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A MICROCALORIMETRIC COMPARISON OF THE EFFECT OF *n*-ALKANE PREADSORPTION ON THE ADSORPTION OF ARGON AND NITROGEN ON SILICALITE-I

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Abstract

The *n*-alkanes of different lengths were preadsorbed to selectively block part of the micropores of a MFI-type zeolite, Silicalite-I. The porosity available to argon and nitrogen was then studied by quasi-equilibrium adsorption microcalorimetry and volumetry at 77 K and compared to what was found for the bare zeolite. Indeed, although partial adsorption of *n*-alkanes does not alter the value of the differential enthalpies of adsorption for both argon and nitrogen, the *n*-butane preadsorption diminishes the adsorption capacity by inducing inaccessible volumes in the micropore network. Moreover, the microcalorimetric experiments clearly show that *n*-butane is not evenly distributed in the zeolite channel network while the longer *n*-alkanes used are.

Keywords: *n*-alkanes, preadsorption, microcalorimetry, Silicalite-I

Introduction

Recently [1], stepped type I adsorption isotherms were obtained during a volumetric study of argon and nitrogen adsorption at 77 K in Silicalite-I, a well known zeolite [2]: one substep was found in the case of argon and two in the case of nitrogen. When examined simultaneously by microcalorimetry and volumetry, these substeps proved to be accompanied with exothermic peaks in the differential enthalpies of adsorption plots [3] that can be seen on Fig. 1.

When the help of neutron diffraction [4, 5], argon was found to be in a mobil fluid phase before the substep and in a crystalline solid-like phase on the plateau of the adsorption isotherm after the substep. Thus, the step in the isotherm accompanied with an exothermic peak in the microcalorimetric signal were assigned to the occurrence of a phase transition β_{Ar} [4] undergone by the adsorbate between the two states described above. Similarly, nitrogen would undergo two phase transitions, from a mobil fluid phase to a mobile slightly organized fluid phase and then to a crystalline solid-like phase (respectively called α_{N_2} and

β_{N_2} in a previous publication [5]). Furthermore, the crystalline solid-like structure for both argon and nitrogen seem to have similar commensurate structures.

The *n*-alkane preadsorption is widely used for the determination of total micropores volume and also to measure the external surface area of catalysts or any microporous adsorbents, as instance zeolites [6–8]. Using the quasi-equilibrium adsorption volumetry at 77 K together with isothermal microcalorimetry, we examine the effect of pore blocking by different *n*-alkanes on the phase transition of argon and nitrogen is Silicalite-I which can be regarded as a 'model' solid.

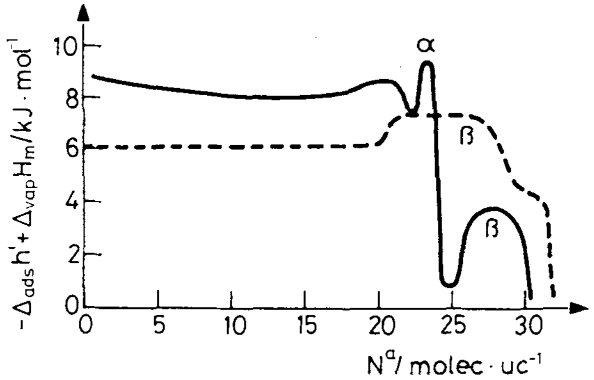

Fig. 1 Net enthalpy of adsorption of nitrogen (—) and argon (---) on Silicalite-I

Experimental

Adsorptives and adsorbents

The *n*-nonane and *n*-hexane used were gas phase chromatography reference samples (99.6% minimum purity) available from Prolabo. They were doubly distilled through a freeze-pump-thaw cycle before use.

The *n*-butane and the other adsorptives used are of a high purity grade (99.995% purity) from Alphagaz (Air Liquide), France.

