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Adsorption of water, methanol and acetonitrile in ZK-5 investigated by temperature programmed desorption, microcalorimetry and FTIR

J. Jänchen[a,*], J.H.M.C. van Wolput[b], W.J.M. van Well[b], H. Stach[c]

[a]*Fachhochschule für Technik und Wirtschaft Berlin (University of Applied Sciences Berlin), Fachbereich 1, Ingenieurwissenschaften I (Elektrotechnik), Treskowallee 8, 10318 Berlin, Germany*

[b]*Schuit Institute of Catalysis, Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

[c]*ZeoSys GmbH, Volmerstrasse 13, D-12489 Berlin-Adlershof, Germany*

Abstract

The adsorption of water, methanol and acetonitrile in ZK-5 was investigated using temperature programmed desorption, microcalorimetry and FTIR spectroscopy. A multi-stage desorption in the TPD, steps in the isotherms and a stepwise decrease of the heat curves with increasing loading was found for H-ZK-5. The potassium form of ZK-5 shows a much less pronounced two step desorption behavior, pointing to the fact that K-ZK-5 is enthalpically less heterogeneous for polar molecules than the H-form. Contrary to the adsorption behavior of *n*-paraffins in ZK-5 the multi-stage desorption in the TPD profile and a step in the isotherm of those polar molecules can be related with the enthalpic heterogeneity of the adsorption sites in the cavities of H-ZK-5. For *n*-paraffins in ZK-5, however, it was found that discontinuities in the sorption behavior were determined by differences in sorption entropy. FTIR measurements with different coverage of methanol and acetonitrile on H-ZK-5 confirm the site heterogeneity of the acidic OH, but no pronounced preference between the HF or LF band could be detected.

Keywords: Adsorption; TG; Microcalorimetry; FTIR; Acidity; Zeolites

1. Introduction

Zeolites are well known for utilization as sorbents, catalysts and are of interest as materials for long-term storage of heat, especially zeolites with a high pore volumes and low Si/Al ratios [1]. In the present paper, we report about the adsorption properties of polar molecules such as water, methanol and acetonitrile in ZK-5 (structure code KFI). ZK-5 is a high alumina zeolite with a high free pore volume to the amount of 0.305 cm^3/g [2]. Water and methanol are often used as agents for thermochemical heat storage or in heat pumps. A high heat of adsorption and a great pore volume are of interest to gain high values for the storage density of heat. Methanol, on the other hand, is an important reactant in catalysis [3] and acetonitrile is frequently used as base to probe acid catalysts [4]. Furthermore, the concentration of the reactants in the narrow pores is a function of the pore size and chemical composition of the zeolite [5]. Thus, information about the adsorption equilibrium of sorbate molecules in a microporous host are generally of high importance for the understanding of the entire process

* Corresponding author.

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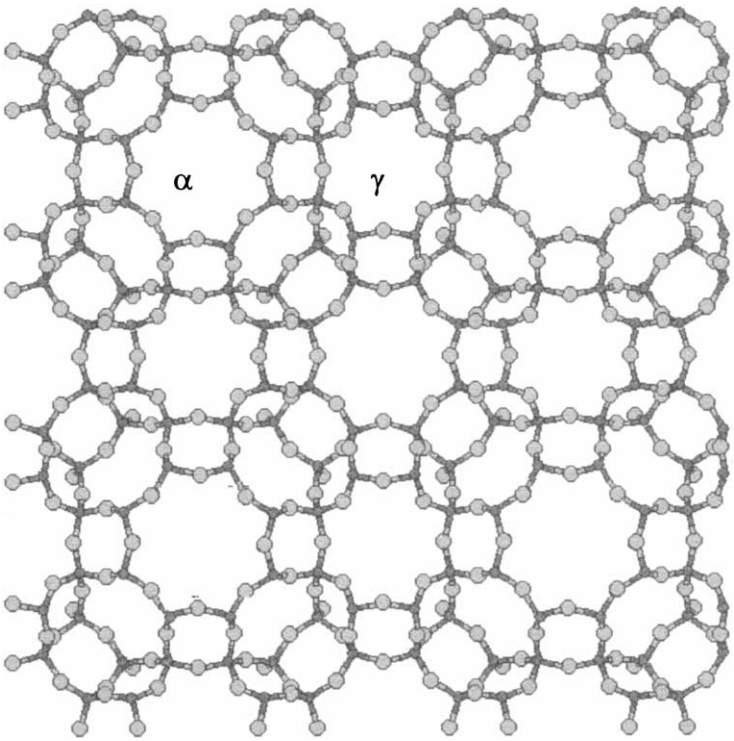

Fig. 1. Structure of KFI viewed along (1 0 0) plan.

no matter it is a catalytic reaction, a separation process or a thermochemical storage.

The KFI structure consists of a three-dimensional network of two larger α-cages (diameter 11.6 Å) and six smaller γ-cages (6.6 Å × 10.8 Å) per unit cell (see Fig. 1). Every α-cage is surrounded by six γ-cages along the octahedral directions. The cavities are connected with each other through eight-membered rings with a diameter of 3.9 Å [6,7]. Many of those rings contain a cation (in the K-form of ZK-5) [8]. As a consequence of the variance in size of the two kinds of cavities and the cation positions, differences in the sittings of the sorbate molecules and adsorption behavior as function of the adsorbed amount can be expected.

