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A MICROCALORIMETRIC STUDY OF THE DIFFERENT STATES OF ARGON AND NITROGEN ADSORBED AT 77 K ON SILICALITE-I AND ZSM-5

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The adsorption of argon and nitrogen on a series of MFI-type zeolites (silicalite-I (Si/Al>1000) and HZSM-5 (16<Si/Al<120)) was studied by isothermal microcalorimetry, volumetry and neutron diffraction.

The adsorption of argon and nitrogen present a 'liquid-like' to 'solid-like' adsorbate phase change. The 'solid-like' structures of both adsorbates are similar and imposed by the zeolite channel system. Increasing the aluminium content produces an overall increase in the enhanced adsorption sites for nitrogen whereas the behaviour of argon is unmodified. On HZSM-5, the phase changes of both adsorbates still occur, but, particularly for nitrogen, in a less distinct manner with increasing aluminium content.

Keywords: adsorption, microcalorimetry, zeolites

Introduction

A study of adsorption of argon and nitrogen on silicalite-I [1] and a series of HZSM-5 [2] samples of varying Si/Al ratios was undertaken. The MFI-type zeolites [3], of which silicalite-I and ZSM-5 number are of interest due to their unusual 3-dimensional pore network system of intersecting sinusoidal and straight channels. For the adsorption of nitrogen, a large substep was discovered in the

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isotherms of silicalite-I and ZSM-5 [4–6] and later a smaller substep was observed with large silicate-I crystals (150 μm) [7]. For argon though, only a single substep has been observed [7]. The large nitrogen substep was initially interpreted as a successive filling of the channels and intersections [6], but more recently owing to microcalorimetric and neutron diffraction [8] measurements both substeps were explained as a series of adsorbate phase transitions [7, 9].

Therefore a deeper investigation of the nitrogen and further study of the argon adsorbate phase within the MFI-type zeolites was proposed. Samples of various aluminium contents and crystal sizes were studied to investigate the influence of these factors on adsorption. A comparison of the adsorption of nitrogen with argon allow the influence of a permanent quadrupole moment to also be studied.

The use of isothermal volumetry is complemented by the use of microcalorimetry which allows one to highlight:

- the successive stages of pore filling
- variations of the mobility and/or density of the adsorbate, and
- the extent of specific interactions, taking into account the existence of a permanent moment of the adsorptive.

Neutron diffraction provides a useful structural study of adsorption to backup the volumetry and microcalorimetry with emphasis on:

- modification of the adsorbent structure
- interference between the adsorbent and adsorbate structure , and
- adsorbate structure changes.

Experimental

Two sources of silicalite-I were examined. The first (3.111.2) was kindly prepared by Professor K. K. Unger's group at the Johannes Gutenberg Universität in Mainz. It was obtained by an alkaline free synthesis [10] and gave large individual crystals (150 μm). This sample was principally used for the neutron diffraction experiments but gave exactly the same results for the low temperature microcalorimetry and volumetric experiments as the second silicalite-I sample described below. All the other samples were prepared at the Laboratoire des Matériaux Minéraux in Mulhouse according to the procedure described by Guth *et al.* [11] in which fluoride anions are used to dissolve the silica and alumina sources. This fluoride route is known to produce large crystals. Tetrapropylammonium cations (TPA^+) were used as templating agents. Five samples with different Si/Al molar ratios and different crystal sizes were prepared (c.f.

Table 1). The as-synthesized samples were then calcined to remove the template at 550°C for four hours under air with a step (2 hours) at 200°C (heating rate = 3 deg·min^{-1}).

Table 1 Si/Al molar ratio and crystal size of the as-synthesized samples

Samples	Si/Al* Molar ratio	Crystal size / μm
I	>10000	600×130×130
II	120	120×30×30
III	60	27×6×6
IV	30	30×6×6
V	20	50×15×15

* by chemical analysis

The samples (around 100 mg) were treated to 200°C by CRTA [12] with a residual water vapour pressure of 1.33 Pa in order to reproduce, independently of the storage conditions, the same surface state of each adsorbent prior to further analysis.

