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QUASI-EQUILIBRIUM ADSORPTION GRAVIMETRY OF WATER ON MFI- AND 'FER'-TYPE ZEOLITES AND ON AN AFI-TYPE ALUMINOPHOSPHATE

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Abstract

Water adsorption at temperatures of 286 and 296 K on silicalite-I, ZSM-5 (Si/Al = 16), ZSM-48 (Si/Al = 50) and $AlPO_4$-5 is followed by gravimetry with a quasi-equilibrium continuous adsorptive introduction.

The results show that all of these samples are characterized by a continuous distribution of strongly energetic water adsorption sites (from 60 to 120 $kJ\cdot mol^{-1}$) for which the adsorption is irreversible at the experimental temperature. This probably justifies the presence of hysteresis on desorption at very low relative pressure values. Adsorption of water in these systems firstly occurs by site. This is then followed by cluster formation and it is suggested that it is the ability of the adsorbent to build up these clusters within the microporous structure which determines intracrystalline uptake. It is put forward that the zeolites, silicalite-I and ZSM-5, do not accommodate cluster formation within its microporous network. However, an external flexible microporous structure, containing Lewis sites, may be present for large crystals. This flexible secondary structure may then be able to opened (swelled) at high relative pressures.

On the other hand, for the aluminophosphate $AlPO_4$-5, it is believed that a change in the aluminium coordination on the formation of a crystal hydrate together with capillary condensation results in a large step in the adsorption isotherm, which is itself preceded by a smaller step, revealing a brutal densification of the adsorbed phase.

Keywords: AFI, aluminophosphate, gravimetry, MFI, water, ZSM-48, zeolites

Introduction

For several decades, zeolite–water interactions have been the subject of numerous studies, including, for instance, those cited in the publications of Barrer

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[1] in 1978 or Ruthven [2] in 1984. For the last five years, research on this subject has essentially dealt with synthetic microporous materials, such as the MFI-type zeolites [3] and the aluminophosphates [3] which are widely used in the catalyst industry, where for example, the adsorption capacity of hydrocarbons on the zeolite ZSM-5 may be greatly modified by 'screening' of its acid sites by the water adsorbed [4].

It stands out from these studies that gravimetry (associated with other techniques: spectrometry, calorimetry...) occupies a choice place for the determination of the adsorption isotherms obtained by the introduction of water vapour to the adsorbent by "successive increments at equilibrium". The use of water as an adsorptive is interesting because it readily sorbs onto active sites and is highly susceptible to the environment for the formation of clusters. Previous studies have used point by point methods of adsorptive introduction for measurement of the isotherm or of heats of adsorption. However, we have previously shown [5] that on introducing the water vapour in a continuous and very slow manner (it is easily checked that the water/zeolite system is always at equilibrium) adsorption gravimetry becomes a technique which is both extremely sensitive and performent. This automated procedure allows the direct and continuous recording of the isotherm with enhanced resolution and thus any 'anomalies' becomes easily exposed as, for instance, a small step disclosing a change of state of the adsorbed phase [5]. We have examined by this procedure, within the scope of an EEC SCIENCE project, two types of model microporous adsorbents (containing three-dimensional and unidirectional channel systems).

The zeolites, silicalite-I and ZSM-5 [6, 7] are isomorphous, consisting of the MFI-type structure [3]. The aluminium content of ZSM-5 may vary such that silicalite-I is the pure silica analogue of ZSM-5. The characteristic three-dimensional pore system of the MFI-type zeolites consists of intersecting straight elliptical channels of cross-section 0.51x0.57 nm and sinusoidal, near-circular channels of 0.54 nm in diameter. Previous work on the adsorption of water on the MFI-type zeolites has been contradictory. Evidence has been put forward for the formation of clusters in the porous network [8, 9] however other studies have argued that water rests on the external surface of silicalite-I (a "hydrophobic adsorbent"), either with the creation of a film blocking the porous system [10] or with adsorption in secondary aggregate pore structure outside of the intracrystalline pores [11].

