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A microcalorimetric comparison of the adsorption of various gases on two microporous adsorbents: a model aluminophosphate and a natural clay [1]

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Abstract

A comparison was made of the physisorption mechanisms of various adsorptives (Ar, CH_4, N_2 and CO) on two microporous adsorbents: an aluminophosphate, $AlPO_4$-5 with an electrically neutral framework and cylindrical pores of 0.73 nm diameter, and sepiolite, a fibrous natural clay with micropores of rectangular cross-section (1.34×0.67 nm^2). Isothermal microcalorimetry at 77 K of probe molecules, either with or without a permanent moment (dipolar or quadrupolar), allowed the determination of the successive steps of micropore filling, an evaluation of their relative importance and, finally, an indication of apparent changes in the phase adsorbed by the aluminophosphate.

In the case of $AlPO_4$-5, the adsorption of the various gases occurred by site in the micropores in only one stage. However, for sepiolite, the adsorption occurred in two steps, initially by site in the intrafibrous structural micropores and then by volume in the interfibrous micropores.

INTRODUCTION

In this study, a comparison is proposed of the adsorption mechanisms of various probe molecules, either possessing a permanent dipole/quadrupole moment or not, on a synthetic aluminophosphate of structure AFI: $AlPO_4$-5 [1] and on a fibrous clay of the Palygorskite group, sepiolite [2]. These adsorbents are microporous, i.e. they contain pores of width less than 2 nm [3]. The micropores of these adsorbents are all rectilinear and mutually parallel without intersections. In contrast to zeolites, $AlPO_4$-5 contains an

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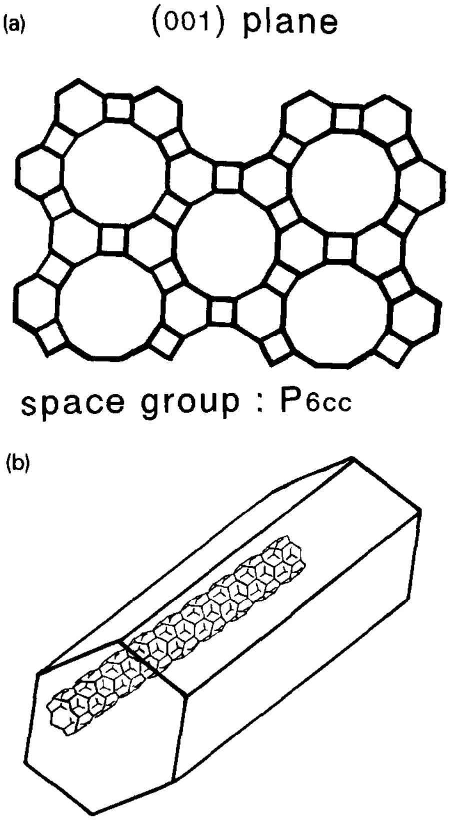

Fig. 1. $AlPO_4$-5: the coupled rings of four and six oxygens forming rings of 12 oxygens (a) which are then stacked to form unidimensional channels 0.73 nm in diameter (b).

electrically neutral framework, and its micropores have a circular cross-section 0.73 nm in diameter (Fig. 1), whereas those of sepiolite have a rectangular cross-section [2] of 1.34 × 0.67 nm^2. The former adsorbent can be considered as a model adsorbent, whereas the latter, of natural origin, is heterogeneous in both structure and texture.

It is anticipated that the combined use of the adsorption isotherms and microcalorimetric data should allow one to highlight the existence of the successive steps of micropore filling, variations of the mobility and/or density of the adsorbate, and, finally, the extent of specific interactions, taking into account the existence of a dipole or quadrupole moment of the adsorbed molecule.

EXPERIMENTAL

Differential scanning calorimetry (DSC990, Du Pont de Nemours) and controlled rate thermal analysis (CRTA [4]) were used for the determina-