The isothermal adsorption microcalorimetry [13] employed with the quasi-equilibrium volumetric procedure [14] allows access to a continuous measurement of the differential enthalpies of adsorption, $\Delta_{ads} h$, during the vertical (or near vertical) parts of the isotherm. The neutron diffraction experiments were carried out at the Institut Laue-Langevin on around 2 g of the silicalite-I sample. The measurements were carried out on a 2-axis diffractometer (D1B) at a constant wavelength of λ=2.524 Å and the results were recorded with a multidetector. The experiments were performed principally at 62 K for nitrogen and 80 K for argon with stability studies undertaken between 10 and 100 K.

Results and discussion

The results of the argon adsorption experiments are shown in Figs 1 to 3 and those of nitrogen in Figs 4 to 6. Figures 1 and 4 show the adsorption and desorption isotherms obtained by static adsorptive introduction. Figures 2 and 5 show the microcalorimetric results for the adsorption on the series of samples plotted as $-\Delta_{ads} h$ the differential enthalpy of adsorption against v^a, which allows a direct comparison with the adsorption isotherm. Figures 3 and 6 show the Clapeyron Diagram for argon and nitrogen on silicalite-I.

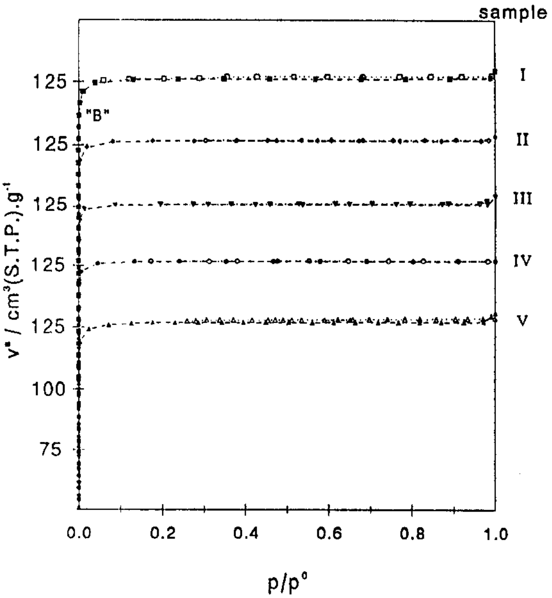

Fig. 1 Argon adsorption and desorption isotherms at 77 K for the series of MFI-type samples. The filled-in symbols indicate the adsorption branch and open symbols indicate the desorption points. Each curve is offset in respect to each other by 25 cm^3 (S.T.P.).g^{-1}

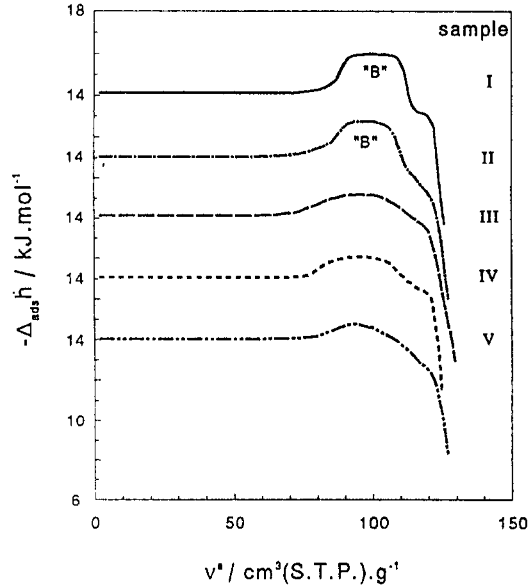

Fig. 2 Argon adsorption microcalorimetric curves at 77 K for each of the MFI-type series. Each curve is offset in respect to each other by 3 kJ·mol^{-1}