ZSM-48 [12] consists of a disordered structure with ferrierite sheets linked via bridging oxygens located on mirror planes. The unidirectional channel system consists of linear, parallel pores with an ideal cross-section of 0.53x0.56 nm. Thus, ZSM-48 has porous system, of a similar dimension to the MFI-type zeolites. The interst of this adsorbent in this study is the comparison of a three-dimensional interlinked porous network with a unidirectional porous system.

The second type of model adsorbent came from the aluminophosphate molecular sieve family [13]. Thus $AlPO_4$-5 with an AFI-type structure whose unidirectional porous system consists of parallel circular channels of 0.73 nm in diameter. $AlPO_4$-5 consists of a porous network, which, like silicalite-I, theoretically is globally electrically neutral although the pore structure is slightly larger than those of the MFI-type zeolites and ZSM-48. The adsorption of water on $AlPO_4$-5 has shown that at low relative pressures a relatively small uptake was observed [14] corresponding to the expected hydrophobic nature of the adsorbent. At a relative pressure of around 0.25 though, a large step in the isotherm has been observed which has been attributed to capillary condensation together with a change in the aluminium coordination from tetrahedral to octahedral [15, 16]. Unfortunately previously published results [14, 17] have not shown a full desorption branch of the isotherm which is a feature that was of interest.

Experimental

Samples

The silicalite-I and ZSM-5 samples were kindly supplied by J. Patarin at the "Laboratoire des Matériaux Minéraux" in Mulhouse, France. They were prepared in a fluoride medium, via a procedure described elsewhere [18]. The silica to aluminium content of the silicalite-I was found to be greater than 10.000 and that of the protonated ZSM-5 to be 16, as determined by chemical analysis. The silicalite-I sample was screen to have a fairly small crystal size distribution, although twinned, with a mean crystal size of 600 μm in length. The ZSM-5 sample was also seen to have a narrow crystal size distribution with mean crystal length of 48 μm. Both samples gave a total BET equivalent surface area in the region of 450 $m^2 \cdot g^{-1}$ a *t*-plot external surface area of around 6 $m^2 \cdot g^{-1}$ and a micropore volume of around 0.19 $cm^3 \cdot g^{-1}$.

The ZSM-48 and $AlPO_4$-5 samples were kindly supplied by K. K. Unger's group at the Johannes-Gutenberg Universität in Mainz. Both samples were prepared in an alkaline free medium [19]. The ZSM-48 sample contained crystals with a mean size of 2 μm and a silicon to aluminium ratio of about 50. The nitrogen BET equivalent total surface area was found to be 220 $m^2 \cdot g^{-1}$. The *t*-plot gave an external surface area of 68 $m^2 \cdot g^{-1}$ and a micropore volume of around 0.06 $cm^3 \cdot g^{-1}$. The $AlPO_4$-5 sample gave crystals of mean length of 150 μm. The sample was found to have a total surface area from nitrogen BET equivalent calculation of 185 $m^2 \cdot g^{-1}$, an external surface area of 50 $m^2 \cdot g^{-1}$ and a micropore volume of around 0.17 $cm^3 \cdot g^{-1}$ from *t*-plot analysis.

Techniques

The gravimetric adsorption isotherms were measured on an apparatus built at the Centre de Thermodynamique et de Microcalorimétrie in Marseille [20]. It consists of a commercial vacuum balance (Setaram) in which the pressure is measured (between 0 and 1.01 MPa) using a silica Bourdon gauge (Texas Instruments) to an inaccuracy of 10^{-5}. The pressure and sample weight may be directly measured on an XY recorder. The balance and water source are housed in a chamber which was kept at constant temperature, typically around 310 K. The sample was put into one of the balance cells and once placed onto the balance a furnace was positioned around the balance wells. The sample was pretreated prior to measurement using the technique of Controlled Rate Thermal Analysis (C.R.T.A.) [21, 22] where the heating of the sample is regulated as a function of the residual pressure above it. The residual pressure attained was $1.33 \cdot 10^{-2}$ Pa and the samples were normally outgassed to 473 K. Once pretreated, the furnace was removed and replaced by a liquid thermostat allowing temperatures to be set between 243 and 373 K. The experiments were carried out at 267, 286 and 296 K to permit the calculation of the isosteric heats of adsorption.