An enthalpic heterogeneity of the structure can lead to discontinuities (steps) in the adsorption isotherms or multi-stage desorption as a result of discontinuities in the heat of adsorption with increasing loading. This effect will especially be pronounced for polar adsorbate molecules. On the other hand, such discontinuities were measured in the adsorption isotherms and desorption patterns of non-polar molecules (C3–C8) in ZK-5 without discontinuities in the heat of adsorption with increasing loading. From these results it was concluded that the adsorption behavior of *n*-alkane molecules in ZK-5 is dominated by entropic effects [9]. Thus, enthalpic as well as entropic reasons can be caused for such behavior in zeolites. An entropically determined adsorption manner was also recently reported by other authors for *n*-paraffin adsorption in the MFI structure [10–13].

In this study, we focus on the adsorption of polar molecules in ZK-5. Temperature programmed desorption (TPD), microcalorimetry, and FTIR spectroscopy are applied to get more insight into the adsorption properties of water, methanol, and acetonitrile in the KFI structure. Some results of the adsorption of methanol in Na-ZK-5 can be found in [14]. Here, we use H-ZK-5 and compare this sample with some results of the as synthesized potassium form of this zeolite.

Table 1
Adsorption capacities of K-ZK-5 and H-ZK-5 for water, methanol, and acetonitrile measured by TG (after saturation of the samples at 303 K and relative pressure of 0.15 in a nitrogen stream)

Molecule	K-ZK-5		H-ZK-5	
	a in cm^3/g	*a* in mmol/g	*a* in cm^3/g	*a* in mmol/g
Water	0.18	9.9	0.23	12.7
Methanol	0.18	4.5	0.245	6.0
Acetonitrile	0.20	3.85	0.265	5.1

2. Experimental

The ZK-5 sample (supplied by EXXON Chemical Europe, Machelen, JP 1320) was synthesized hydrothermally in the potassium form. The complete H-form was obtained through triple ion exchange with ammonium nitrate. The Si/Al ratio of the sample amounts to 3.3. The material has been proven by XRD and SEM to be of high crystallinity. Table 1 gives information about the adsorption capacities for different molecules. The high adsorption capacity of methanol in the H-form of KFI with 0.28 cm^3/g (corresponding to about 7 mmol/g at a relative pressure of 0.8, see isotherm later), compared to the theoretical free pore volume of the H-ZK-5 (0.305 cm^3/g), confirms the good crystallinity.

The differential molar heats of adsorption and the isotherms of methanol and acetonitrile in H-ZK-5 were measured using a Calvet-type microcalorimeter (SETARAM C 80) at 303 K (and 423 K for methanol) which was connected to a standard volumetric adsorption apparatus with MKS Baratron pressure sensors. Before application, the sample (about 450 mg) was calcined in high vacuum ($<10^{-5}$ hPa) at 673 K for 8 h. An additional isotherm was measured gravimetrically for methanol in K-ZK-5 at 298 K in a McBain quartz spring balance.

The temperature programmed desorption was performed on a SETARAM TG-DSC 111 equipment (after saturation at 303 K and a relative pressure of 0.15) with a heating rate of 5 K/min to a temperature of 673 K in a nitrogen stream of 1 l/h. Water was adsorbed off-line in a desiccator at a relative pressure of 0.3 at room temperature overnight.

IR spectra were measured at room temperature on a Bruker FTIR spectrometer IFS 113v equipped with a vacuum cell. Self-supporting discs with a thickness of 4 mg/cm^2 were used. The compaction pressure exerted to the powder was 750–1500 kg/cm^2. Activation of the samples was performed at 723 K in high vacuum (10^{-6} hPa) for 1 h. After cooling down to room temperature the spectrum of the unloaded sample was taken, followed by adsorption of methanol/acetonitrile at an equilibrium pressure of about 0.5 hPa for 30 min. Then again a spectrum was recorded. After this the loading of the samples were reduced by lowering the equilibrium pressure to 0.05 hPa as well as by desorption (30 min) at room temperature, 353, 453, 573, and 723 K, respectively, followed again by taking room temperature spectra after each step.

3. Results and discussion

3.1. TPD, DSC

The Figs. 2 and 3 summarize the results of the thermogravimetric measurements (TG) for all three sorbate molecules investigated. Fig. 2a shows the TG curves for K-ZK-5, part b of the figure gives the DTG curves (differential mass loss). Water desorbs in a single step from K-ZK-5 with a maximum at about 410 K showing not any discontinuity. Methanol and acetonitrile show a discontinuity resulting in a weak three stage (methanol) or two stage (acetonitrile) desorption behavior possibly related to differences in the position of the potassium ions in the structure [8]. If a one-to-one ratio for the interaction of methanol with the potassium ions is assumed, then the amount of desorbed methanol represented by the maximum at 410 K and the shoulder at about 500 K can be related to methanol interacting with those cations. This amount (3.4 mmol/g) correlates with the number of cations of K-ZK-5 (compare with the isotherm in Fig. 4 also). The remaining weaker bound methanol which is first desorbed in the TG experiment (and last adsorbed in the isotherm at high equilibrium pressure) should be ''bulk methanol''. The total amount of acetonitrile adsorbed in K-ZK-5 corresponds with the amount of K^+. Thus, all acetonitrile molecules should find ''their'' cation. According to the shape of the desorption profile, a maximum at 370 K and a long range of desorption from 450 to 650 K, at