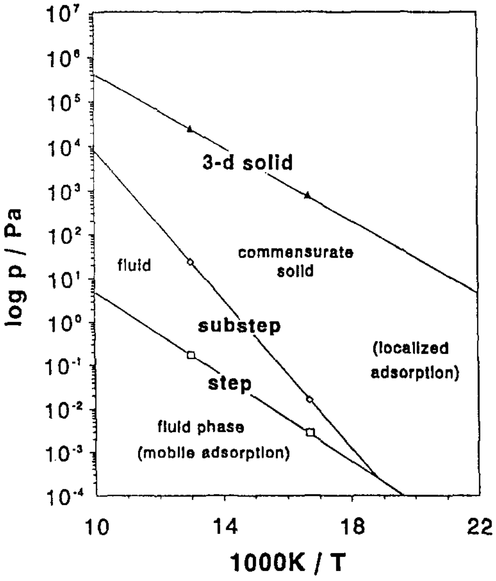

Fig. 3 Clapeyron Diagram for the adsorption of argon on silicalite-I

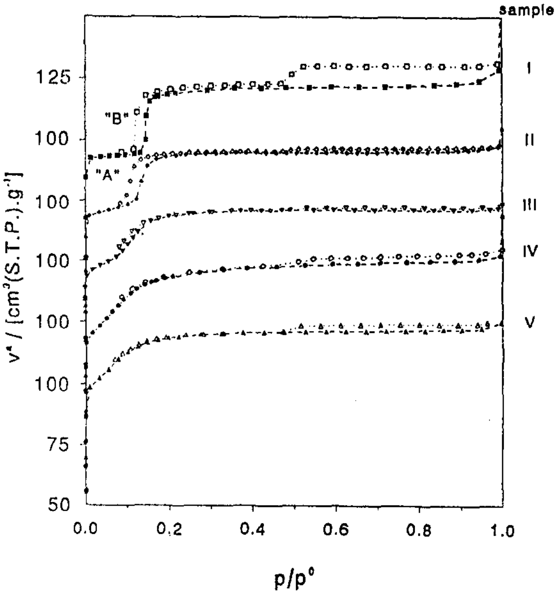

Fig. 4 Nitrogen adsorption and desorption isotherms at 77 K on the series of MFI-type samples. Filled symbols indicate adsorption points and open symbols indicate the desorption points. Each curve is offset to each other by 25 cm^3 (S.T.P.).g^{-1}

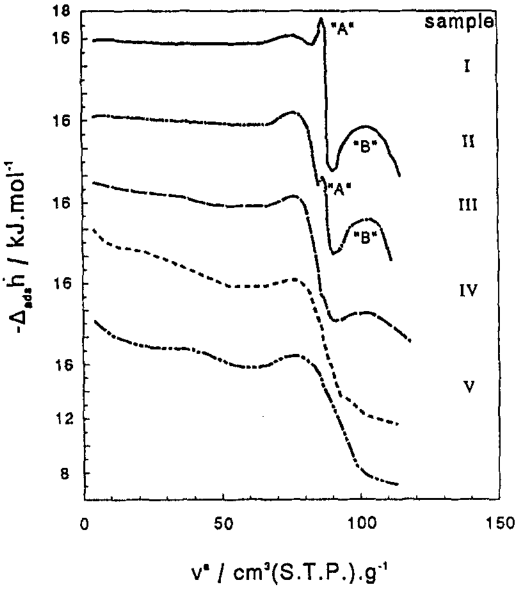

Fig. 5 Nitrogen adsorption microcalorimetric curves at 77 K for each of the MFI-type series. Each curve is offset in respect to each other by 6 kJ·mol $^{-1}$