Results and discussion

A comparison of the adsorption isotherms obtained on the four samples at 296 K after CRTA treatment to 473 K can be seen in Fig. 1.

Silicalite-I (Fig. 1a) has the lowest water uptake over the whole pressure range. This quantity adsorbed is approximately one tenth of those of nitrogen and argon at 77 K (approximately 5.8 $mmol \cdot g^{-1}$ on the plateau of the isotherm at a relative pressure of 0.9) [23]. It would seem that adsorption in the zeolitic micropores is limited. As has been previously suggested [11, 17], this may be because the clustered configuration preferred by water is unable to be developed in the silicalite-I micropores. The isosteric heat of adsorption during the initial uptake to a relative pressure of 0.25 can be seen in Fig., 2a. Even though the low pressure isotherm is not reversible, the calculated isosteric heats are in good agreement with published results obtained by direct calorimetric measurement [24]. It can be seen that initially water strongly sorbs on energetically favourable sites, probably giving rise to chemisorption. It may be seen however, that the isosteric heat quickly reaches the value for the enthalpy of vaporization of water (44 $kJ \cdot mol^{-1}$). Thus adsorption initially occurs on energetically pre-

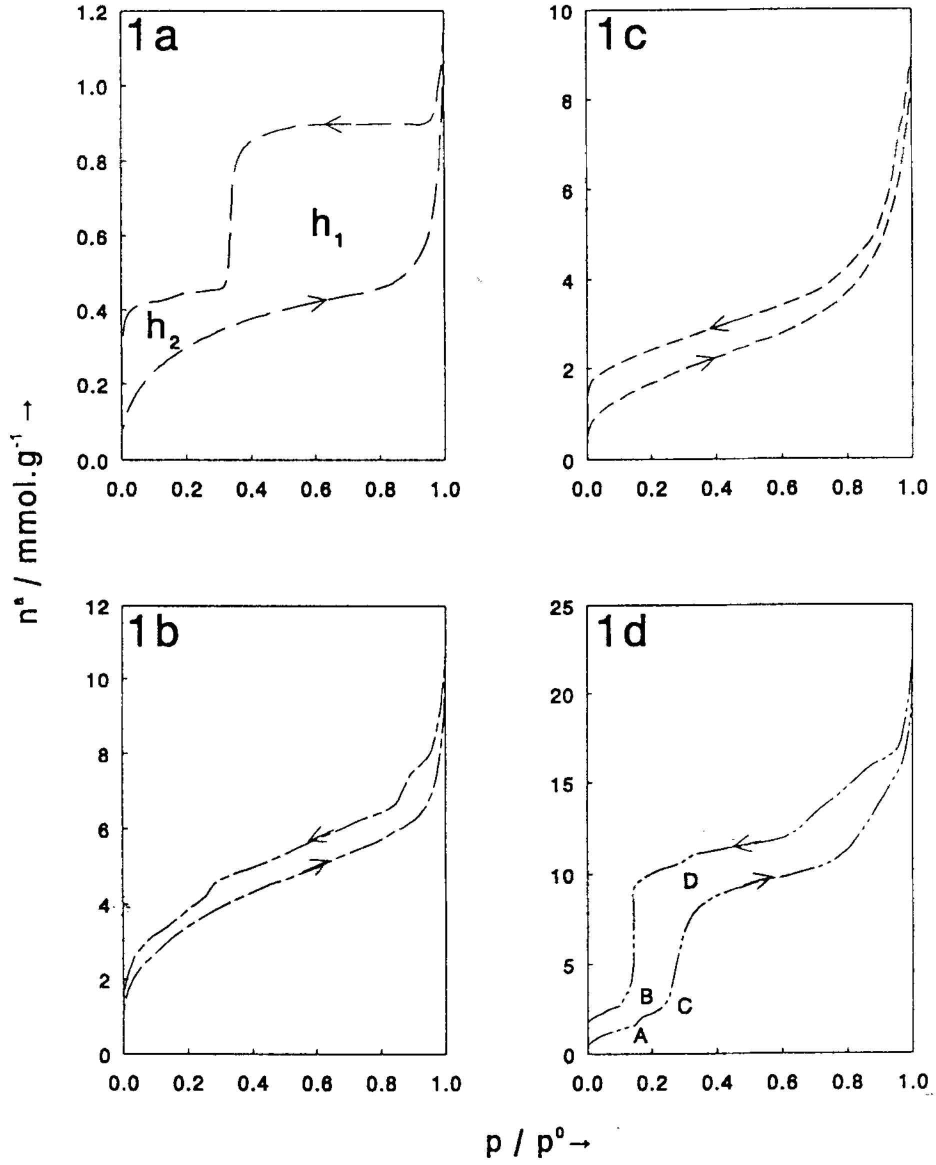

Fig. 1 Adsorption and desorption isotherms of water obtained at 296 K after pretreatment at 473 K; 1a: silicalite-I; 1b: ZSM-5; 1c: ZSM-48; 1d: AlPO$_4$-5

ferred centres. Those within the crystal may be at the channel intersections where hydroxyl groups have been observed as a consequence of preparation in a TPA$^+$ medium [25]. However, any further increase in sorption may thus be due to cluster formation of water on the external surface.

The desorption branch of silicalite-I shows two distinct hysteresis regions, h_1 and h_2. The first, h_1, at high relative pressures between 1 and 0.32, seems to have the same form as that of nitrogen at 77 K and argon at 87 K. As has previously been remarked [11], this may be interpreted as adsorption in a secondary aggregate pore structure outside of the intracrystalline porous network. The desorption branch for water falls sharply at a relative pressure of 0.32 and it would seem that the hysteresis is due to liquid water in this secondary pore structure whose miniscus is not stable below this relative pressure.

