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Evaluation of the n-nonane preadsorption method with a well characterized model adsorbent: Silicalite-I

*Y. Grillet, P. L. Llewellyn, M. B. Kenny, F. Rouquerol & J. Rouquerol**

Centre National de la Recherche Scientifique, Centre de Thermodynamique et de Microcalorimétrie, 26 Rue du 141ème R.I.A., 13003 - Marseille, FRANCE

Abstract

The n-nonane preadsorption technique is analysed here, using a well characterized model adsorbent : silicalite-I.

Controlled Rate - Evolved Gas Analysis allows the precise quantity of n-nonane retained to be known. In this case the n-nonane totally blocks the microporous channels of silicalite-I without allowing diffusion of the adsorbate. Quasi-equilibrium microcalorimetry shows that the adsorbent nature is not modified by the n-nonane and also supplies supplementary information on previously noted argon and nitrogen adsorbate transitions. However, initial desorption of the n-nonane renders certain void regions of the microporous network inaccessible to the adsorbate.

INTRODUCTION

The n-nonane preadsorption method (NP-method) has long been recognised as one of the standard method for the characterization of microporous solids. This technique, introduced by Gregg and Langford [1], arose from the observation that n-nonane desorbs infinitely slowly from micropores at ambient temperatures. It is widely used for the determination of total micropore volume, particularly for activated carbons. It is also used as a method to measure the external surface area of a sample, catalysts for example. This explains why it has been recommended by both Gregg and Sing and the IUPAC as a technique to estimate micropore distribution [2,3].

Many people however, have voiced caution to the blind use of the NP-method. Sing for instance, has pointed out that this technique is not always 'direct' and that precautions should be taken in the interpretation of results [4] and above all he recommends that this technique be used with the adsorption of probe molecules at low temperatures (e.g. nitrogen and argon at 77 K) as at ambient temperatures, diffusion past the n-nonane may occur [2]. Rodríguez-Reinoso related the quantity of n-nonane taken up by activated carbons at a certain temperature with the various proportions of larger micropores [5]. He thus concluded that this method 'fails' if at a carbon has a large range of micropores biased towards the larger end.

Carrott and Sing have proposed a relationship between the temperature and the size of pores from which n-nonane desorbs [6]. This is, however, a first approximation as seen from the work of Guerrero-Ruiz and Grillet [7]. In taking examples of carbosieve and the zeolites 5A and 13X, they show that the desorption of n-nonane is governed by a diffusion process related to the adsorbent micropore size and thus is not liberated at a defined temperature.

* The manuscript was received in the editorial office of this journal before the symposium. However, it was not presented because of the lecturer's inability to attend the meeting due to unavoidable circumstances.

The aim of this study therefore, is to test the validity of this NP-method in taking a well crystallized "model microporous adsorbent", silicalite-I [8], for which the physisorption effects observed depend only on van der Waals forces (the structure is electrically neutral in theory). More importantly however, this study has employed an adsorbent whose adsorption characteristics with nitrogen and argon are well documented and thus a secondary aim is to further understand the physisorption observed.

In order to closely follow the stages of physisorption of argon and nitrogen as well as the modifications on n-nonane preadsorption, three specific techniques are employed. The n-nonane desorption is precisely determined with Controlled Rate Evolved Gas Analysis (C.R.-E.G.A.[9]). adsorption is followed by both the widely used method of static volumetry and by quasi-equilibrium volumetry itself coupled with isothermal microcalorimetry [10]. This latter technique proffers the simultaneous tracing of the adsorption isotherm and the curve of differential enthalpies of adsorption during the micropore filling process.

EXPERIMENTAL

Adsorptives and adsorbents

The **n-nonane** employed is a gas phase chromatography reference sample (99.6 % minimum purity) obtainable from Prolabo. Before use it is doubly distilled to ensure purity. The other adsorptives used are of high purity grade (99.995 % minimum purity) from Alphagaz (Air Liquide), France.

Silicalite-I is the pure silica end member of the zeolite MFI-structure series [11]. Its well characterized microporous network consists of straight channels, elliptical in cross section (0.52 x 0.56 nm) and sinusoidal shaped channel which are quasi-circular (0.54 x 0.56 nm) in cross section. These two channel systems connect with each other, giving rise to intersections of around 0.8 nm in diameter.