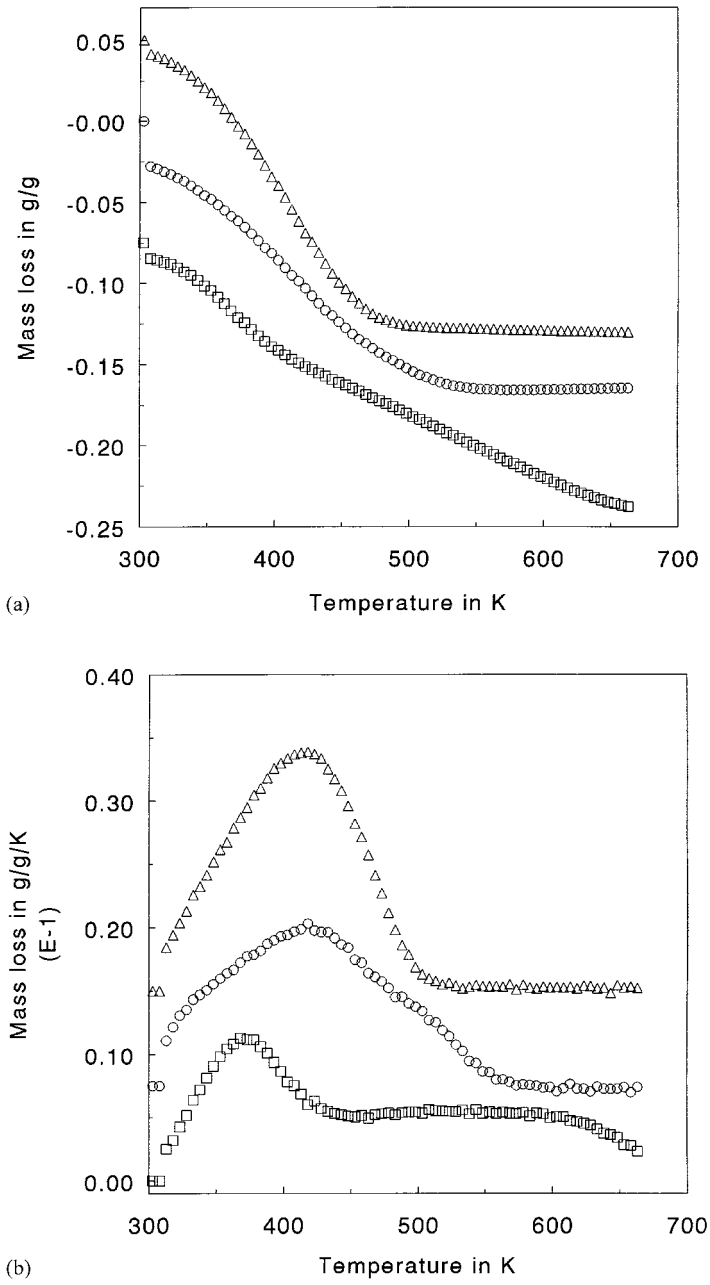

Fig. 2. TG (a) and DTG ((b) differential mass loss $-\mathrm{d}m/\mathrm{d}T$) profiles of acetonitrile (□), methanol (○), and water (△) adsorbed in K-ZK-5.

least two different energetic surroundings of the cations must exist. The broad range of temperature needed to desorb acetonitrile may be due to kinetic rather than energetic reasons because the integral heat of desorption is comparable with the value of methanol (see Table 2) and taking into account the fact that adsorption is slow too. It seems to be not that easy for the bigger acetonitrile to enter or leave the structure through the eight-membered rings partially blocked by a cation [8].

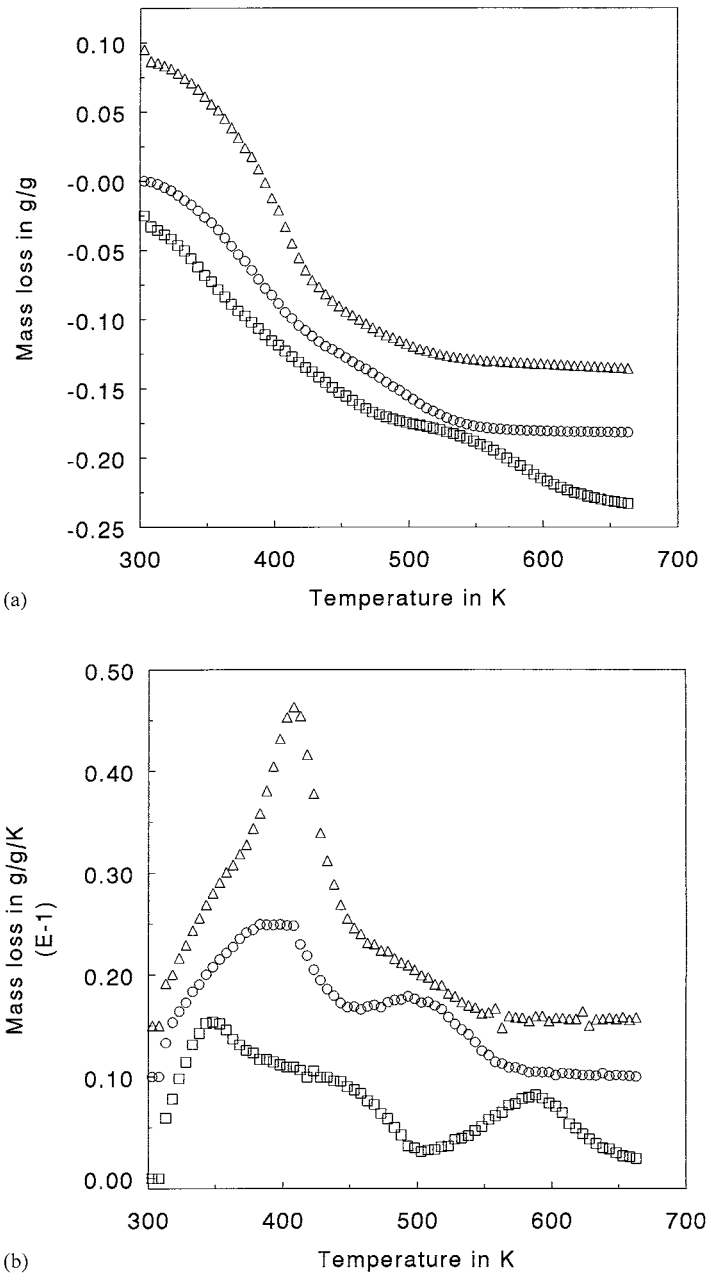

Fig. 3. TG (a) and DTG ((b) differential mass loss $-\mathrm{d}m/\mathrm{d}T$) profiles of acetonitrile (□), methanol (○), and water (△) adsorbed in H-ZK-5.

