused in both zeolites exclusively by desorption of water. The course of desorption from 300 K to 700 K corresponds to the TPD results (Fig. 1). The desorbed amount of water is (75 ± 10) mg g^{-1}. Beside the water desorption at 1210 K resulting from the dehydroxylation of the HZSM-5 sample (removal of the bridging SiOHAl groups), for both zeolites slight water desorption was detected at temperatures exceeding 700 K. An accurate determination of this amount was, however, not possible. But it can be estimated to be lower than 5 mg g^{-1}. TG allowed, additionally, the determination of the water amount which desorbs already isothermally at room temperature in the He gas stream. This amount was about 50 mg g^{-1} (16 water molecules per u.c.) for both zeolites.

The amount of water desorbing in the temperature range 400–700 K was separated from desorption up to 400 K by a combination of isothermal and non-isothermal

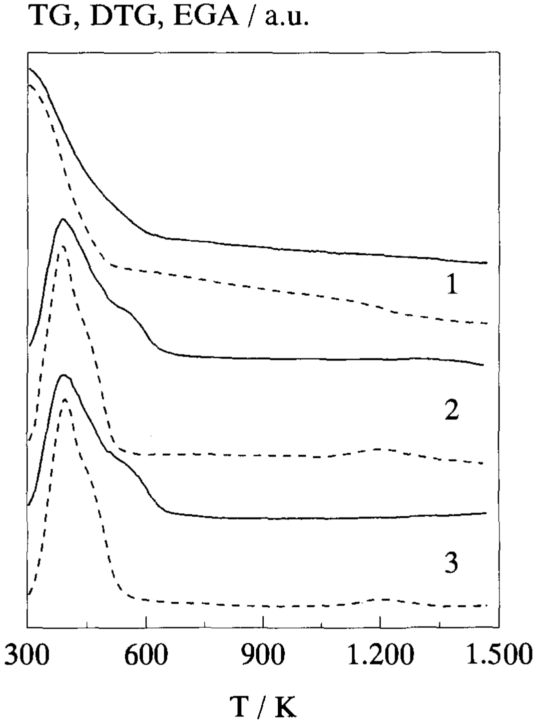

Fig. 2. TG, DTG and EGA curves for zeolites NaZSM-5 (—) and HZSM-5 (- - - -) (10 K min^{-1}) 1: TG, 2: DTG, 3: EGA (18 AMU).

desorption. For that purpose, heating was carried out up to the peak maximum of 360 K and then the temperature programme was stopped. When no further desorption was observed at this temperature, the temperature programme was restarted. Results for NaZSM-5 are shown in Fig. 3. Whereas the HZSM-5 shows only one simple desorption peak, the NaZSM-5 has a structured desorption profile with two separated regions (see Fig. 3, curve 2). Therefore the described treatment was repeated at 425 K. The desorbed amount in the temperature range 400–700 K is about 6 water molecules per unit cell, corresponding to the Na^+ content of NaZSM-5 and the number of bridging SiOHAl groups of HZSM-5, respectively. This experimental result suggests that this water interacts specifically with these adsorption sites. In case of NaZSM-5 both parts of the structured desorption curve (Fig. 3, curve 2) represent about three water molecules per u.c.

The experimental adsorption isotherms at room temperature for water on both zeolites are presented in Fig. 4. For NaZSM-5 two branches can be distinguished: first, a stronger increase in adsorption up to 50 mg g^{-1} at $p = 270$ Pa, and further a smoother one from 50 to 90 mg g^{-1}. A comparison of the adsorbed amounts with the TG results shows that the second branch of the isotherm belongs to weakly bonded water, which