Silicalite-I is the pure silica form of the ZSM-5, a MFI-type structure zeolite [2]. Its microporous network consists of two sets of channels intercrossed; along the [010] crystalline direction run the straight channels that have an elliptical cross section (0.51×0.56 nm) while the sinusoidal channels run along the [100] direction and have a nearly circular cross section (0.54×0.56 nm). Therefore, an unit cell can be described in terms of 4 straight channels sections (4×0.46 nm long), 4 sinusoidal channels sections (4×0.66 nm long) and 4 nearly circular channel intersections (4×0.54 nm in diameter).

The sample was obtained from Pr. K. K. Unger laboratory at the J. Gutenberg Universität, Mainz, Germany. The crystals have a homogeneous size distribution of approximately 120×30×30 μm. It was initially outgassed at 473 K by means of Controlled Rate Thermal Analysis or CRTA [9]: the rise in temperature and the constant rate of outgassing are controlled by a set residual pressure above the sample (c.a. 0.133 Pa). This method allows the obtention of a reproducible surface state or preadsorbed state.

N-nonane and n-hexane preadsorption

A known weight of sample is first saturated by *n*-nonane or *n*-hexane vapour at 296 K for 16 h. The excess vapour is then evacuated at ambient temperature up to a chosen residual pressure and the sample cell weighed, so the total amount of vapour adsorbed is known.

The CRTA method is then used to obtain a thermal desorption curve. Since the outgassing rate is maintained constant this method allows a reproducible desorption of a fixed known amount of *n*-nonane or *n*-hexane and the CRTA experiment can be stopped at various desorption stages.

Volumetric preadsorption of n-butane

The *n*-butane was adsorbed onto the sample by means of a volumetric apparatus constructed 'in house' [10]. The vapour is introduced on the sample through a sonic leak in a slow (c.a. 0.5 $cm^3 \cdot h^{-1}$) continuous and constant manner, so the system is always in quasi-equilibrium, and the pressure above the sample is monitored. The gas flow rate being known, the amount adsorbed at any time can be deduced. Again, the adsorption was stopped at various stages.

Isothermal microcalorimetry coupled with quasi-equilibrium volumetry at 77 K

The microcalorimetric data for argon and nitrogen at 77 K were obtained on an apparatus also constructed 'in house' [10] which is coupled to a quasi-equilibrium volumetric rig: the adsorptive introduction is, again, slow (2.5 $cm^3 \cdot h^{-1}$), continuous and constant. It is worth noting that in the vertical part of the type I adsorption isotherms, i.e. at very low relative pressure, the heat flow is directly proportional to the differential enthalpy of adsorption; on reaching the adsorption isotherm plateau, a correction must be made due to the gas compression in the sample cell.

Results and discussion

N-alkanes preadsorption

The maximum loadings of the various *n*-alkanes used are listed in Table 1. The liquid volumes were calculated by taking the bulk liquid density at ambient temperature. It is worth noting that the liquid volumes adsorbed at saturation are not equal which seems in discrepancy with the Gurvitsch rule which states that the liquid volume of all adsorbates should be equal at saturation. This effect was already noticed [11] and assigned to a molecular sieve effect, since, for a given microporous sample, the larger molecules give the smaller liquid volume.

Furthermore, although the theoretical microporous volume available in Silicalite-l is reported to be 0.19 $cm^3{}_{liq}\cdot g^{-1}$, the liquid volume calculated for *n*-butane stands 8% above this value. This probably means that the density of the adsorbate phase in the micropores differs from the 3d-liquid density. Moreover, it is likely that the average density of *n*-butane (and the other *n*-alkanes used) in the pores is somewhat higher than the bulk value because of the strong potential field due to the pores walls [12].