An isotherm obtained at 267 K did not give any hysteresis in this relative pressure region indicating that water needs to be above its triple point to be able to penetrate this structure. A further experiment carried out directly after an adsorption–desorption water isotherm, without heating, gave a lower uptake but showed the same isotherm shape and hysteresis height as previously. This indicated a screening of the high energy sites but that the high pressure hysteresis was repeatable. In an attempt to eliminate some of the hydroxyl groups the sample was pretreated to 623 K. The resulting water isotherm is plotted in comparison with that of a sample pretreated at 473 K (Fig. 3). It would seem that the adsorption branches are very similar although the desorption branch is diminished in height with the increased pretreatment temperature.

In view of these aforementioned results it would seem logical to view this external microporous structure as flexible. Thus a liquid sorptive at high enough pressures may be able to force its way into this porous structure. However as some of these flexible regions may contain hydroxyl groups, these could be eliminated with heat treatment thus leading to a restructuration of this intercrystalline region rendering these secondary pores more rigid.

The low relative pressure hysteresis h_2, was found to be at equilibrium as it was seen that on isolating the sample cell for 24 h, no change in the pressure and quantity adsorbed of the branch was observed. Thus the shape of this region h_2 may be explained more in terms of the rehydroxylation of the sample on water adsorption and not of a slow diffusion of desorbed species within the structural micropores as previously suggested [26]. Not all of the adsorbed water was able to be recovered, even under a residual pressure of $1.33\cdot10^{-2}$ Pa for 12 h which would seem to further indicate chemisorption or strong physisorption on the sample. CRTA of a sample after desorption at the experimental temperature (293 K) was carried out to 1273 K. The curve can be seen in Fig. 4.

Three main regions of weight loss may be distinguished. The region I between 296 K and 310 K is interpreted as the loss of physisorbed water (corresponding to the range of isosteric heats between 44 and 60 $\mathrm{kJ\cdot mol^{-1}}$). The weight loss in the region II between 350 and 400 K was found to be equal to 0.17 $\mathrm{mmol\cdot g^{-1}}$ of water. This corresponds to the amount of water initially ad-