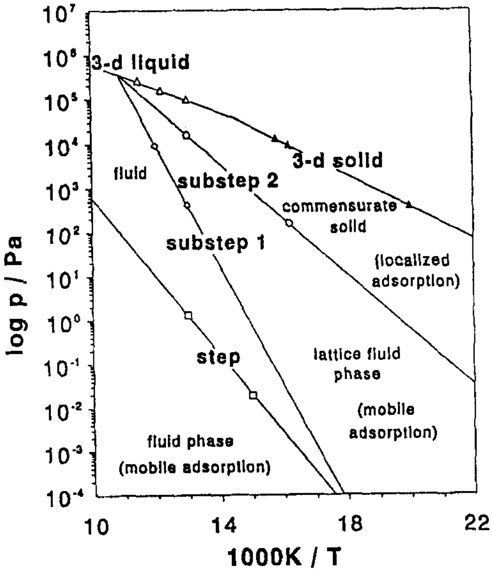

Fig. 6 Clapeyron Diagram for the adsorption of nitrogen on silicalite-I

Argon adsorption on silicalite-I

The isotherm and microcalorimetric plots for silicalite-I are in good agreement with previously published results [7]. The argon isotherm on silicalite-I exhibits a step at a relative pressure of 1×10^{-3}. The microcalori- metric curve for the adsorption of argon on silicalite-I shows an exothermic phenomenon 'B' (Fig. 2) in the range of v^a from 100 to 120 cm^3 (S.T.P.). g^{-1} which corresponds to this step. This exothermic phenomenon is likely to be caused by a rearrangement of adsorbate giving an increase in adsorbate density and therefore allowing an increase in uptake giving the sharp step in the isotherm. The neutron diffraction spectra taken just after this step show the appearance of several intense peaks in the range of the scattering vector, Q from 1.8 to 2.1 $Å^{-1}$ ($Q = \{4\pi/\lambda\}\sin\theta_B$, where θ_B is the Bragg diffusion angle). The positions of these peaks are stable in the temperature range from 10 to 100 K. This may indicate the large role played by the interaction between the adsorbent channel structure and argon molecule and would seem to confirm a densification of the adsorbate phase at this point from a 'fluid-like' to a stable 'solid-like' phase. Furthermore the configuration of this 'solid-like' phase seems to be imposed by the zeolite itself indicating that a commensurate argon structure exists.

Argon adsorption on HZSM-5

The initial adsorption of argon in the range of v^a from 0 to 95 cm^3 (S.T.P.). g^{-1} observed by microcalorimetry show that for all the samples studied, the exothermic signal is constant at around $\Delta_{ads}h=-14$ $kJ\cdot mol^{-1}$. The fact that this region is horizontal for all the samples implies that the argon adsorbs in a homogeneous manner even in the presence of aluminium. All of the ZSM-5 samples in the series show the exothermic phenomenon 'B' between $v^a=100$ to 120 cm^3 (S.T.P.). g^{-1} previously described for silicalite-I. This phenomenon occurs to varying degrees but is less distinct as the aluminium content increases. It is believed that at high adsorbate loading, the aluminium exerts an induced moment in the argon molecule. Thus, in the region of the aluminium atoms, a preferential orientation of argon occurs therefore 'smoothing out' the distinct phenomenon observed on silicalite-I.

The total loading of the argon at the plateau region on the series of samples is approximately the same (126–127 cm^3 (S.T.P.). g^{-1}) thus implying that in this region a 'solid-like' structure exists in all of the samples.

Nitrogen adsorption on silicalite-I

The nitrogen adsorption isotherm and microcalorimetric curve obtained for silicalite-I are similar to results previously published [7]. The exothermic peak 'A' (Fig. 5) at coverage, v^a around 100 cm^3 (S.T.P.). g^{-1} is thought to be caused by the appearance of a preferential configuration leading to an increase in adsorbate density. This 'fluid like' to 'lattice fluid like' phase transition thus allows an increase in adsorbate loading. The neutron diffraction spectra show a strong increase of a peak at Q=1.63 Å^{-1} and the appearance of two new peaks at 1.88 and 2.06 Å^{-1} which are not temperature dependent indicating that this 'lattice fluid like' phase is stable in the temperature range between 10 and 100 K.