Theodorou and al. [13] modelised the adsorption several alkanes in the Silicalite-I pores. They found out that linear alkanes such as *n*-butane and *n*-hexane prefer to reside in the channels and avoid the channels intersections; on the contrary, bulky side groups in branched alkanes, such as 2- and 3-methyl pentane, force these molecules toward the more spacious channels intersections. They also showed that the molecules are perturbated from the ideal gas dihedral angle distribution toward the more linear trans states when confined in Silicalite-I. These calculations may be another proof for a denser packing of the molecules in the zeolite channels since, as opposed to a 3-*d* liquid state, the molecules are more likely to adopt a single configuration when adsorbed in Silicalite-I. X-ray diffraction experiments [14] have also shown that *n*-hexane resides preferentially in the straight channels.

Eventually, Nicholas *et al.* [15] found that both adsorbate-adsorbate and adsorbent-adsorbate interactions influence the packing of the *n*-alkane molecules in the zeolite and even more, that, around the maximum loading, the molecules have a solid-like behaviour. Thus, when using the 3-*d* density of the *n*-alkanes at their normal melting temperature, one found liquid volumes in accordance with the theoretical volume of the zeolite framework (Table 1).

Therefore, the use of liquid densities should then be very cautious and instead we used the effective total chain length of sorbate molecules per unit cell or eftcl (expressed in $nm\cdot uc^{-1}$), as suggested by Richards and Rees [16], to compare the adsorbed amounts between the *n*-alkanes and argon and nitrogen. The effective total chain length of sorbate molecules adsorbed by unit cell is simply

Table 1 Size and maximum loadings in Silicalite-1 at 296 K for the various *n*-alkanes

n-alkane	Size**/nm	Max. loading/ molec.uc $^{-1}$	Liquid volume/$cm^3_{liq}\cdot g^{-1}$ (3-d liquid density *at 293 K)	Liquid volume/$cm^3_{liq}\cdot g^{-1}$ (3-d liquid density at $T_{melting}$)
n-butane	0.778	12	0.208 (0.579)	0.615 (0.730)
n-hexane	1.05	7.64	0.171 (0.659)	0.149 (0.762)
n-nonane	1.45	4.64	0.144 (0.715)	0.133 (0.772)

* The liquid densities are taken from D.M. Small: 'The physical chemistry of lipids from alkanes to phospholipids', Plenum Press. New York and London 1988.

**The molecules length were taken from reference [12] the product of the chain length of sorbate molecules and the number of molecules adsorbed by unit cell.

N-alkanes controlled rate thermal analysis

The curves shown on Fig. 2 are the desorption extent of the *n*-alkanes as a function of the temperature (the lighter the *n*-alkane and the lower the range of temperature at which it desorbs). These curves are characteristic of a desorption governed by a diffusion process and assert the molecular sieve effect detected through the non obedience to the Gurvitsch rule.

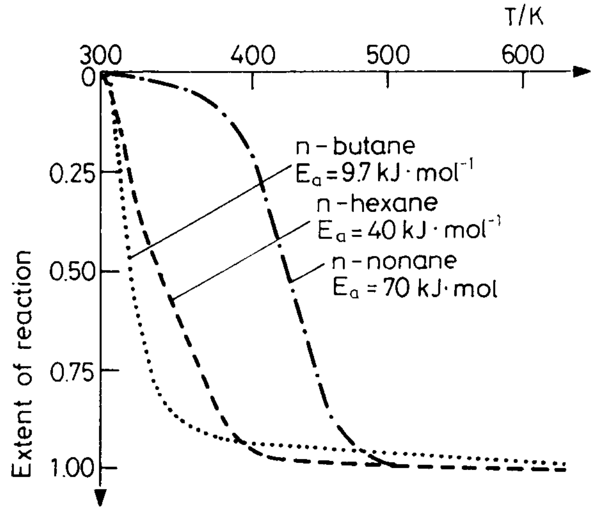

Fig. 2 Extent of desorption of *n*-butane, *n*-hexane and *n*-nonane as a function of temperature

The activation energies for the different *n*-alkanes can be calculated by linking the extent of the reaction to an equation derived from Ficks law and Arrhenius law [17], considering a 3-*d* diffusion process. The activation energies calculated in this way leads to the values listed on Fig. 2.