The silicalite-I samples used are from two sources. The first was obtained via the alkaline free synthesis route [12] and kindly prepared at K. K. Unger's laboratory at the Johannes Gütenberg Universistät in Mainz, Germany. The crystals obtained have a homogeneous size distribution of approximately 120 x 30 x 30 μm in dimension. The second sample was kindly prepared at J. L. Guth's laboratory at the Ecole de Chimie in Mulhouse, France. This sample was obtained in a fluoride medium [13] and consists of crystals approximately 600 x 120 x 120 μm in dimension with a narrow size distribution. Both samples were calcined up to 823 K. The two samples give exactly the same adsorption isotherms and microcalorimetric results for argon and nitrogen.

Outgassing

The samples are initially outgassed using Controlled Rate - Evolved Gas Analysis (C.R.-E.G.A. [9]) developed by Rouquerol. It may also be described as Controlled Rate - Temperature Programmed Desorption (CR-TPD) in that it keeps the a constant rate of outgassing (under a residual pressure which is here 0.133 Pa) by appropriate heating of the sample. This technique permits a reproducible and homogeneous preparation of the surface state of a sample and reduces the part of the storage conditions.

N-nonane preadsorption

The NP-method, as developed by Gregg and Langford [1] is used as a base for the modified procedure using C.R.-E.G.A. [7].

Firstly the n-nonane is preadsorbed onto the sample at a temperature of 296 K for 16 hours. Then the excess n-nonane is removed from the sample cell by evacuating up to a vacuum pressure of 1.33 x 10^{-2} Pa at 296 K. The n-nonane is then treated via C.R.-E.G.A. to gradually *desorb* the n-nonane allowing a ***precise control of the rate and extent*** of this thermal desorption process. This control is usually lacking in the case of the conventional isothermal outgassing commonly used with the preadsorption method. Once the total thermal desorption curve is obtained, the sample is again left to preadsorb n-nonane with the excess again removed under vacuum at 296 K. The second C.R.-E.G.A. treatment is then stopped at various points, to allow adsorption of argon or nitrogen, and then restarted from the very point left off without any problem.

Adsorption gravimetry, volumetry and microcalorimetry

The adsorption - desorption isotherms of n-nonane vapour at 296 K on silicalite-I are obtained on a gravimetric apparatus developed 'in house' with a continuous quasi-equilibrium method of vapour introduction [14]. This method allows a continuous collection of data via a microcomputer increasing the resolution of the isotherm several fold compared to normal static introduction techniques.

The adsorption - desorption isotherms of nitrogen at 77 K are obtained via a commercial apparatus (Omnisorp 100, Coultronics S. A., France) where a static, 'point by point' introduction of adsorptive was used.

The microcalorimetric data for argon and nitrogen at 77 K are obtained on an apparatus also constructed 'in house' [10] employing a quasi-equilibrium adsorptive introduction procedure allowing adsorption up to a pressure of around 35 kPa. This apparatus permits the direct continuous measurement of the differential enthalpies of adsorption $\Delta_{ads}\hat{h}$ (or the "net" enthalpies of adsorption if the relevant enthalpy of liquefaction or sublimation at 77 K is subtracted from $\Delta_{ads}\hat{h}$), during the vertical (or near vertical) parts of the isotherm, i.e. at very low relative pressure and also when other adsorption phenomena occur within micropores.

At several points after the adsorption, the samples are re-heated under vacuum pressure to eliminate the adsorbate. The sample is then re-cooled to 77 K, thus re-freezing the n-nonane, and the experiment repeated to confirm the result.

RESULTS AND DISCUSSION

The ***adsorption of n-nonane*** on silicalite-I at 296 K as followed by gravimetry reveals an isotherm of essentially type-I character [2] (figure 1) with a small substep shown by the arrow at a relative pressure around 0.2. This substep has not, to the authors knowledge, been previously observed and is most likely to be the result of a reorganization of the adsorbate phase. Desorption of the n-nonane gives rise to a hysteresis of type H4 [2]. This phenomenon being due to the nature of adsorptive and adsorbent may be resultant of adsorption in microporous defect regions within this large crystal sample as has been put forward elsewhere for other zeolitic adsorption systems [15-17]. The final point reached, after desorption for 16 hours at the experimental temperature under a vacuum pressure of 1.33 x 10^{-2} Pa, is an uptake of 3.74 molecules per unit cell. This value coincides well with both the point at which the adsorption branch parts from $p / p^0 = 0$ and also the values obtained during the separate preadsorption experiments with the volumetric sample cells.