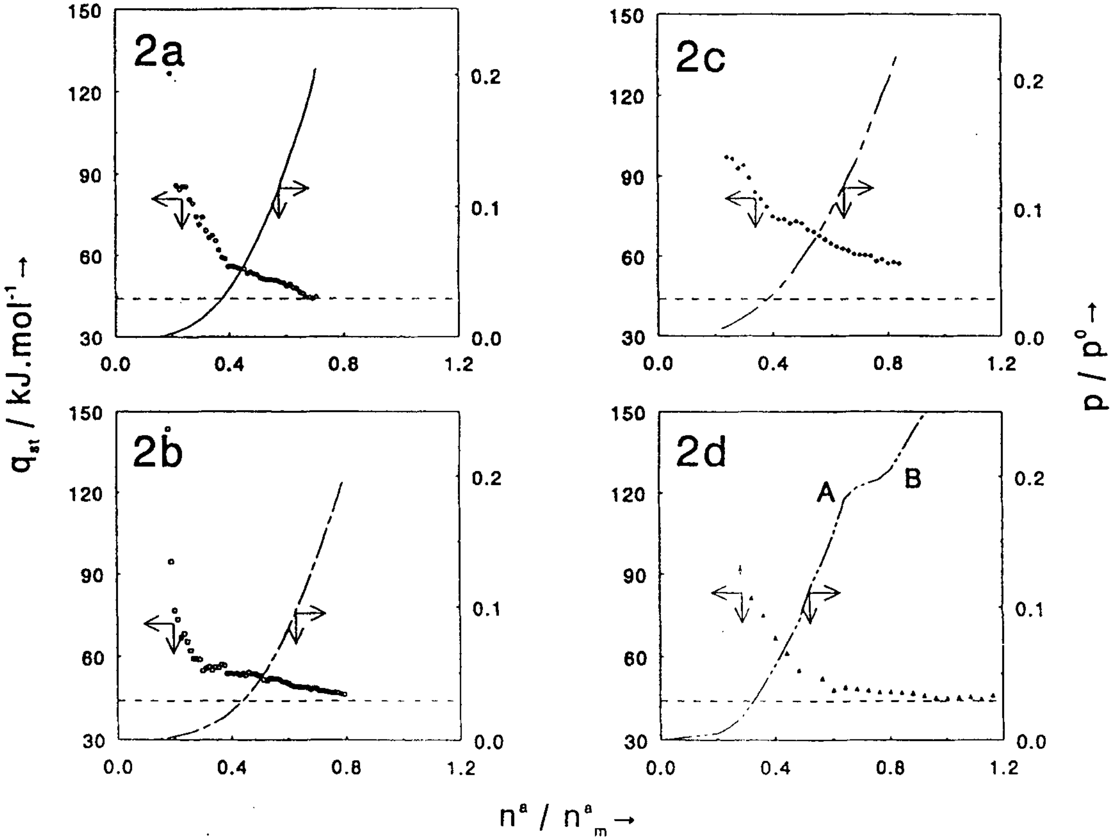

Fig. 2 Comparison of the isosteric heats of adsorption and initial adsorption isotherms as a function of relative coverage (n^a_m is the quantity adsorbed at the point B as proposed by Brunauer, Emmett and Teller); 2a: silicalite-I; 2b: ZSM-5; 2c: ZSM-48; 2d: $AlPO_4$-5