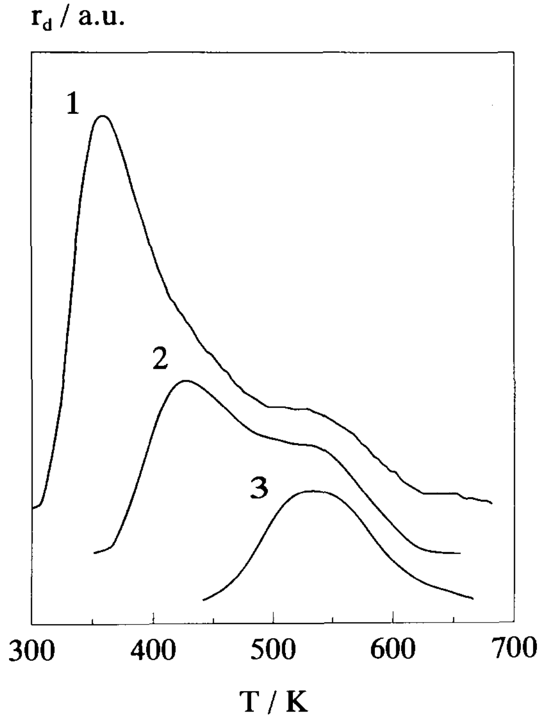

Fig. 3. Desorption curves (10 K min^{-1}) for zeolite NaZSM-5 for different initial amounts of adsorbed water 1: 16.5 H_2O/u.c, 2: 6.5 H_2O/u.c, 3: 3 H_2O/u.c.

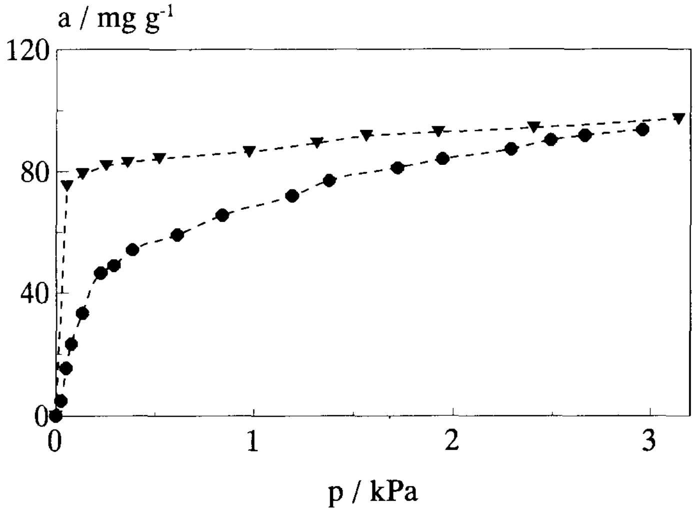

Fig. 4. Adsorption isotherms at 298 K (●): NaZSM-5, (▼): HZSM-5.

can not be detected in the TPD experiments, because it already desorbs at room temperature in an helium gas stream. In HZSM-5 the pore filling up to 80 mg g^{-1} already takes place at lower pressures ($p = 70$ Pa). Therefore it seems likely that the development of the weakly bound water clusters in the channel system is inhibited in the presence of sodium ions.

A kinetic analysis of the TPD data assuming a rate law with constant pre-exponential factor and constant desorption energy was not possible. This simple model failed also for the experimental separated desorption peaks. Therefore a rate law of first order with a distribution function f(E) of desorption energy E was considered [10]:

$$r_d(T) = -\mathrm{d}\theta(T)/\mathrm{d}t = A\int_{E_{\min}}^{E_{\max}} \theta_l(E,T)\exp(-E/RT)\mathrm{f}(E)\mathrm{d}E \tag{1}$$

where r_d is the overall desorption rate, θ is the overall degree of coverage, and A the pre-exponential factor. θ_l is the local coverage of sites characterized by a desorption energy E. From the mathematical point of view, Eq. 1 is a linear Fredholm integral equation of the first kind. The calculation of f(E) from Eq. 1 is a numerically ill-posed problem [11]; i.e., small changes in $r_d(T)$ caused by experimental errors can significantly distort the calculated distribution function. In the current paper, the program INTEG [11], which involves a regularization method for solving such numerically unstable integral equations was used. The pre-exponential factor A required to solve Eq. 1 was estimated by using the dependence of the temperature of the peak-maximum on the heating rate [12, 13]. Additionally, for selected desorption peaks the pre-exponential factor A was determined using non-linear regression with a rate law assuming a logarithmic dependence of the desorption energy on the coverage θ. The values differ only within one order of magnitude (A = 1×10^6–1×10^7 min^{-1}). This variation is consistent with the error of this calculation.

The calculations with the INTEG program to solve Eqs. (1) and (2, see later) were carried out without any assumptions or constraints about the resulting distribution functions. Thus negative parts in the distributions are possible. They fail to possess any physical meaning, but if the distribution is dominated by the negative parts then the used local model does not describe the experimental data appropriately. The negative parts are neglected in the interpretation of the distribution functions.