H-ZK-5 contains no large cations and shows much more pronounced steps in the TG curves of acetonitrile, methanol and water corresponding to maxima of mass loss in the DTG profiles as well. Three different stages of desorption can be identified. The amount desorbed in the higher temperature range corresponds to 1.4, 1.6 or 2 mmol/g for acetonitrile, methanol and water, respectively, most probably related to the interaction with the strongest acidic sites of the zeolite. Acetonitrile reveal two steps in the DTG curve

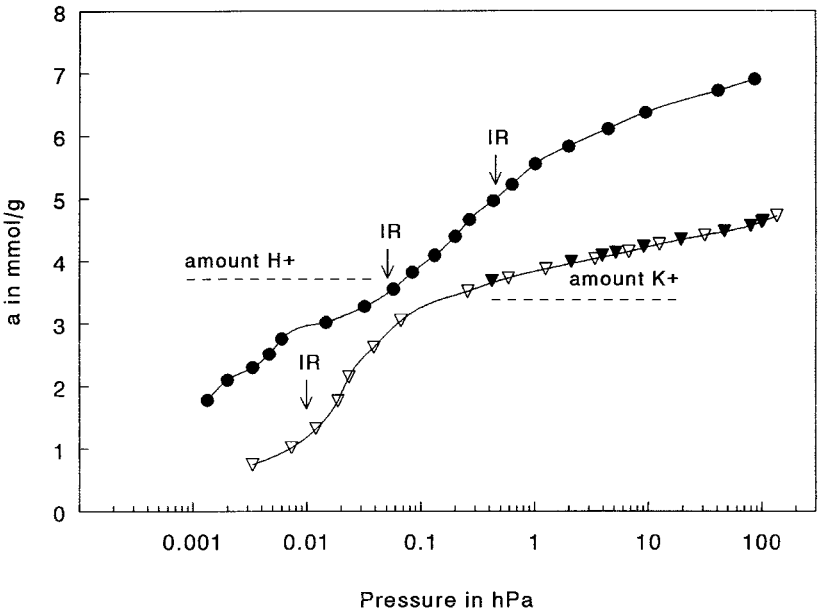

Fig. 4. Adsorption isotherms of methanol in H-ZK-5 at 303 K (●) and in K-ZK-5 at 298 K ((▽), filled symbol desorption).

(maxima at 580 and 420 K, Fig. 3b) due to the amount of acidic sites (3.8 mmol/g) and a third at 350 K probably the physisorbed portion (see isotherm later). Obviously, only the strongest sites give a step in the DTG profile for all three molecules. It has to be mentioned that the maxima in Fig. 3b are shifted to higher temperatures with increasing size of the probe molecule indicating some kinetic problems during the desorption. Differences in the heat of sorption do not explain the sequence of these maxima as can be seen in Table 2.

Table 2 shows the results of the DSC measurements on K- and H-ZK-5. The integral heats of desorption are given as molar values related to the sorbate and as values related to the amount adsorbent in kilogram. For water/K-ZK-5 a value of 64 kJ/mol is found for the integrated heat of adsorption. These results are comparable with results of microcalorimetric measurements on KX in [15] with values of the differential molar heats of adsorption starting at 75 kJ/mol and decreasing to 55 kJ/mol.

No significant differences in the molar integral heats of desorption between the K- and H-form of ZK-5 were found. But this is not true comparing the heat values related to the amount of zeolite. Because of the bigger pore volume accessible in the H-form compared to the K-form the heat per kg adsorbent is larger as well. Further, whereas water gives the lower molar values compared to the bigger molecules such as methanol or acetonitrile the heat necessary to desorb water from a certain amount of zeolite is higher than for the other two molecules. Consequently,

Table 2
Integral heats of desorption of water, methanol, and acetonitrile in K-ZK-5 and H-ZK-5 measured by DSC (after saturation of the samples at 303 K and relative pressure of 0.15 in a nitrogen stream)

Molecule	K-ZK-5 $-Q_{int}$ in kJ/mol (adsorbate)	K-ZK-5 $-Q_{int}$ in kJ/kg (adsorbent)	H-ZK-5 $-Q_{int}$ in kJ/mol (adsorbate)	H-ZK-5 $-Q_{int}$ in kJ/kg (adsorbent)
Water	64	591	63	778
Methanol	90	402	88	485
Acetonitrile	86	333	84	425

because of the larger molar amount of water which can be adsorbed in the pores of KFI (see Table 1) the energy storable per gram zeolite is higher than for methanol or acetonitrile though the molar integral heats of adsorption of the latter two are bigger. Therefore, water as sorbate is the better choice from a point of view of a high energy density in thermochemical storage of heat. However, the larger values for Q_{int} of the H-ZK-5/water system for instance is still somewhat lower than was found for a CaNaA/water combination with 950 kJ/kg adsorbent [16].

Another advantage of water compared to the other two sorbates is the fact that most of the water can be desorbed at a lower temperature as can be seen from the Figs. 2b and 3b. Thus, the level of the temperature for charging the storage system can be lower which influences the kind of source of the heat, for instance the application of solar heat.