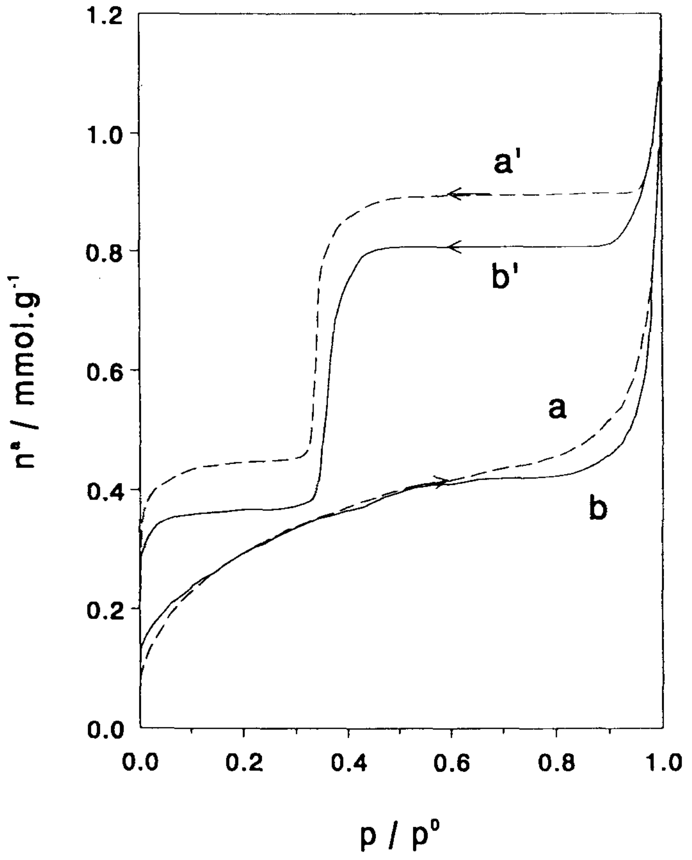

Fig. 3 Comparison of silicalite-I isotherms obtained at 296 K after different pretreatment temperatures; Solid curve (a: adsorption; a': desorption) pretreated to 623 K and dashed curve (b: adsorption; b': desorption) pretreated to 473 K

sorbed gravimetrically (Fig. 1a, from zero uptake to where the adsorption branch parts from zero pressure). This corresponded to isosteric heats in the range form 60 to 120 kJ·mol^{-1} and may be due to the chemisorbed water mentioned earlier. The third region III between 400 K and 920 K may be due to the liberation of water resulting from the dehydroxylation of isolated silanol groups on the external surface of the structure.

Finally, region IV may therefore be due to the loss of water from hydroxyls found in the internal porous structure. These hydroxyls may be those associated with preparation with a TPA$^+$ template [26]. In the regions III and IV around 0.15 –OH·nm^{-2} was liberated from the total calculated BET surface area. Thus the concentration of active sites for water is low giving a further indication of the hydrophobicity of the sample.

For the case of ZSM-5, a type II adsorption isotherm (Fig. 1b) was obtained and it can be seen that the quantity adsorbed is very much greater than for its pure silica analogue. In comparison with the adsorption of nitrogen and argon at 77 K, the quantity adsorbed of water on this ZSM-5 sample is about half of that of nitrogen and argon at a relative pressure of 0.1. However, the water uptake steadily increases and at a relative pressure of 0.9, the quantity of water adsorbed is comparable to that of nitrogen and argon. The hydroxyl groups associated with the aluminium content in addition to the hydroxyl groups associated with defect structure provide further high energy centres for individual water molecules to sorb. In analogy with silicalite-I though, it would be logical to expect strong adsorption on specific centres throughout the sample with further cluster formation to take place on the outer surface as the shape of the intracrystalline porous network would seem to hinder cluster formation. This is further confirmed as the shape of the curve of isosteric heat of adsorption with relative uptake (Fig. 2b) is almost identical to that of silicalite-I indicating initial strong interactions associated with chemisorption. A *t*-plot analysis on the nitrogen isotherms has shown that the external surface areas of the two samples is about the same (in the region of 6 $m^2 \cdot g^{-1}$). Therefore assuming that clusters