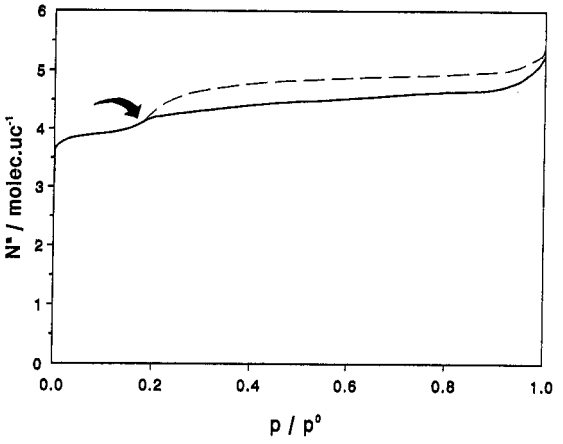

Figure 1 : Adsorption (full line) - desorption (broken line) isotherm of n-nonane on silicalite-I at 296 K.

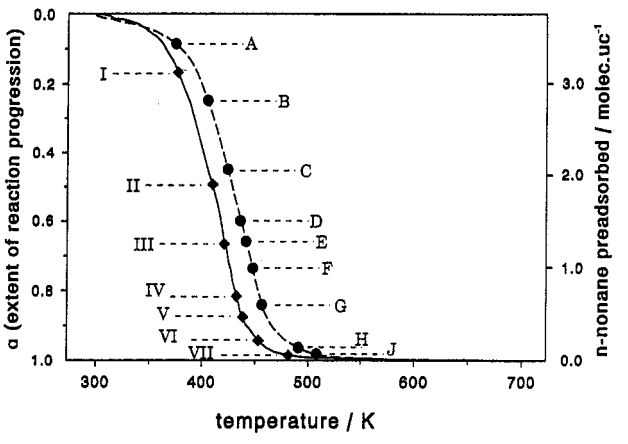

Figure 2 : C.R.-E.G.A. curves for the thermodesorption of n-nonane from silicalite-I. The full line correspond to the static volumetry experiments and the broken line corresponds to quasi-equilibrium microcalorimetry experiments. The points mark where the thermodesorption was stopped and correspond to the curves in later figures.

The ***C.R.-E.G.A. curves*** shown in figure 2 represent the liberation of n-nonane with temperature. These results support the conclusions of Carrott *et al* [6] on microporous carbons in that the n-nonane, with a minimum kinetic diameter of 0.43 nm, desorbs from the silicalite-I micropores essentially at a temperature of 400 - 450 K. However, it should be appreciated that the C.R.-E.G.A. technique proffers a more precise determination of n-nonane desorbed. The two curves shown in figure 2 are of the same general shape, typical of diffusion processes, and similar to those presented elsewhere for the desorption of n-nonane from zeolites 5A and 13X [7]. However, the shift in temperature results from a difference in the residual pressure above the sample due to sample cell geometry (the sample cell used for microcalorimetry has a much longer capillary than a normal volumetric cell [10] resulting in a somewhat higher residual pressure above the sample.

The activation energy is calculated from a transformation of the C.R.-E.G.A. curves in figure 2. This transformation of α (the extent of reaction progression) by an equation derived from Ficks Law and the Arrhenius Law ***implying a 3-d diffusion process*** leads to a plot of $\ln[f(\alpha)]$ against 1 / T (figure 3). This gives a value of around 70 kJ.mol^{-1} which compares well with values calculated for smaller homologous molecules on the MFI-type zeolites [17,18].

Previously, the ***adsorption of argon and nitrogen at 77 K*** on well crystallized samples of silicalite-I has given rise to unusual stepped isotherms [20-25]. In the case of argon, the isotherm obtained is of type I character with one additional substep 'β' (figure 4a). This substep has been further examined via isothermal microcalorimetry [21-24] and neutron diffraction [24] revealing an adsorbate phase transition of the type :

"mobile fluid phase" $\Leftrightarrow$ "crystalline solid-like phase" ....."β"