3.2. Isotherms and microcalorimetry

DSC measurements give fast information about the overall properties of the adsorption system. For a more detailed understanding of the interaction of a particular molecule in a zeolite, the isotherms and differential molar heat curves are needed. In the following the H-form of ZK-5 will be subject of closer inspection. The isotherms and heat curves for methanol and acetonitrile on H-ZK-5 are shown in the Figs. 4–6. Fig. 4 considers additionally the adsorption isotherm of methanol on K-ZK-5. As can be seen this isotherm is a very common s-shaped type I isotherm, is partially reversible and does not show any step. Accordingly, the desorption profile in Fig. 2 shows weak steps only. H-ZK-5, however, does show a step in the isotherm which corresponds with the amount of H^+ (3.8 mmol/g) of the sample and indicates stronger specific interaction of the methanol with the acidic sites below 0.1 hPa. The arrows in the figure indicate the equilibrium pressure applied for the recording of the FTIR spectra, see later.

Fig. 5 compares the adsorption isotherm of methanol at 303 and 423 K and acetonitrile on H-ZK-5 at 303 K. With increasing temperature the isotherm of methanol is shifted to higher pressure by three orders of magnitude and the shape of the isotherm changes. The step at about 3.8 mmol/g becomes less pronounced pointing to the fact that enthalpic reasons may be the explanation. If the entropy of adsorption would be the reason of the kink it must become more pronounced with increasing temperature as found for paraffins in ZK-5 [9]. The inflection point at

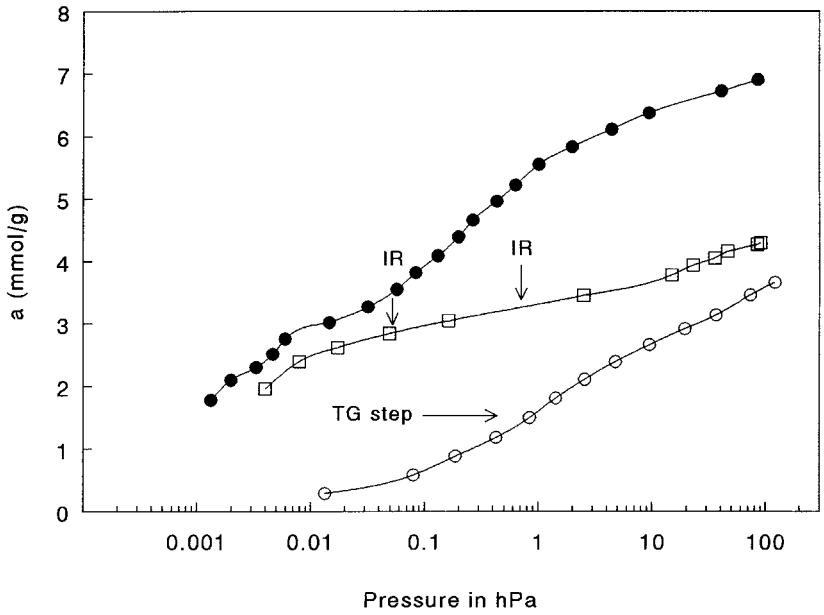

Fig. 5. Adsorption isotherms of methanol in H-ZK-5 at 303 (●) and 423 K (○) and of acetonitrile in H-ZK-5 at 303 K (□).

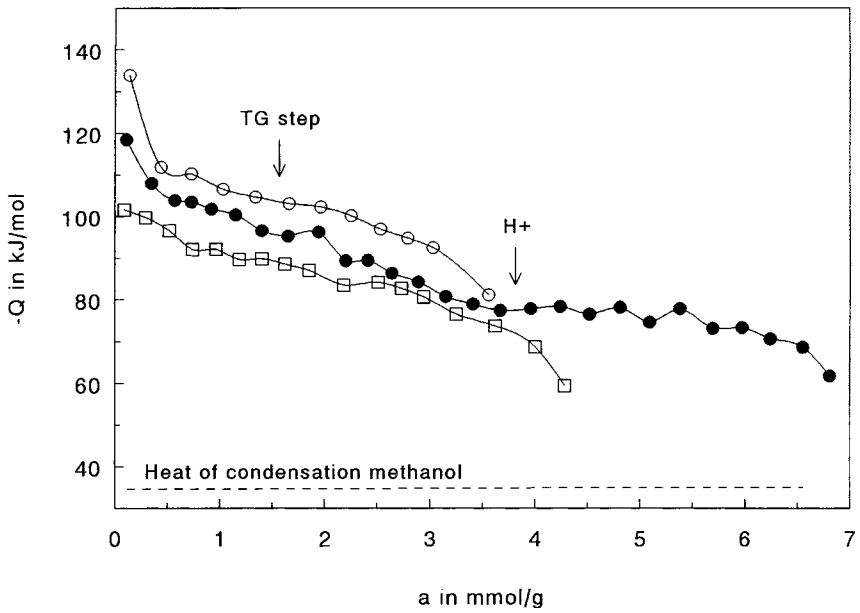

Fig. 6. Differential molar heats of adsorption of methanol in H-ZK-5 at 303 (●) and 423 K (○) and acetonitrile at 303 K (□).

1.6 mmol/g in the isotherm at 423 K corresponds with the maximum at about 490 K of the TG curve of methanol in Fig. 3b due to the strongest acidic sites of the sample.

The isotherm of acetonitrile (at 303 K) confirms the information got from the data of the methanol and is in accordance with the shape of the TG profile. Specific interaction of the base occurs at an equilibrium pressure <1 hPa and up to a loading of 3.8 mmol/g. This first part of the isotherm has to be compared with the part of the TG/DTG curves >370 K in Fig. 3. The weaker bonded acetonitrile desorbs first in the TG (<370 K) and adsorbs last in the determination of the isotherm at $p > 10$ hPa indicated by a small step. Unfortunately, the equilibrium pressure of acetonitrile at 303 K and low coverages is out of the range of the manometers. Thus the shape of the isotherm at the beginning (low loadings) cannot be compared with the last part of the TG curve.