Fig. 5 represents distributions f(*E*) of desorption energies for NaZSM-5 calculated from desorption profiles with different initial coverages of water. For the whole desorption in the temperature span 300–700 K (see Fig. 3, curve 1) three energy ranges can be clearly distinguished (Fig. 5, curve 1). The part with the maximum at about 45 kJ mol^{-1} can be related to water physisorbed more or less independently of the type of cation. This range of energy (40–50 kJ mol^{-1}) comparable to the heat of vaporization for water (41 kJ mol^{-1}) agrees with previous results of thermoanalytical investigations concerning other zeolites [8]. Similar values have been found for heats of adsorption of water at higher coverage on different zeolites [14–16]. Further support for the

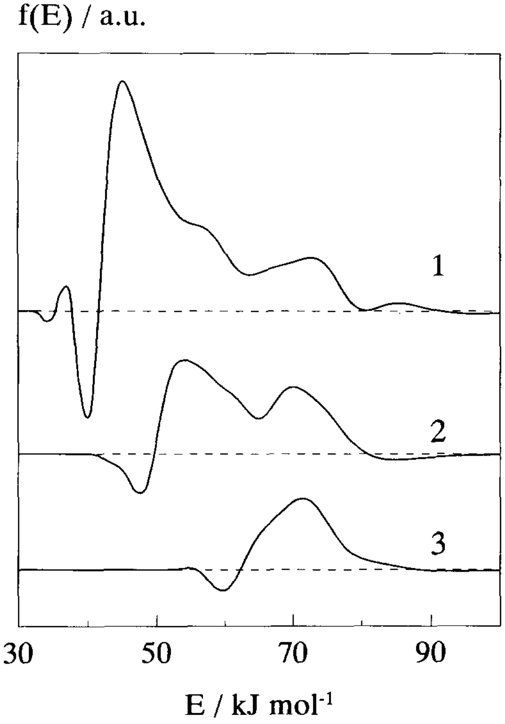

Fig. 5. Desorption energy distribution for zeolite NaZSM-5, adsorbed amount ($A = 2 \times 10^6$ min^{-1}) 1: 16.5 H_2O/u.c, 2: 6.5 H_2O/u.c., 3: 3 H_2O/u.c.

interpretation of this energy range as an unspecific interaction with the zeolitic framework results from theoretical calculations for the interaction of water with silicalite. Vigné-Maeder and Auroux [15] calculated an average interaction energy of nearly 52 kJ mol^{-1} for water located near the pore wall of both types of channel. The energies belonging to both areas of higher desorption energy (50–60 kJ mol^{-1} and 60–80 kJ mol^{-1}) which are related to an interaction with Na^+ cations, correspond to heats of adsorption and desorption energies, respectively, determined earlier for other zeolites [4, 8, 16]. The observed bimodal distribution for the specific interaction in the case of NaZSM-5 can be explained by two different adsorption states of water on Na^+ ions. In recent dielectric and ^{23}Na–MAS–NMR studies of a NaZSM-5-zeolite with Si/Al = 13 Ohgushi et al. [17, 18] found two kinds of Na^+ ion which show different behaviour in respect of water adsorption. Additionally, the type which interacts more strongly with water shows two different interaction mechanisms which are dependent on temperature. However, without further information a detailed assignation of the TPD results is not possible.

The heterogeneous structure of the zeolites is also responsible for the failure of the simple isotherm fits to describe the adsorption isotherms of water. If a continuous distribution $f(U)$ of adsorption sites with respect to the adsorption energy U is accepted as a quantitative characteristic of an adsorbent's heterogeneity, then the overall coverage $\theta(p)$ is expressed by the integral equation [19, 20]:

$$\theta(p) = \int_{U_{\min}}^{U_{\max}} \frac{K^0(T)\exp(U/RT)p}{1 + K^0(T)\exp(U/RT)p} f(U)\,\mathrm{d}U \qquad (2)$$