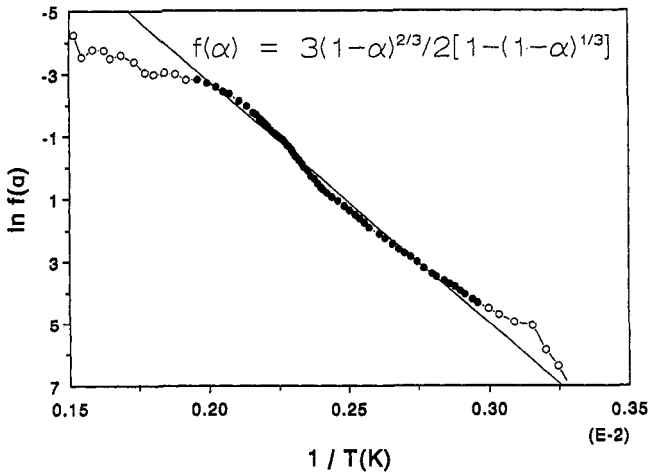

Figure 3 : Curve showing the transformation of α against 1/T for the calculation of the desorption activation energy.

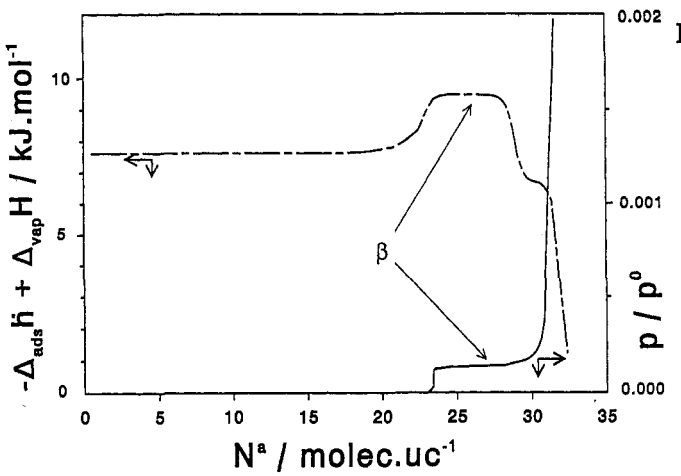

Figure 4a : The net enthalpy curves and initial isotherm for ***a, argon*** and ***b, nitrogen*** on silicalite-I obtained by quasi-equilibrium volumetry and microcalorimetry at 77 K. Note the regions in each curve which correspond to the respective phase changes 'α' & 'β'.

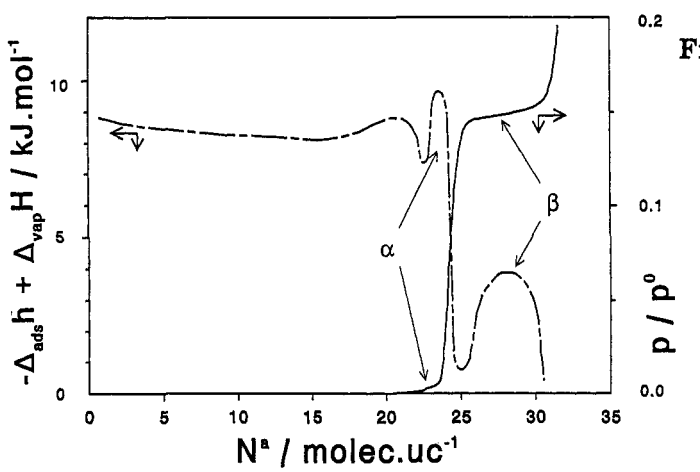

Figure 4b : The net enthalpy curves and initial isotherm for ***a, argon*** and ***b, nitrogen*** on silicalite-I obtained by quasi-equilibrium volumetry and microcalorimetry at 77 K. Note the regions in each curve which correspond to the respective phase changes 'α' & 'β'.

Nitrogen adsorption however, reveals a type I isotherm with two substeps 'α' and 'β' (figure 4b). Again, further examination by isothermal microcalorimetry [20-22,24] and neutron diffraction [24] reveals two adsorbate phase transitions of the type :

"mobile fluid phase" ⇔ "mobile, slightly organized fluid phase" ....."α"

"mobile, slightly organized fluid phase" ⇔ "crystalline solid-like phase" ....."β"

The solid-like adsorbate phases obtained for both argon and nitrogen are similar in structure and furthermore *structure directed or commensurate* with the adsorbent micropore network [24,25].