The second, larger step 'B' on the silicalite-I isotherm, observed between v^a=100 and 120 cm^3 (S.T.P.). g^{-1} corresponds to the appearance of the crystalline order in the adsorbate phase or a 'lattice fluid like' to 'solid like' adsorbate phase transition as the neutron diffraction experiments have already confirmed [8, 9].

Nitrogen adsorption on HZSM-5

The curves of derived enthalpy of adsorption on the HZSM-5 samples in this initial region show a variation from the horizontal which is in contrast with the argon adsorption. It can be seen that the differential enthalpy of adsorption decreases to a region at approximately v^a=90 cm^3 (S.T.P.). g^{-1} where the value of $\Delta_{ads}h$ in each case in approximately the same. The initial values of $\Delta_{ads}h$ in the region of v^a=0 to 5 cm^3 (S.T.P.). g^{-1} seem to vary in correlation to the Si/Al ratio and may reflect the number of hydroxylated defect sites in the structure.

It is thought that the aluminium in the MFI structure creates more active sites to which the nitrogen is preferentially attracted imposing this 'lattice fluid like' phase from the beginning of the initial adsorption and so broadening out the effect of the step or peak on the isotherm or microcalorimetric curve respectively.

As the aluminium content increases a gradual inclination of this second substep can be clearly observed on the corresponding isotherms. The series of microcalorimetric curves also shows a gradual change as aluminium content increases. The distinct effect seen for silicalite-I becomes more obtuse with its depart shifting to lower relative pressure. As the amount adsorbed after this step is approximately the same for each isotherm (120 cm^3 (S.T.P.). g^{-1}), it can be deduced that a 'solid like' phase exists in this region for every sample as for argon adsorption. The 'lattice fluid like' to 'solid like' phase transition shown for silicalite-I can then be thought to occur in the other samples. The 'smoothing out' of this phase change may be due to preferential orientation of the nitrogen adsorbate near to the aluminium sites creating regions of this denser 'solid like' phase at a lower pressure than the corresponding substep observed for silicalite-I.

The high pressure hysteresis loops between $p/p^{\circ}=1$ and 0.4 for each sample are given and it can be seen that they do not vary in respect to the aluminium content. It can be seen though, that with the exception of sample 'II', the size of the hysteresis loop corresponds to the crystal size. It is therefore thought that crystal defects are created during calcination due to the violent depart of water and organic material from within the crystal structure. In the larger crystals, this depart is more important which may lead to fissures or cracks as can be clearly seen by SEM.

Conclusion

Isothermal volumetry, low temperature microcalorimetry and neutron diffraction results have shown that during argon adsorption on silicalite-I the adsorbate undergoes a 'fluid like' to 'solid like' adsorbate phase change and that nitrogen undergoes two phase changes, from a 'fluid like' to 'localized-fluid' phase and then from a 'localized fluid' to a 'solid like' phase. It is seen that for all the MFI-type samples, approximately the same amount of either argon or nitrogen is adsorbed on the plateau region after the large substep. This would seem to indicate that the adsorption of both argon and nitrogen on ZSM-5 also undergo the phase transitions observed on silicalite-I leading to a dense 'solid like' phase at the plateau region. The neutron diffraction results indicate that the structure of the argon and nitrogen 'solid like' phases are dictated by the adsorbents and therefore commensurate in nature and furthermore that the commensurate structures of argon and nitrogen are probably similar. It would seem also that the adsorption of both adsorbates occurs at designated regions or by site. The phase transitions become less distinct with an increasing aluminium content of the sample. Transition 'A' observed for the adsorption of nitrogen on silicalite-I is still visible for the sample 'II' with Si/Al=120 but it is not distinguishable for the other samples. On the other hand, the second nitrogen transition 'B' and argon transition are visible for all the samples. It seems that at the regions where the aluminium is sited, a preferred configuration of the adsorbate occurs thus smoothing out the prompt phase transitions observed for silicalite-I.