where the energy-dependent local adsorption isotherm has the simple Langmuir form and $K^\circ(T)$ is the pre-exponential factor of the Langmuir constant. $K^\circ(T)$ is expressed in terms of the partition functions for an isolated molecule in the gas and surface phase. The above factor was estimated according to the Adamson method [21, 22]. Again using the INTEG-program to solve Eq. 2 the adsorption energy distribution $f(U)$ was calculated (see Ref. [23] for further details) for water on NaZSM-5. A comparison with the desorption energy distribution $f(E)$ given in Fig. 6 shows agreement of $f(E)$ and $f(U)$ in the range of non-specific interactions (40–50 kJ mol^{-1}). On the other hand, the appearance of an additional range in the distribution at lower adsorption energies (30–40 kJ mol^{-1}) means that part of the water is adsorbed more weakly than the amount desorbing at temperatures exceeding 300 K. The weakly bound water should be the one which is found to desorb at room temperature (ca. 50 mg g^{-1}) in the TG experiments. This interpretation is supported by calculated potential maps for water in silicalite [15] showing that water located in the middle of the channel intersections is adsorbed with a small interaction energy of about 33 kJ mol^{-1}. A comparison of the distribution functions at higher energy values ($>$ 50 kJ mol^{-1}) was not possible because of missing experimental adsorption data in the corresponding low pressure range.

The calculation of the desorption energy distribution for HZSM-5 (Fig. 7) shows only a bimodal distribution. According to expectations, the distributions in the range of 40–50 kJ mol^{-1} correspond to the one for NaZSM-5. The higher energy span between

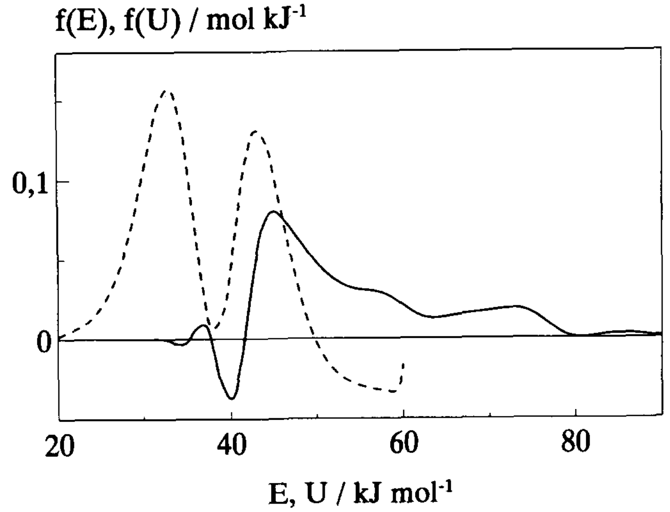

Fig. 6. Comparison of the desorption energy distribution f(E) (—) with the distribution function of the adsorption energy f(U) (– – – –) for zeolite NaZSM-5.

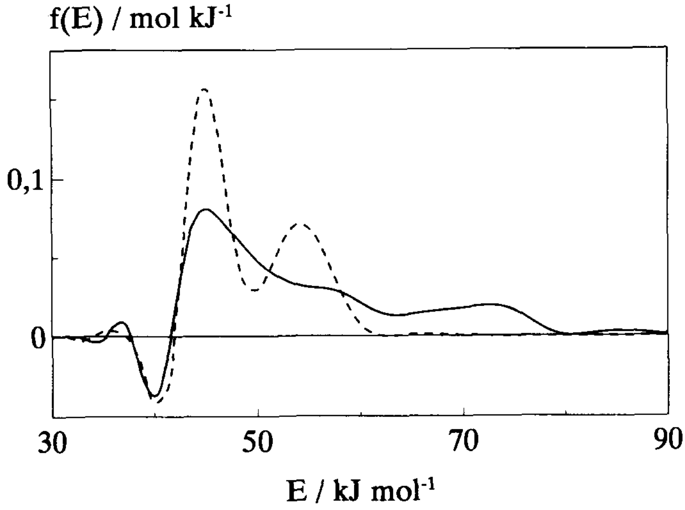

Fig. 7. Distribution function of the desorption energy for zeolites NaZSM-5 (—) and HZSM-5 (– – – –) ($A = 2 \times 10^6$ min^{-1}).

50 and 60 kJ mol^{-1}, related to the interaction with SiOHAl groups, corresponds to heats of adsorption of water on HZSM-5 zeolites at low coverage. In Ref. [14] a value of 51 kJ mol^{-1} is given for the heat of adsorption of the first molecule of water per site. Both the span of energy and the position of the maximum show that water is adsorbed

on SiOHAl groups as strongly as on one type of Na^+ cation. A determination of the corresponding adsorption energy distribution from the experimental adsorption isotherm for energies > 40 kJ mol^{-1} was not possible, because in the relevant pressure range only one data point could be measured.