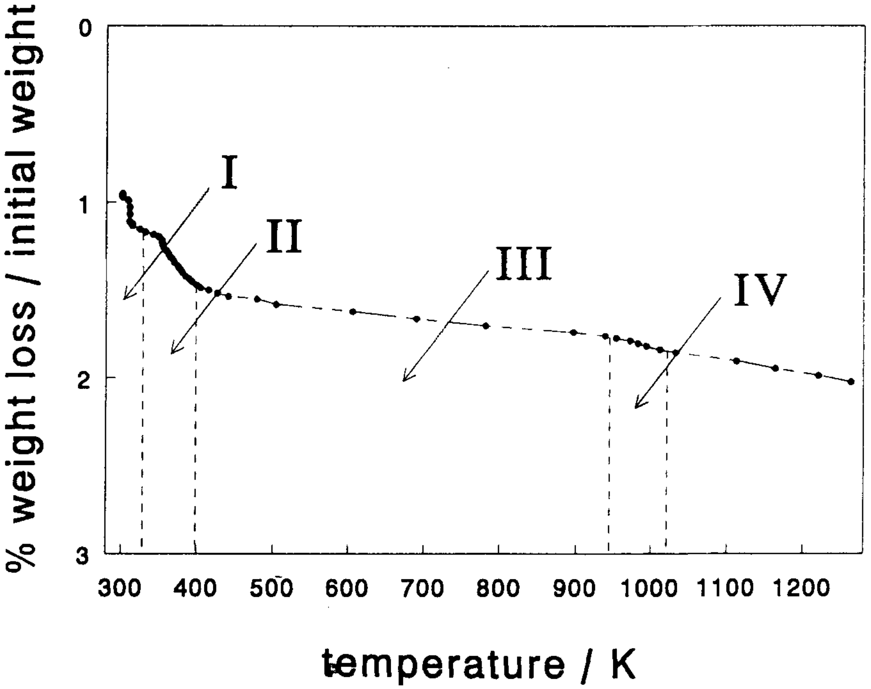

Fig. 4 C.R.T.A. curve of a silicalite-I sample taken after water adsorption at 296 K followed by evacuation to $1.33 \cdot 10^{-2}$ Pa for 12 h at the same temperature

do not form in the porous network it can be seen that the slope of the adsorption branch is more inclined than that of silicalite-I due to cluster formation on a higher concentration of high energy centres on the outer surface, as would be expected.

The desorption branch of the ZSM-5 isotherm shows similar features to that of silicalite-I. This may suggest that a flexible microporous structure exists in addition to the intracrystalline porous network. Thus liquid water at a high enough pressure would 'inflate' this external structure during adsorption and therefore during desorption at a relative pressure of 0.32 this liquid becomes unstable and vaporizes out of the pores which accordingly 'deflate'. The lower pressure hysteresis would also, in analogy to silicalite-I, seem to be a consequence of sample rehydroxylation.

ZSM-48 also gave an irreversible type II isotherm (Fig. 1c). No distinct adsorption features could be distinguished which may have been a consequence of the relatively small crystal size (2 μm). The shape of the isotherm (that is, the addition of type I character and type II character) would suggest an initial adsorption in the micropores followed by adsorption on the external surface. The isosteric heats of adsorption (Fig. 2c) do not attain the value of water liquefaction in the initial part of the adsorption isotherm indicating a range of adsorption phenomena occurring which is again characteristic of an intercrystalline structure.

The $AlPO_4$-5 isotherm (Fig. 1d) has the general shape and uptake as that previously reported [14, 17]. Again from the plot of the isosteric heat (Fig. 2d) it can be seen that sorption initially occurs strongly at specific centres, may be at structure defects. However the initial uptake is low until a small step AB at a relative pressure of around 0.15 which we believe has not previously been reported. This step AB corresponds to an increase in uptake from 2.8 to 4.0 molecules per unit cells. The isosteric heat of adsorption during this step was found to be 47.6 $kJ \cdot mol^{-1}$. The step AB is followed by a second, much larger step CD at a relative pressure of 0.25. The isosteric heat of adsorption in this region is found to have dropped to the values of the enthalpy of liquefaction of water. It has previously been put forward that this step CD is due to the formation of a crystal hydrate and furthermore accompanied by a change in aluminium coordination from 4 to 6 as viewed by NMR [27]. However, this step CD has also been suggested to be resultant of capillary condensation with an aluminium co-ordination change in analogy with the results with $AlPO_4$-17 [15]. What is more, it is interesting to note that $AlPO_4$-11 [28, 29] and $AlPO_4$-17 [30] also undergo structural changes during water adsorption.

From our results of the isosteric heat it would seem likely that the first step AB may be attributed to a brutal densification of the sorbed phase accompanied by a probable cluster formation (clathrate-type structures [31]).