The isotherm obtained after the n-nonane preadsorption (3.74 molec.uc^{-1}) is of type III character [2] (figure 5). This is indicative of weak adsorbate - adsorbent interactions and shows the total inaccessibility of the nitrogen to the microporous structure of silicalite-I after n-nonane preadsorption. This also indicates the very small external surface area of the sample (less than 0.2 $m^2.g^{-1}$) and thus the phenomena observed later may be taken to be due to the microporous structure. At point 'A' in the C.R.-E.G.A. curve (figure 2), the adsorption of nitrogen did not give rise to any appreciable adsorption and thus is not presented.

Gradual removal of the n-nonane allows accessibility to the silicalite-I channel network resulting in Langmuir type-I isotherms without any substep (figure 6a, curves 'I', 'II', 'III' & 'IV'). The uptake of nitrogen at $p / p^0 = 0.8$ for curve 'I' is less than the volume available (see table 1). This highlights a major disadvantage of this n-nonane preadsorption procedure in that the volume of silicalite-I liberated on desorption of the n-nonane is ***not totally*** accessible to the nitrogen adsorptive. It can be appreciated that this problem would be even greater for microporous solids with a unidimensional channel system where only two molecules are required to block the totality of the pore. However, for curves 'II', 'III' and 'IV' the total uptake of the 'fluid-like nitrogen phase' and n-nonane at $p / p^0 = 0.8$ is constant and equal to the value obtained for n-nonane at the same relative pressure (figure 1). This shows that ***the total volume liberated on desorption of n-nonane is accessible to the nitrogen*** via the three dimensional silicalite-I microporous network. Curves 'B',

Table 1 : Various principal uptakes at $p / p^0 = 0.8$ obtained from the gravimetric, C.R.-E.G.A., volumetric and microcalorimetric curves for the adsorption of n-nonane and nitrogen on silicalite-I.

point	N^a (n-nonane) molec.uc^{-1}	N^a (nitrogen) molec.uc^{-1}	V_{total} (N-C9 + N_2) $cm^3_{(liq)}.g^{-1}$
end of n-nonane des^n	3.74	-	0.116
n-nonane ads^n ($p/p^0 = 0.8$)	4.64	-	0.144
I	3.12	4.7	0.125
II	1.89	14.0	0.143
III	1.25	17.6	0.145
IV	0.67	20.8	0.146
G	0.60	*21.1*	*0.144*
V	0.47	*21.9* 25.8	*0.146* ***0.148***
VI	0.21	*24.2* 29.9	*0.152* ***0.161***
VII	0.05	*24.2* 31.0	*0.147* ***0.161***
O	-	*24.3* 31.4	*0.146* ***0.161***

* total theoretical micropore volume 0.19 $cm^3 . g^{-1}$ (from [8]).

* values in simple italics are those taken before the sub-step 'β' where observed (the nitrogen adsorbate phase is taken to be of 3-d liquid density) whereas the values in bold italics indicate that the 3-d solid density of nitrogen is taken.

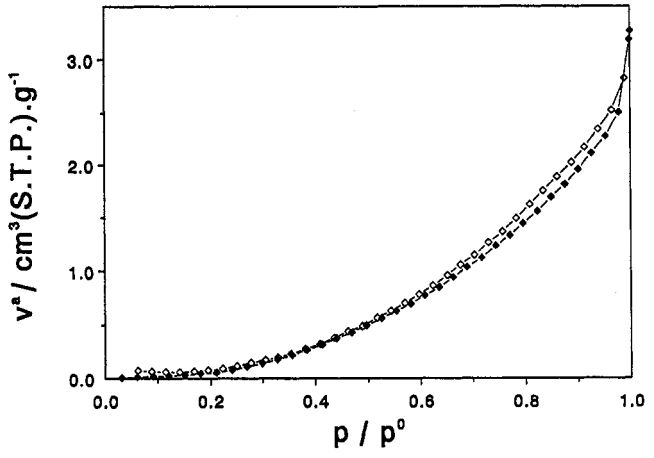

Figure 5 :
Nitrogen adsorption - desorption isotherm obtained at 77 K on silicalite-I initially preadsorbed with n-nonane