The activation energy found for *n*-butane is well in agreement with those obtained by other methods [18]. However, Jobic *et al.* [19] have found similar values for both *n*-butane and *n*-hexane activation energies by means of quasi-elastic neutron scattering. They also state that the activation energy of any *n*-alkane ranging from C_1 to C_6 should be c.a. 5 kJ·mol^{-1}.

Measurements for *n*-paraffins with $n = 6$ were reported by Ruthven [20] and the activation energy was c.a. 17 kJ·mol^{-1}. He also reported that the diffusional activation energy becomes almost independent of carbon number when $n > 10$.

The discrepancies observed between our values and the literature have then to be assigned to processes different from the intra-crystalline self diffusion such as the long range diffusion which is a combination of inter- and intra-crystalline diffusion [19–20].

As the *n*-alkanes desorption is governed by a diffusion process, the CRTA method used to determine the amounts adsorbed ensures that the residual pressure of *n*-alkane above the sample will be very small (< 0.133 Pa) and therefore, no or very little 3-*d* solid condensation should occur when the sample cell will be transferred into the cryogenic bath.

Argon and nitrogen adsorption

As shown in the example on Fig. 3, the zero coverage differential enthalpies of adsorption or argon or nitrogen are not affected significantly (experimental error: $\Delta h'_{ads}$ $(\theta = 0) \pm 0.5$ kJ·mol^{-1}) by the presence of any of the *n*-alkanes chosen for this study. This indicates that even though the *n*-alkanes molecules interact with the framework, they do not interact with neither argon nor nitrogen and they do also not modify the interaction of the two latter adsorptives with the framework.

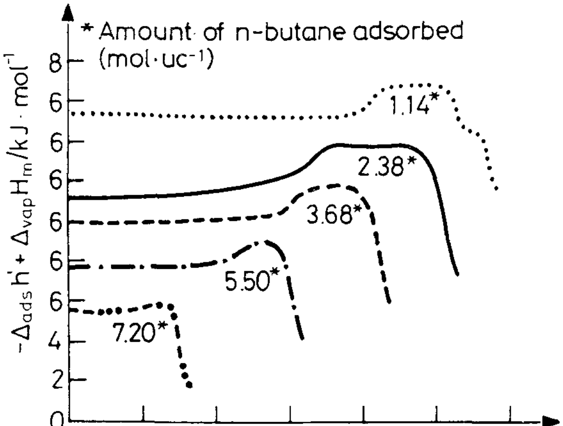

Fig. 3 Net enthalpy of adsorption of argon adsorbed on Silicalite-1 with *n*-butane preadsorbed (the scale is offset for clarity)

Gradual removal of the *n*-alkanes allows accessibility to the zeolite channels network, resulting in type I adsorption isotherms becoming progressively stepped. At the same time, the exothermic peaks on the microcalorimetric curves reappear.

For each experiment, using the volumetric data, we have calculated the effective chain length of adsorbate in the pores for the argon or nitrogen and plotted it *vs*. the *n*-alkane contribution. These calculations are plotted in Fig. 4.