The hysteresis loops observed for the adsorption of nitrogen seem to correspond, with one exception, to the size of the zeolite crystals. This may well be due to the calcination process where the heating rate is related to time. Thus the pressure above the sample may vary considerably and thus the violent depart of organic matter or water can occur so creating fissures in the crystal where defect sites may appear. The use of a technique such as controlled rate thermal analysis [12], where the rate of heating is related to the pressure above the sample, may avoid this phenomenon and so produce crystals with fewer defects.

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References

1 E. M. Flanigen, J. M. Bennett, R. W. Grose, J. P. Cohen, R. L. Patton, R. M. Kirchner and J. V. Smith, Nature 271 (1978) 512.
2 G. T. Kokotailo, S. L. Lawton, D. H. Olson and W. M. Meier, Nature, 272 (1978) 437.
3 W. M. Meier and D. H. Olson, Atlas of Zeolite Structure Types, 2nd Ed., Butterworths, London 1987, p. 100.
4 U. Müller and K. K. Unger, Forschr. Mineral., 64 (1986) 128.
5 P. J. M. Carrot and K. S. W. Sing, Chem. Ind., (1986) 786.
6 P. A. Jacobs, H. K. Beyer and J. Valyon, Zeolites, 1 (1981) 161.
7 U. Müller, H. Reichert, E. Robens, K. K. Unger, Y. Grillet, F. Rouquerol, J. Rouquerol, Dongfeng Pan and A. Mersmann, Fresenius Z. Anal. Chem., 333 (1989) 433.
8 ILL experimental report, No.9-07-196, 1990.
9 H. Reichert, U. Müller, K. K. Unger, Y. Grillet, F. Rouquerol, J. Rouquerol and J. P. Coulomb, Characterization of Porous Solids II, Eds. F. Rodriguez-Renso, J. Rouquerol, K. S. W. Sing and K. K. Unger, Elsevier, Amsterdam 1991, p. 535.
10 U. Müller and K. K. Unger, Zeolites, 8 (1988) 154.
11 J. L. Guth, H. Kessler and R. Wey, New Developments in Zeolite Science and Technology, Eds. Y. Murakami, A. Iijama and J. W. Ward, Elsevier, Amsterdam 1986, p. 121.
12 J. Rouquerol, J. Thermal Anal., 2 (1970) 123.
13 J. Rouquerol, Thermochimie, C.N.R.S., Paris 1971, p. 537.
14 Y. Gillet, J. Rouquerol and F. Rouquerol, J. Chim. Physique, 2 (1977) 179.

Zusammenfassung — Mittels Mikrokalorimetrie, Volumetrie und Neutronendiffraktion wurde die Adsorption von Argon und Stickstoff an einer Reihe von MFI-Zeolithen ((Si/Al1000) und HZSM-5 (16<Si/Al<120)).

Die Adsorption von Argon und Stickstoff stellt einen Phasenübergang von einem "flüssigkeitsartigen" zu einem "feststoffartigen" Adsorbat dar. Die "feststoffartigen" Strukturen beider Adsorbate sind einander ähnlich und durch das Zeolith-Tunnelsystem geprägt. Die Erhöhung des Aluminiumgehaltes verursacht bei Stickstoff eine allgemeine Zunahme der belegten Adsorptionsstellen, während das Verhalten von Argon unverändert bleibt. An HZSM-5 vollzieht sich zwar die Phasenumwandlung bei beiden Adsorbaten, aber – insbesondere bei Stickstoff – durch Erhöhung des Aluminiumgehaltes in einer weniger ausgeprägten Weise.