The FTIR spectra of the NaZSM-5 samples pretreated at different temperatures are shown in Fig. 8. Curves 1 and 2 (1.5 and 3 water molecules per u.c., corresponding to desorption ranges of 550–650 K and 450–650 K (curve 3, Fig. 3), respectively) exhibit four bands due to the adsorbed H_2O: the two relatively narrow bands at (3677 ± 4) cm^{-1} and (3584 ± 4) cm^{-1} are assigned to free antisymmetric and symmetric OH stretching vibrations of water molecules adsorbed on Na^+ cations without intermolecular interactions [24]. This adsorption form cannot be the only one since there appear two additional bands at (3420 ± 20) cm^{-1} and (3260 ± 4) cm^{-1}. According to Jentys et al. [24], they are associated with hydrogen bonded OH stretching vibrations of the H_2O molecules within clusters. It should be mentioned that one could also expect to observe the overtone of the H_2O bending vibration (1630 cm^{-1}) in the region of the latter absorption band ((3260 ± 4) cm^{-1}). Another explanation concerning only the bands at 3420 cm^{-1} and 3677 cm^{-1} is suggested in Ref. [25] resulting from the comparison with NaX zeolites; the low frequency band is assigned to the OH stretching vibration of H_2O molecules hydrogen bonded with lattice oxygen. The narrow band at higher wavenumbers is due to the corresponding free OH stretching

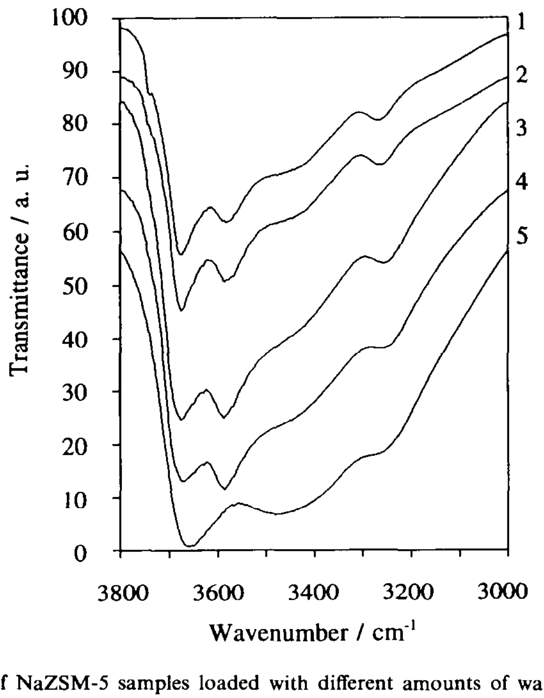

Fig. 8. FTIR spectra of NaZSM-5 samples loaded with different amounts of water 1: 1.5 H_2O/u.c., 2: 3 H_2O/u.c., 3: 4 H_2O/u.c., 4: 6.5 H_2O/u.c., 5: 16.5 H_2O/u.c.

vibration. Further studies will be required to decide whether the narrow bands at 3677 cm^{-1} and 3584 cm^{-1} correspond to the two modes of freely vibrating water molecules in the presence of water clusters [24] or indicate two different adsorption forms of water on Na^+ cations (as suggested in Ref. [17]) with hydrogen bonding to the framework partially occurring.

The fifth weak band in spectra 1 and 2 in Fig. 8 at 3745 cm^{-1} is caused by SiOH species (about 0.5 per u.c.). Its decreasing intensity demonstrates the increasing interaction of these SiOH groups with water molecules.

While the spectra 1 and 2 described above show similar water band shapes and positions, differences arise for the higher loaded samples (curves 3 and 4 with 4 and 6.5 H_2O molecules adsorbed per u.c., corresponding to desorption ranges of about 450–650 K and 350–650 K (curve 2 Fig. 3), respectively); in the region of the free water OH stretching vibrations, an additional shoulder at about 3690 cm^{-1} is observed. While the broad band at about 3420 cm^{-1} reflecting hydrogen bonding of the water molecules remains unchanged, the band at 3260 cm^{-1} is shifted by about 15 cm^{-1} to lower wavenumbers. Further investigations should be performed in order to clarify this phenomenon.