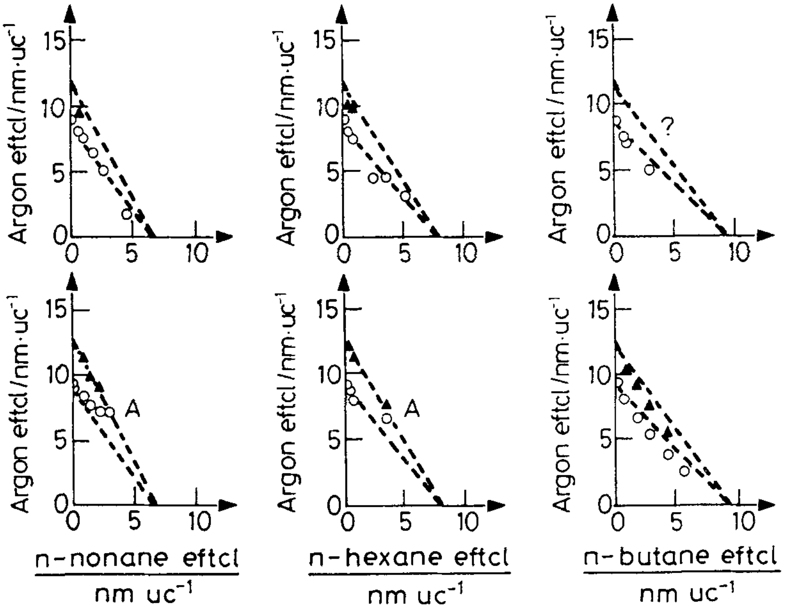

Fig. 4 Effective total chain length of nitrogen and argon plotted versus the effective total chain length of *n*-butane, *n*-hexane and *n*-nonane (o and ▲ values before and after the transition β respectively; the broken lines represent the 'ideal' linear correlation)

In an ideal case, a linear relationship should exist between the two extrema of these plots, i.e. the zeolite is fully loaded with the *n*-alkane (no argon or nitrogen molecule is present in the micropores network) or the zeolite is fully loaded with argon or nitrogen (no *n*-alkane molecule is present). As both adsorption isotherms for argon and nitrogen possess a substep and a plateau corresponding to the beginning and the end of the β transition, two sets of linear relationships can be obtained, linking the maximum loading of *n*-nonane to the loading before and after the β transition. A linear correlation would simply mean that, when a *n*-alkane molecule is desorbed from the zeolite pores, it leaves an empty space that can be completely filled with argon or nitrogen molecules. Moreover, if an experimental point is found lying below these lines, then it will mean that some of the micropore volume liberated by the *n*-alkane molecule is inaccessible for argon or nitrogen.

Indeed, for the system *n*-nonane/nitrogen, this linear relationship between the effective chain length of nitrogen at the substep and the effective chain length of *n*-nonane is observed: all the experimental values but one lay on a straight line. The latter disagreement is easily explained; thus, when nitrogen is adsorbed on the Silicalite-I containing about 3.12 molecules of *n*-nonane preadsorbed per unit cell, on average three out of four intersections are blocked and, therefore, part of the micropores is inaccessible to the nitrogen molecules and therefore the nitrogen effective chain length is smaller than it would be if the nitrogen was able to occupy the entire pore space. However, when less *n*-nonane molecules are preadsorbed, the whole channel network is available for the nitrogen molecules. Furthermore, when the β_{N_2} transition reappears, the values obtained for the maximum loading lay on the straight line that can be traced between the effective chain length of nitrogen after β_{N_2} for an empty zeolite and the effective chain length of *n*-nonane at maximum loading.

For that first system the expected linear correlation is found for both sets of data. However, for the system *n*-nonane/argon, a different behaviour is observed: the set of values calculated before β_{Ar} do not follow a linear correlation with the *n*-nonane effective chain length. Moreover, they lie above the 'ideal' straight line until they slowly rejoin it when very few *n*-nonane molecules remain in the zeolite pores: the argon effective chain length at the substep is larger than it would be if a *n*-nonane chain length was simply replaced by an argon chain length in the zeolite pores. On the other hand, contrastingly, the plateau set of values follow the expected linear correlation. Furthermore, the point labelled *A* on Fig. 3 which belong to the substep set of values is lying in the plateau correlation line.

The *n*-hexane systems reveal similar features to the *n*-nonane systems: while the effective chain length linear relationship is obeyed by the system *n*-hexane/nitrogen it is not by the system *n*-hexane/argon. However, as far as the phase transitions of argon and nitrogen are concerned, differences emerge in the thermodynamics data that will be discussed later.

It is also worth noting that when the β_{N_2} occurs, the height of the isotherm step is constant (6 molec·uc^{-1}) while the height of the step corresponding to β_{Ar} increases when the *n*-alkane is further desorbed.