The desorption branch was found to be at equilibrium except at the large step at a relative pressure of 0.12. This also seems to have been the case in previous studies [14] and is to be expected if it is due to the breakup of a crystal hydrate. However, before this large step a smaller step can be distinguished at a relative pressure of 0.32 which, in analogy with the previous results, may be associated with external defect structure. A third small step was observed at a relative pressure of 0.1 and seemed to correspond to the reverse of the adsorption phenomenon at a relative pressure of 0.15. The hysteresis was seen to continue to very low pressures and again not all of the water was desorbed at the experimental temperature for 12 h at a residual pressure of $1.33\cdot10^{-2}$ Pa, which again points to rehydroxylation of the sample during adsorption.

Conclusions

It has been shown that the adsorption of water on silicalite-I, ZSM-5, ZSM-48 and $AlPO_4$-5 does not occur in the manner expected of a small probe molecule in a well defined microporous system due to the chemical nature of this sorption and to the existence of defect structure within the samples.

For silicalite-I, strong water-zeolite interactions have been observed. However the overall quantity of water adsorbed is about one tenth of that previously observed for nitrogen and argon at 77 K. This highlights that the sorption sites for argon and nitrogen at 77 K and for water at ambient temperatures are not the same. It is therefore suggested that water initially chemisorbs on specific sites throughout the crystal but that further cluster formation is unable to take place in the intracrystalline micropores, however water clusters do form on the external surface. The hysteresis loop observed at relative pressures between 1 and 0.32 suggest that physisorption occurs in a secondary intercrystalline microporous structure. This flexible secondary structure may be reorganized with heat treatment to become more rigid.

ZSM-5 with more adsorption sites was seen to have a greater uptake than silicalite-I but it is suggested that again this occurs as chemisorption on these sites followed by cluster formation mainly on the external surface and physisorption in a secondary porous structure at high relative pressures. The ZSM-48 showed intercrystalline phenomena expected of a sample with a relatively small crystal size. This highlighted the requirement for large crystals for the fundamental study of intracrystalline adsorption phenomena.

Finally $AlPO_4$-5 was seen to give an adsorption isotherm with two steps. The first is believed to be due to a brutal densification of the adsorbed water whilst the second seems to be due to a gradual co-ordination change of the aluminium from 4 to 6 accompanied by capillary condensation. All four samples retained water after vacuum pumping after 12 h under a residual pressure of

$1.33 \cdot 10^{-2}$ Pa at the experimental temperature, indicating a degree of chemisorption and that dehydroxylation of the samples occurs during pretreatment at 473 K.

It can thus be seen that water firstly chemisorbs on specific sites in these microporous samples. Secondly, it is the ability of these adsorbents to accommodate the formation of clusters within the pores which determines further intracrystalline uptake.

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Zusammenfassung — Mittels Gravimetrie wurde die Wasseradsorption bei den Temperaturen 286 und 296 K an Silikat-I, ZSM-5 (Si/Al=16), ZSM-48 (Si/Al=50) und an $AlPO_4$-5 verfolgt. Die Ergebnisse zeigen, daß alle untersuchten Proben von einer stetigen Verteilung sehr energiereicher Wasseradsorptionsstellen (zwischen 60 und 120 $kJ \cdot mol^{-1}$) gekennzeichnet sind, für die die Adsorption bei der im Versuch angewandten Temperatur irreversibel ist. Wahrscheinlich wird hierdurch das Auftreten einer Hysterese bei der Desorption für sehr geringe relative Druckwerte gerechtfertigt. Die Adsorption von Wasser erfolgt in diesen Systemen zuerst an der Oberfläche. Dem folgt eine Clusterbildung und es scheint, daß die Fähigkeit des Adsorbens zum Aufbau dieser Cluster in der Mikroporenstruktur es ist, was die intrakristalline Aufnahme bestimmt. Es ergibt sich, daß Zeolithe, Silikat-I und ZSM-5 keine Clusterbildung in ihrem Mikroporennetz beherbergen. Unabhängig davon kann bei großen Kristallen eine externe flexible Mikroporenstruktur mit Lewis'schen Stellen existieren. Diese flexible Sekundärstruktur kann dann bei hohen relativen Drücken geöffnet werden.