It was already mentioned that changes in the adsorption enthalpy with the adsorbed amount should be responsible for discontinuities in the isotherms which can be seen in Fig. 6. Different to the *n*-alkanes [9,17] in H- and K-ZK-5 the heat curves of methanol and acetonitrile in the H-ZK-5 show a stepwise decrease with increasing loading. The heat curve of acetonitrile has basically the same shape but it is shifted to lower values of heat because of the less strong basic properties. Compared to HY [18], however, the first part of the heat curve of acetonitrile in H-ZK-5 is about 10 kJ/mol higher because of the higher Si/Al ratio and the smaller γ-cages not viable in the Y structure. Both facts contribute to a stronger interaction [18,19]. Arrows in Fig. 6 indicate the position of the last step/inflection point of the TG/DTG curves in Fig. 3 and the total amount of acidic sites of the H-ZK-5, respectively.

There is a not expected small shift of the heat curve of methanol towards higher heats of adsorption with rising temperature. It might be that at higher temperature some catalytic reaction contribute very little to the heat measured calorimetrically. The heat curve at 423 K stops at the loading which corresponds to the amount of H^+. Because of the limits of the experimental set up (see isotherm) no higher pressure (up to the saturation) could be applied. The heat curve at 303 K starts, after a strong decrease at the very beginning, at a level of about 100 kJ/mol up to a coverage of 3.8 mmol/g, most probably the 1:1 complex. For $a > 3.8$ mmol/g the heat curve continues on

a level of about 80 kJ/mol. This could be due to a second methanol molecule per site as sufficient space is available in the structure which is the case for ZK-5. Interestingly, results of quantum chemical calculations suggest a 20 kJ/mol lower heat of adsorption for the interaction of a methanol molecule to an already occupied site [20]. In the case of acetonitrile it is different. Acetonitrile is larger and only a few more molecules than just as many as acidic sites can be adsorbed.

In conclusion, the heat curves of both probe molecules indicate heterogeneity of the acidic sites in H-ZK-5. Thus, as can be expected for polar molecules different to the *n*-paraffins, enthalpic heterogeneity must contribute to the multi-stage desorption profile of the TG/DTG as well as is the reason for the step in the isotherm.

The IR spectra of H-ZK-5 show two bands in the OH stretch region, the so-called HF and LF bands [21] as well known for the faujasites type zeolites. Now the question arises whether or not these bands can be assigned to the weaker or stronger sites identified by the TG and microcalorimetric measurements. Therefore, FTIR spectra of the H-ZK-5 upon adsorption of different amounts of methanol and acetonitrile have been taken.

3.3. FTIR

Fig. 7 shows a set of difference spectra recorded at room temperature upon adsorption of methanol. The spectra were taken with decreasing coverage (from top to bottom) as described in the experimental section. Since the methanol interacts with the Brønsted sites of the H-ZK-5 their stretch modes at 3568 (LF band) and 3609 cm^{-1} (HF band) disappear and negative peaks appear in the difference spectrum at the same wavenumbers. The disturbed OH stretch mode arises in the spectra as a very broad band indicated with A (2900 cm^{-1}), B (2500 cm^{-1}), and C (1700 cm^{-1}) in Fig. 7. This well-known A–B–C pattern [4] is in fact one broad band due a shifted OH stretch mode, forming combination and difference bands with stretch modes of the base molecule with respect to the OH group, including overtones of this mode. The dips at 2650 and 2000 cm^{-1} are assigned to the so-called Evans windows due to Fermi resonance of the broadened OH stretch band with the first overtones of

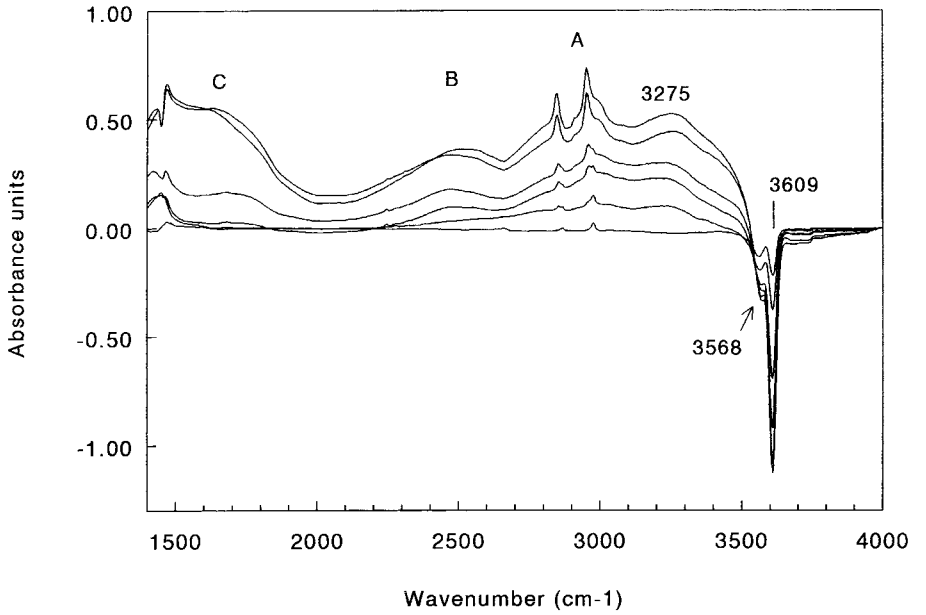

Fig. 7. FTIR difference spectra at room temperature of H-ZK-5 with decreasing adsorbed amounts of methanol from top to bottom: equilibrium pressures 0.5, 0.05 hPa, desorption at room temperature, desorption at 353, 453 and 573 K.

the OH in-plane and out-of-plane bending modes, respectively [4,22,23].