The non linear correlations obtained for the substep effective chain length plots have suggested that the space occupied by the argon atoms is larger than expected. When the steps in the adsorption isotherms accompanied with the peaks in the microcalorimetric traces were observed for the first time, two explanations were suggested [1]. Firstly, a relaxation of the zeolite framework could be induced by the adsorbate allowing more molecules to adsorbe; thus, minor reversible structural changes of Silicalite-I upon adsorption have already been observed for large and rigid molecules [21, 22]; moreover, recent neutron diffraction experiments [23] of ^{40}Ar adsorbed on Silicalite-I do not allow to exclude the possibility of minor structural changes of the zeolite framework upon argon adsorption. Secondly, a phase transition of the adsorbate was suggested and this assumption was supported by neutron diffraction results [4, 5].

The points labelled *A* on Fig. 4 lead to consider the first hypothesis: it seems that, at this stage of *n*-hexane desorption, argon occupies as much space as if the β transition had already occurred. It may then be assumed that the large alkane molecules used may induce a framework relaxation leading to the observed argon behaviour: when removing the *n*-alkane the relaxation of the framework is more and more due to argon alone.

The *n*-butane systems stands apart of the two others. Though, as far as both substeps sets of values are concerned, when the argon or nitrogen effective chain length are plotted *vs.* the *n*-butane effective chain length, a linear correlation can be found. However, these straight lines lie below the 'ideal' line. Therefore, *n*-butane creates inaccessible volumes for argon and nitrogen in the pore network.

In the case of *n*-butane/argon system plateau values, again, some striking differences with the two systems previously examined may be spotted. While the argon plateau set of values was not following a linear correlation with the *n*-alkane effective chain length neither for *n*-hexane nor *n*-nonane, it does for *n*-butane. Moreover, the straight line that can be drawn through the experimental data lies the 'ideal' line which is in agreement with the above statement that *n*-butane leaves inaccessible volumes for the adsorbed molecules.

Argon and nitrogen differential enthalpies of adsorption

As far as the *n*-nonane/nitrogen system is concerned, the transition β_{N_2} is already visible in the microcalorimetric trace when an average of c.a. 0.60 molecules of *n*-nonane per unit cell are still preadsorbed. At this stage of the desorption, the *n*-nonane molecule effective length is 0.8 nm·uc^{-1} that can be split in two contributions: 0.46 nm can be fitted in a straight channel section while the remaining 0.34 nm can be fitted in 31% of two intersections. The space remaining in each of these two intersections is just sufficient to accomodate 1 nitrogen molecule, which is the difference in amount of nitrogen adsorbed between this desorption stage and the previous one. This phenomenon highlights the intersection role in the β_{N_2} transition.

The transition α_{N_2} only becomes visible when an average c.a. 0.07 molecule of *n*-nonane per unit cell remain in the channels or so when only one molecule of *n*-nonane is present in 14 unit cells. This behaviour is highly different from β_{N_2}. However, at this stage of this study, it cannot be affirm that α_{N_2} would not be seen by a more direct technique such as neutron diffraction.

The β_{Ar} transition has already reappeared when 1.5 *n*-nonane molecules per unit cell (or 1 *n*-nonane molecule in every 0.66 unit cell) are present in the Silicalite-I. This is surprising since argon is bulkier than nitrogen and would be expected to need more room to adopt a denser packing than nitrogen One can assume that this transition may be sensitive to the relative orientation of the molecules: argon being spherical, no particular orientation is needed while for nitrogen, especially at high loading, the relative orientation of the molecules may be crucial for β_{N_2} and also α_{N_2} to occur. Simulations studies undertaken recently by Nicholson and Pellenq [24] indicate that this assumption (relative orientation of the adsorbed molecules) is very probable in the case of α_{N_2}.