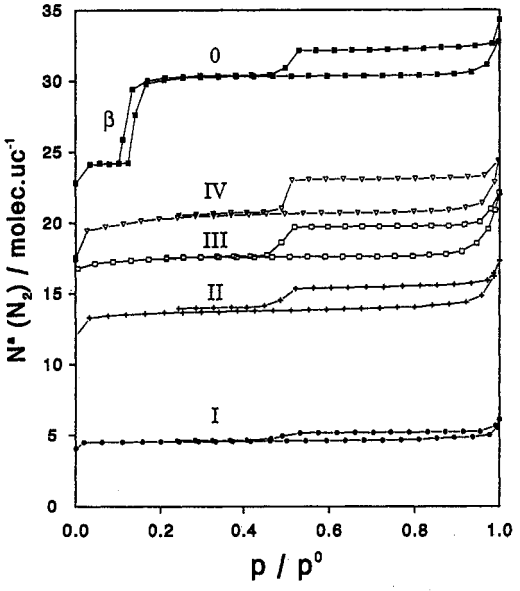

Figure 6a : *Nitrogen* adsorption - desorption isotherms obtained at 77 K on silicalite-I after preadsorption of various quantities of n-nonane corresponding to the points (I to IV) marked in figure 2.

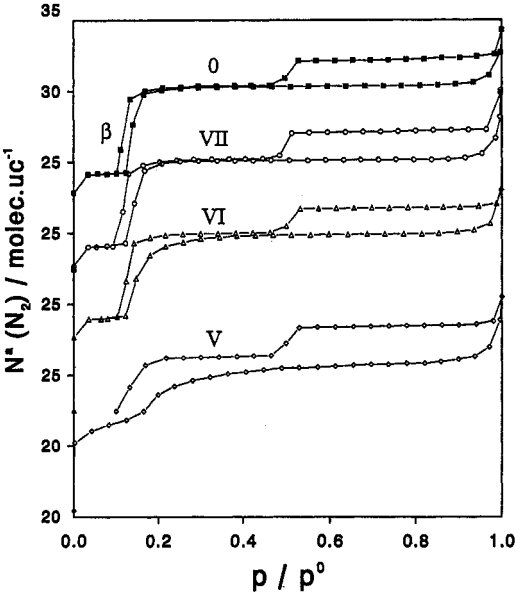

Figure 6b : *Nitrogen* adsorption - desorption isotherms obtained at 77 K on silicalite-I after preadsorption of various quantities of n-nonane corresponding to the points (V to VII) marked in figure 2. The points are offset for clarity.

'C', 'D' and 'E' (figure 7) also reflect the increasing adsorption volume available with the gradual liberation of n-nonane. It may be noted here, that the near horizontal region for each curve presented is of the same value (around -9.7 $kJ.mol^{-1}$) as that obtained without preadsorption (curve '0'). This indicates both immediate liberation of the structural micropores by the n-nonane (in which the nitrogen preferentially adsorbs) and more importantly that neither chemical modification nor specific interaction occurs due to the n-nonane.

The appearance of the high pressure hysteresis during initial liberation of the n-nonane further highlights the conclusions noted elsewhere [26] in that it is caused by large microporous defect regions within the crystal structure (for example between internal crystallites), accessible after partial liberation of the n-nonane (practically no hysteresis is evident when the pores are totally blocked by the n-nonane : figure 5).

Between curve 'IV' in figure 6a and 'G' in figure 7, a liberation of ***only 0.07 molecules of n-nonane per unit cell of silicalite-I*** which is enough to view the appearance of a nitrogen adsorbate transition. The isotherm substep and microcalorimetric peak observed are obviously relative to 'β' mentioned previously and thus due to an adsorbate transition of the type 'fluid-like phase' ⇔ 'solid-like phase'[25]. The quantity of n-nonane liberated between 'IV' and 'G' (see figure 2) corresponds to the space required for adsorption of an additional **0.3 nitrogen molecules per unit cell** : 20.8 in 'IV' to 21.1 in 'G' before the transition (see table 1). This may be explained in terms of the number of adsorption sites liberated. Atom-atom potential calculations have shown that 12, 8 and 4 potential minima are located within the sinusoidal channels, straight channels and intersections respectively per unit cell [21]. Thus assuming that the n-nonane rests preferentially within the channel intersections suggested [27], the difference in uptake between 'IV' and 'G' corresponds to the initial global connection of the nitrogen located within the channels (20 in total) by nitrogen within the intersections. This highlights the ***global continuity*** of the adsorbate phase in three dimensions that is required to provoke this phase change. This effect may be more clearly appreciated for curves 'VI', 'VII' and O where all the adsorption sites are taken up both in the channels and intersections (24 in total) indicating a total integrality of the liquid-like adsorbate required before transition occurs.