Another broad OH stretch band can be found at 3275 wavenumbers due to the disturbed OH stretch vibration of the adsorbed methanol. According to results of quantum chemical calculations it can be assigned to the end-on interaction with the OH of the zeolite which means that the methanol OH oxygen interacts with the zeolitic proton and the methanol OH proton interacts with the basic oxygen of the lattice next to the OH of the zeolite [24]. Because the assignment is based on a 1:1 complex it supports our supposition in Fig. 4 that at low coverage of methanol on H-ZK-5, the step up to 3.8 mmol/g, an 1:1 complex exists.

Quite different is the situation for K-ZK-5 in Fig. 8 because of the missing Brønsted sites. The difference spectra of K-ZK-5 upon adsorption of methanol reveal just a broad band at 3400 wavenumbers, due to the disturbed OH of the methanol, as well as two sharp bands at 2951 and 2839 cm^{-1} due to the C–H stretch modes. Of course, the latter bands can be found in Fig. 7 too. The OH of the methanol is less shifted compared to the wavenumber of the undisturbed molecule in the gas phase (3687 cm^{-1}) and in comparison with H-ZK-5 because of the specific interaction with the acid sites in H-ZK-5. The nature of the shoulder of the band at 3400 cm^{-1} (K-ZK-5) is not clear yet.

Fig. 9 shows the difference of a difference FTIR spectrum of H-ZK-5 and a difference spectrum of K-ZK-5 upon adsorption of methanol. As can be seen this way the O–H stretch of the methanol and the C–H stretch (not complete) can be suppressed. The remaining pseudo bands in Fig. 9 are due to the A–B–C pattern of the disturbed OH modes of H-ZK-5.

The same pattern can be found in Fig. 10 upon adsorption of deuterated acetonitrile. Acetonitrile is the weaker base compared to the methanol. Consequently, the intensity of the A–B–C pattern is less concentrated on the C-band side [4,23]. This is in good agreement with the results of the microcalorimetric measurements given in Fig. 6. The heat of adsorption of methanol is higher compared to acetonitrile.

The acid strength of the sites determine the size of the A, B and C parts as well. Thus, the center of gravity of the A–B–C pseudo bands are a measure of the acid strength of a certain zeolite probed with a particular base molecule. Table 3 lists the shift of the disturbed OH stretch bands, $\Delta\nu$(OH), upon adsorption of deuterated acetonitrile for some zeolites with

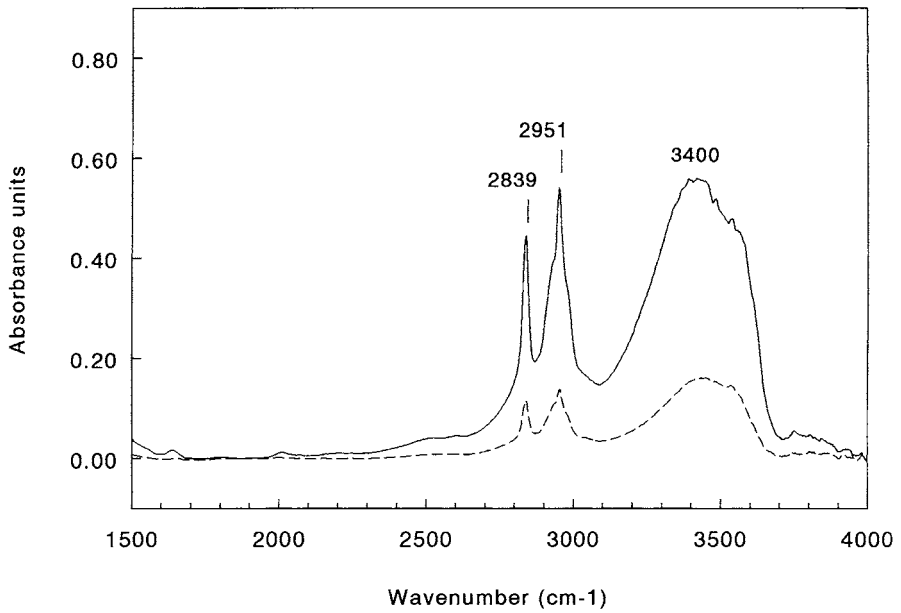

Fig. 8. FTIR difference spectra of K-ZK-5 at room temperature upon adsorption of different amounts of methanol, from top to bottom: equilibrium pressure 0.01 hPa, 30 min desorption at room temperature.

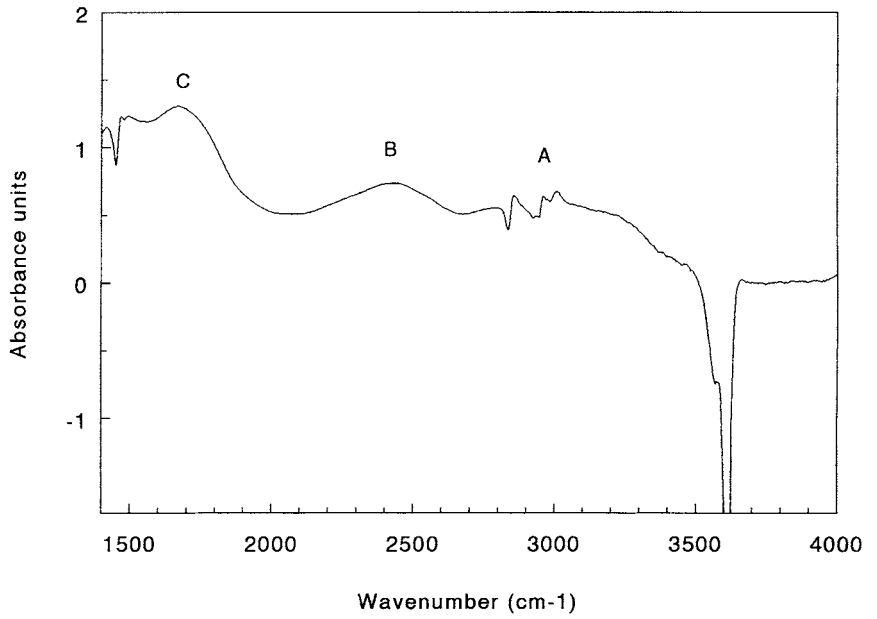

Fig. 9. Difference of the FTIR difference spectra of H-ZK-5 and the FTIR difference spectra of K-ZK-5 at room temperature upon adsorption of methanol.