While the β_{N_2} transition reappears when the *n*-hexane and *n*-nonane molecules occupy roughly the same effective chain length in the zeolite channels (an average of c.a. 0.8 nm·uc^{-1}), the step in the isotherm is much more developped for the nitrogen/*n*-hexane system than it was at the same stage for the nitrogen/*n*-nonane system, which suggests that the β_{N_2} transition could arise before this desorption stage. As far as the α_{N_2} transition of the *n*-hexane/nitrogen system is concerned, the microcalorimetric signal shows that it reappears when an average of c.a. 0.57 molecules of *n*-hexane per unit cell still remain in the pore network (or 0.58 nm·uc^{-1} or also 1 *n*-hexane molecule in every 1.75 unit cell) and so a lot earlier for the nitrogen/*n*-hexane system than for the nitrogen/*n*-nonane system. The same trend is followed by the *n*-hexane/argon system since the peak corresponding to β_{Ar} also shows up earlier than it did for the *n*-nonane/argon system (for 1 *n*-hexane molecule in every 0.30 unit cell or 3.44 nm·uc^{-1} occupied).

As suggested previously, the channel intersections could play a major role in the β_{N_2} transition: *n*-hexane being shorter than *n*-nonane, more space in the intersections is vacant for nitrogen to adsorb. However, no explanations can be suggested yet to take into account the surprising α_{N_2} behaviour.

For the *n*-butane/argon system, the β_{Ar} transition is already visible when as much as 5.54 molecules of *n*-butane per unit cell (or 4.31 nm·uc^{-1}) are adsorbed. This phenomenon yields to assume that some unit cells are perfectly empty of *n*-alkane while others contains much more than 5.54 molecules per unit cell of the *n*-paraffin. The observed adsorption isotherms and microcalorimetric signals being then averaged.

The *n*-butane/nitrogen system reinforces this assumption and is also interesting on its own. Though, the adsorption isotherms obtained contrast strongly with the usual stepped type-I that is observed for the nitrogen adsorption on the bare zeolite and also with the adsorption isotherms that were obtained for Silicalite-I loaded with *n*-hexane or *n*-nonane. Firstly, in this case, the adsorption isotherms appear to be mixed type-I/type-II adsorption isotherms: there is no plateau after the substep nor after the step but a steady increase of the amount adsorbed, which could mean that the adsorption is actually taking place on a non-porous surface as well as in the micropores of the zeolite. Secondly, the number of molecules adsorbed per unit cell after β_{N_2} is well above the zeolite capacity when empty. It may be assumed that nitrogen can displace the *n*-butane present in the channels to the zeolite surface when a sufficient pressure is reached in the sample cell. Thus, a simple calculation, assuming that both *n*-butane and nitrogen are spherical with a Lennard-Jones diameter, shows that at least 5 molecules of nitrogen could be fitted around a molecule of *n*-butane and at least 18 molecules when assuming that the two molecules are cylindrical. Therefore, it does not seem impossible that the *n*-butane rejected from the channels offer enough surface for the nitrogen to adsorb on. One has to keep in mind that the adsorption capacity after the transition α_{N_2} was not unusual and so the pressure in the sample cell needed to displace the *n*-butane would be at least c.a. 300 Pa. In the case of argon adsorption, such a pressure was to reached since the experiment was stopped nearly after the occurrence of the β_{Ar} transition when the pressure in the sample cell is c.a. 130 Pa. Therefore, this behaviour might not be specific of the *n*-butane/nitrogen system but simply a phenomenon due to thermodynamic equilibrium.

No straightforward conclusion can be drawn up to now and more experiments have to be carried on such as determining full adsorption-desorption isotherms for both argon and nitrogen.