This substep, viewed in curve 'V' (figure 6b) is well inclined and offset to a higher pressure when compared to curve '0' (with no n-nonane preadsorbed). This indicates the role of the steric hindrance of the n-nonane on the adsorbate phase transition where the adsorbate may be imagined to pass through a maze-like channel network, partly blocked by n-nonane, then taking up the available adsorption sites and finally reaching the continuity needed for the phase transition to occur. This effect compares and contrasts with that viewed on the adsorption of nitrogen by HZSM-5 [23,25]. Similarly with this result, the substep becomes more inclined with increasing aluminium content and thus increasing cation concentration within the sample structure and micropores respectively. However, in contrast, the substep is offset to lower pressures. This shows both the role of steric hindrance from the compensatory cation and also the effect of preferential adsorption towards these sites.

Further removal of n-nonane results in the 'redressing' of the substep to a more vertical position and lower pressure (figure 6b). The low pressure hysteresis (below $p / p^0 = 0.42$) associated with this substep also seems to redress with the increased liberation of n-nonane. However, the form of the desorption branch seems to vary much less than that of the adsorption. This may indicate that once the 'solid-like' phase is formed, its structure is similar to that viewed on a sample without n-nonane, thus commensurate, and it acts independently of the n-nonane present.

Curve 'H' (figure 7) is the first in the series to show a peak corresponding to the transition 'α' : a transition of the type 'fluid-like phase' ⇔ 'localized fluid-like phase' [25]. Unfortunately the phenomenon remarked in the net enthalpy curves, obtained via a constant adsorptive introduction, is not able to be detected via the static, point by point, method of introduction employed in the volumetric experiments due to the lack of resolution attainable. The importance of this transition increases with n-nonane removal. However, it can be appreciated that at 'J', the importance of 'α' is greatly reduced by the presence of only 0.07 molecules of n-nonane per unit cell and furthermore at 'H', this transition is almost unobservable with less than 4 % of the original quantity of n-nonane present. These features again highlights the sensitivity of the adsorbed nitrogen phase transition to extend the continuity of this phase.

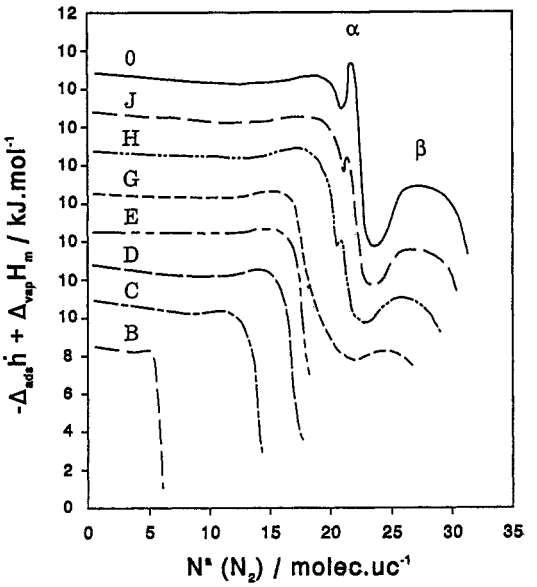

Figure 7 : Net enthalpy curves for the adsorption of ***nitrogen*** at 77 K on silicalite-I preadsorbed with various quantities of n-nonane corresponding to the points marked in figure 2. The curves are offset for clarity.

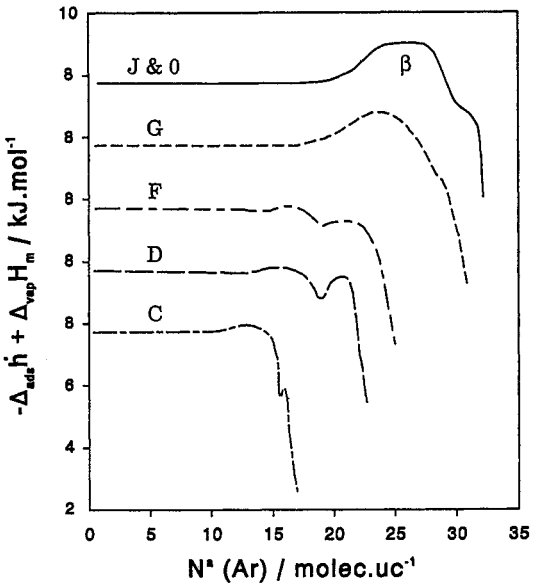

Figure 8 : Net enthalpy curves for the adsorption of ***argon*** at 77 K on silicalite-I preadsorbed with various quantities of n-nonane corresponding to the points marked in figure 2. The curves are offset for clarity.