In Fig. 9 the FTIR spectra of the HZSM-5 zeolite corresponding to different desorption steps are presented. Spectrum 1 (about 0.5 H_2O per u.c.) resembles that of the activated HZSM-5 zeolite which exhibits five different hydroxyl stretching vibra-

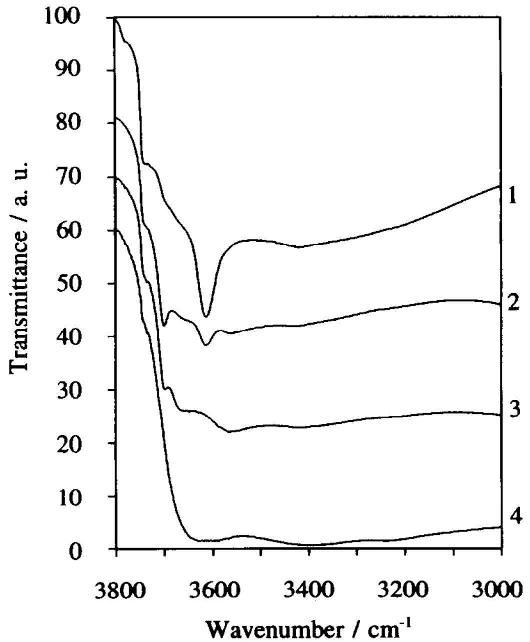

Fig. 9. FTIR spectra HZSM-5 samples loaded with different amounts of water 1: 0.5 H_2O/u.c., 2: 4 H_2O/u.c., 3: 6.5 H_2O/u.c., 4: 16.5 H_2O/u.c.

tion bands; the well-known absorption at 3613 cm^{-1} is attributed to SiOHAl groups (bridging hydroxyls, Brønsted acid sites) [26]. Those bridging hydroxyl groups showing an additional interaction with the zeolitic framework give rise to the broad band at about 3250 cm^{-1} [27]. Beside the well-known band at 3745 cm^{-1} due to SiOH groups at the crystallite surface, on defects in the crystallites or in amorphous phases, a further weak SiOH band is observed at 3725 cm^{-1}, this is associated with defect sites in dealuminated HZSM-5 zeolites. Another proof of the slight dealumination is the weak vibration band at 3780 cm^{-1} assigned to AlOH groups of unknown structure [28]. The number of the respective non-framework Al atoms is less than the minimum number detectable by ^{1}H MAS NMR spectroscopy [29]. Therefore, it can be estimated to be less than 10% of the total number of Al atoms. The number of SiOH groups per unit cell is determined to be (0.9 ± 0.3) [29, 30].

The AlOH band and both the SiOH bands corresponding to defect sites are almost completely shifted due to the adsorbed water content of about 0.5 molecules per u.c. whereas the SiOHAl groups are hardly influenced. It should be noted that such an effect was mentioned earlier by Jentys et al. [24] without any explanation. In contrast to the AlOH (3780 cm^{-1}) and SiOH (3725 cm^{-1}) species, one type of SiOH groups, those causing the band at 3745 cm^{-1}, fails to interact with the water molecules. The respective weak band can be detected even if the sample is saturated with water (curve 4 in Fig. 9). This can be explained by their inaccessibility to water molecules rather than by low acidity effect since all the SiOH groups are influenced by H_2O adsorbed on NaZSM-5 (see curve 4 in Fig. 8).

Using the spectra 2 and 3 in Fig. 9 (4 and 6.5 H_2O per u.c., respectively) one can conclude from the decreasing intensity of the band at 3613 cm^{-1} that the adsorbed water molecules mainly interact with bridging SiOHAl groups. This result strongly supports the attribution of the water desorption between 400 and 500 K on HZSM-5 to the bridging SiOHAl groups as adsorption sites (see Fig. 1).

The value of the corresponding band shift cannot be given presently. This question is connected with the interpretation of the following bands left out of consideration up to now (cf. for example spectrum 2): $(3700 \pm 4)\ cm^{-1}$, $(3660 \pm 5)\ cm^{-1}$, $(3558 \pm 4)\ cm^{-1}$ and $(3420 \pm 10)\ cm^{-1}$. Concerning their assignments we refer to Refs. [24, 31, 32] where three different models of the water adsorbed on bridging hydroxyls are proposed in order to interpret the IR data.

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