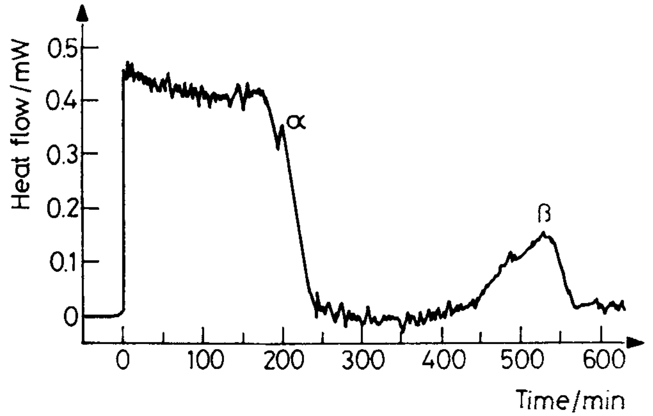

Fig. 5 Recording of the heat flow during nitrogen adsorption on Silicalite-I preadsorbed with *n*-butane

The microcalorimetric curves show striking features as well. Firstly the α_{N_2} transition is present although 1.14 molecules of *n*-butane per unit cell (or 0.88 nm·uc^{-1}) are still adsorbed: once again, this could be the result of some cells being full of *n*-butane and others being absolutely empty of the pre-adsorbate. Secondly, the β_{N_2} transition exothermic peak is split (Fig. 5). Similar effects have been observed for the nitrogen and carbon monoxide adsorption but not for argon adsorption on MFI-type zeolite possessing a distinct zoning of aluminium or iron [25]. An analogous feature was obtained by the authors by mixing a sample of Silicalite-I with a ZSM-5 sample: the structure of these zeolites is similar, only the aluminium contents varies ($Si/Al = \infty$ and $Si/Al < 100$ respectively). As our sample is purely siliceous, the zoning revealed by the microcalorimetry has to be due to the *n*-butane. Therefore, it has to be concluded that *n*-butane is not evenly present in the structure and that it blocks some channels in such a way that the access to some unit cells is prevented, living empty spaces in the micropores. Such a β_{N_2} transition splitting was not observed for the systems *n*-hexane/nitrogen and *n*-nonane/nitrogen. Therefore it may be assumed that *n*-hexane and *n*-nonane are evenly distributed thorough the sample unit cells and, unless at high loading, they do not leave inaccessible voids in the channels.

Conclusion

Neutron diffraction studies have suggested that β transitions of argon and nitrogen adsorbed in Silicalite-I have similar structures. However, in this study, they are found to behave differently when *n*-nonane and *n*-hexane have been preadsorbed onto the zeolite. Thus, argon seems less sensitive to the presence of the *n*-alkanes, suggesting that α_{N_2} and β_{N_2} could be a matter of relative orientation of the adsorbed nitrogen molecules. Moreover, the effective total chain length plots suggest that the zeolite could undergo a structural phase transition under argon adsorption that could be involved for the step in the adsorption isotherm. On the other hand, the preadsorption of *n*-butane in Silicalite-I was shown to give rise to inaccessible volumes in the pores; furthermore, the *n*-butane is not evenly adsorbed in the channel network, as revealed by nitrogen differential enthalpy of adsorption. Eventually, in the case of the *n*-butane/nitrogen system, the adsorption isotherms suggest that *n*-butane can be displaced by nitrogen.

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Zusammenfassung — Zur selektiven Blockung eines Teiles der Mikroporen von Silicalite-I, eines MFI-Zeolithen, wurden *n*-Alkane verschiedener Kettenlänge präadsorbiert. Anschließend wurde mittels Quasigleichgewichts-Adsorptionsmikrokalorimetrie und Volummetrie bei 77 K die für Argon und Stickstoff zugängliche Porösität untersucht und mit den Werten für unbelegtes Zeolith verglichen. Obwohl eine partielle Adsorption von *n*-Alkanen den Wert von Adsorptionsenthalpiedifferenzen weder für Argon noch für Stickstoff verändert, reduziert die Präadsorption von *n*-Butan die Adsorptionskapazität durch die Schaffung unzugänglicher Porenvolumina im Mikroporennetz. Außerdem zeigen die mikrokalorimetrischen Versuche eindeutig, daß *n*-Butan im Gegensatz zu längeren *n*-Alkanen ungleichmäßig im Kanalsystem des Zeolithen verteilt ist.