The ***argon net enthalpy curves*** (figure 8), all exhibit an initial horizontal region of the same value indicating both an adsorbate homogeneity to argon and also that the n-nonane does not affect the nature of argon adsorption. However, these curves reveal a contrasting behaviour of argon compared to that of nitrogen. It can be seen that all of the curves presented exhibit a region suggesting an adsorbate density change. The region 'β', corresponding to a transition of the type 'fluid-like phase' ⇔ 'solid-like' phase [21,22,24], is practically not at all affected by the presence of a small amount of n-nonane : curve 'J' is very similar to curve '0'. This contrasts greatly with the behaviour of nitrogen (figure 7, curve 'J'). The preadsorption of n-nonane at point 'G', sufficient to almost cause the disappearance of the substep 'β' for nitrogen, shows only a small effect on the adsorption of argon (figure 8, curve 'G'). The curves 'F', 'D' and 'C' in figure 8 show a decreasing importance of the corresponding exothermic effect with increasing n-nonane preadsorption. However, it is possible to interpret a sterically hindered argon transition which most probably does lead to the same 'solid-like phase' as observed without n-nonane present. It would thus seem that the argon 'fluid-like' adsorbate does not require the same degree of global, three dimensional continuity as that of nitrogen.

CONCLUSIONS

The use of a well crystallized and previously characterized sample of the model adsorbent, silicalite-I, has allowed a study of the validity of the n-nonane preadsorption method (NP-method). This study was greatly aided by the techniques developed 'in house' : C.R.-E.G.A. and quasi-equilibrium microcalorimetry.

From a positive point of view, C.R.-E.G.A. highlights the diffusion controlled desorption process and provides a precise determination of the n-nonane retained by the silicalite-I. The n-nonane lends itself well to this study as it totally blocks the void space occupied (no diffusion effects are detectable for nitrogen or argon) and does not chemically affect the adsorption. Quasi-equilibrium microcalorimetry allows a high resolution tracing of the net enthalpy curve which proves essential in verifying both the lack of interaction of the preadsorbate with the adsorbent and also for detecting certain physisorption phenomena difficult to observe in the adsorption isotherm. What is more, this technique allows supplementary information to be obtained on the physisorption phenomena present : in this case, the phase transitions of argon and nitrogen.

However, from a negative stand-point, the n-nonane initially rendered certain regions of the microporous structure inaccessible to the adsorbate however at later stages of the desorption the volume liberated by the n-nonane becomes available to the adsorbate. Furthermore, for $AlPO_4$-5, with pores of 0.74 nm in dimension, n-nonane does not totally block the porous system to argon as diffusion is detectable. This shows the requirement of the molecule used in preadsorption to be ***compatible***, both chemically inert in the adsorption process and also large enough to totally block the porous system and even so, care should be taken in using this technique.

The previously noted ***nitrogen adsorbate transitions*** are greatly affected by the presence of n-nonane. 0.07 molecules of n-nonane per unit cell of silicalite-I are sufficient to diminish drastically the importance of the first transition ('α') and 0.67 molecules per unit cell are sufficient to hinder the second ('β'). The transition 'β' seemed to occur only after adsorption within the channel intersections started. It would therefore seem that the nitrogen adsorbate phase requires a three dimensional global continuity to undergo these transitions. That is to say that it is both the micropore size and moreover the three dimensionality of the silicalite-I microporous network that leads to the nitrogen adsorbate transitions.

The case for ***argon adsorption*** however, contrasts greatly with that of nitrogen. With over 50 % of the total argon uptake impeded by the n-nonane, a signal in the microcalorimetric curve still indicates a transition, although greatly affected by n-nonane confinement. It would thus seem in this case that the argon is not as exigent as nitrogen and does not require the three dimensional continuity like nitrogen. Moreover, the argon adsorbate transition seems to be driven by the spatial confinement of the micropores themselves rather than the three dimensionality of the silicalite-I channel system.

Acknowledgements

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