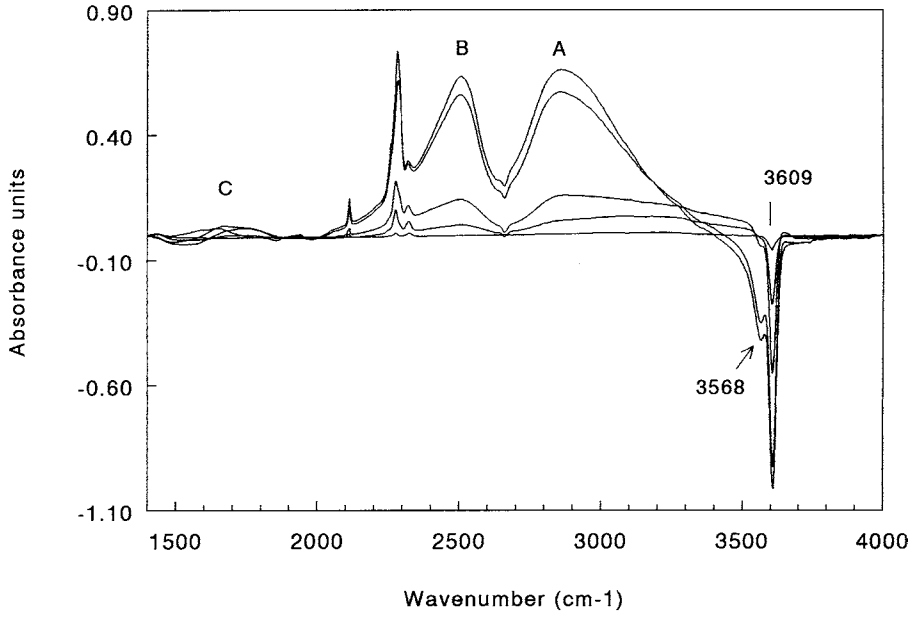

Fig. 10. FTIR difference spectra of H-ZK-5 at room temperature upon adsorption of deuterated acetonitrile with decreasing adsorbed amounts from top to bottom: 0.8, 0.05 hPa, desorption at room temperature, desorption at 353, and 573 K.

Table 3
The OH shift of $\Delta\nu$(OH) upon adsorption of deuterated acetonitrile, based on the center of gravity the disturbed OH stretch mode, for H-ZK-5 compared to other faujasite type zeolites with different Si/Al ratio

Sample	Si/Al ratio	ν(OH) in cm^{-1}	$\Delta\nu$(OH) in cm^{-1}
HY(18)	18	3629, 3550	1039
HY(5)	5	3630, 3550	950
H-ZK-5	3.3	3609, 3568	887
NaHY(2.4)	2.4	3647	747

different Si/Al ratios. As can be seen H-ZK-5 fits well with other zeolites in respect to the Si/Al ratio [19]. Consequently, the heat of adsorption of acetonitrile in H-ZK-5 (Fig. 6) is higher compared to HY ($Si/Al = 2.4$) in [18].

The spectra in Fig. 10 show sharp bands of the deuterated acetonitrile in the region between 2100 and 2300 cm^{-1}. The mode at 2114 cm^{-1} is assigned to the symmetric CD_3 vibration and the CN stretch to bands at 2286 and 2322 cm^{-1}. The CN modes can be used to identify the nature of acid sites. According to [4] the band at 2322 cm^{-1} represents a small amount of weaker Lewis sites (five coordinated extra lattice alumina) and the other the CN stretch of acetonitrile interacting with Brønsted sites. The negative bands again depict the disappearing OH stretch modes. As can be seen the acetonitrile as well as the methanol (Fig. 7) interact with both kinds of acid sites even at low loadings. A comparison of the HF/LF ratio (the heights of the bands) amounts to about 2 for all coverages and reveal no clear preference of any band of a site covered by the base molecules. Thus, the site heterogeneity has to do with the site location in the structure and changes of the strength of the acid sites with the coverage.

4. Conclusions

- Acetonitrile and methanol show a discontinuous desorption behavior from H-ZK-5 and a step in the isotherm related to the specific interaction on the H^+. This behavior is much less pronounced for K-ZK-5. The integral heats of adsorption of water, related to the amount of adsorbent, are higher than those of the bigger methanol and acetonitrile though the integral molar heat of adsorption of water is the lowest of the three.
- The differential molar heats of adsorption of methanol and acetonitrile in H-ZK-5 show a stepwise decrease with increasing loading. This points to enthalpic heterogeneity of the adsorption sites in the cavities which is not the case for *n*-paraffins. The adsorption sites for *n*-paraffins in ZK-5 are entropically heterogeneous where an increase of the differential heat of adsorption with increasing loading was found.
- FTIR measurements confirm the energetic heterogeneity of the acidic OH in H-ZK-5. However, no clear preference of the HF band compared with the LF band can be found.

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