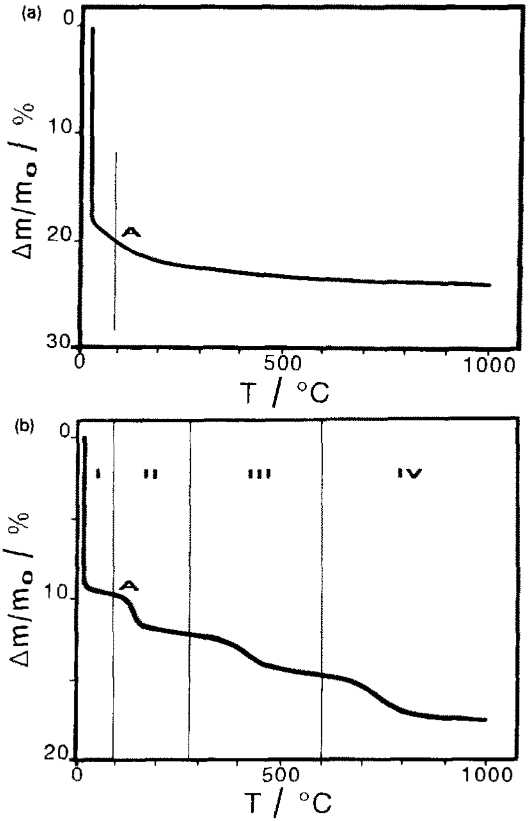

Fig. 2. Thermogravimetric curves of (a) $AlPO_4$-5 and (b) sepiolite.

tion of the outgassing temperature, i.e. that sufficient for the elimination of physisorbed (or zeolitic) water within the solids but without causing dehydroxylation of the surface.

It would seem in looking at Figs. 2 and 3 that the DSC results indicate more clearly the temperature of the departure of physisorbed water from the samples. However, the scanning rate used in DSC (5–20°C min^{-1}) leads to a temperature shift which is essentially avoided in the CRTA experiments. Thus CRTA is preferred to determine the actual outgassing temperature, which is why, before each adsorption experiment, the samples (approx. 100 mg) were treated up to 80°C using CRTA with a residual water vapour pressure of 1.33 Pa in order to reproduce, independently of the previous storage conditions, the same surface state of the adsorbent before further analysis.

The adsorption measurements were carried out either by point by point automatic static volumetry [5] or by quasi-equilibrium volumetric adsorption [6], in which the introduction of the adsorptive was both continuous and extremely slow, of the order of 2 cm^3 h^{-1}, a condition for which it has

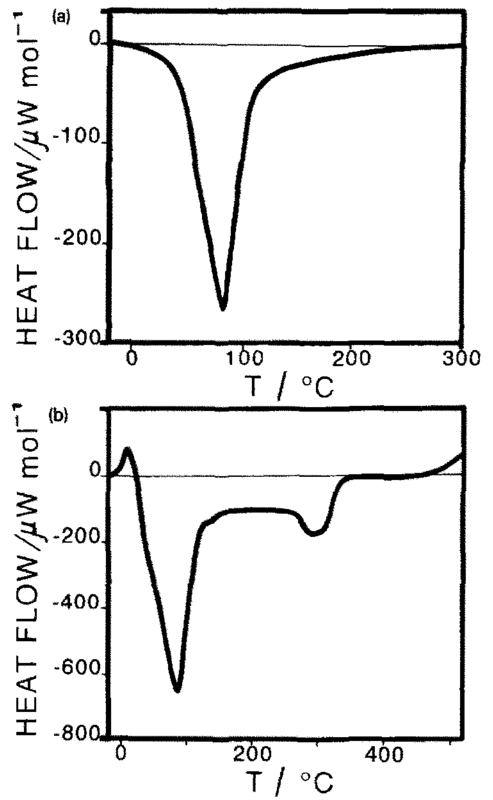

Fig. 3. Analytical curves from differential scanning calorimetry of (a) $AlPO_4$-5 and (b) sepiolite.

been checked that all of the systems studied were "at equilibrium" [6]. This latter technique associated with isothermal adsorption calorimetry at 77 K [7] allows one to obtain directly a continuous measurement of the derived enthalpies of adsorption $\Delta_{ads}\dot{h}$ during the vertical parts of the isotherm, i.e. at the very beginning and also when the adsorption phenomena occur within the micropores.

The $AlPO_4$-5 sample was synthesized at the laboratory of Professor K.K. Unger in Mainz (Johannes-Gutenberg Universität). The sample designated (5.2) consists of "large" crystals (150 μm) which are well defined. This aluminophosphate consists of TO_4 tetrahedra in which the T-sites are occupied by aluminium and phosphorous atoms alternately. According to Wilson and Regent [8], the structure itself consists of alternately coupled rings of four and six oxygen atoms stacked in columns parallel to the highest crystal symmetry axis, which thus form rings of 12 oxygen atoms producing cylindrical channels of 0.73 nm in diameter. $AlPO_4$-5 crystallizes in a hexagonal arrangement (Fig. 1) with unit cell dimensions $a = 1.37$ nm and $c = 0.84$ nm. The crystal may exhibit some structural defects, giving rise to the presence of Al–OH and P–OH groups [9].

Sepiolite is a fibrous magnesium silicalite which crystallizes in an orthorhombic arrangement with a general formula for half the unit-cell of $Si_{12}Mg_8O_{30}(H_2O)_4 \cdot 8H_2O$ and whose dimensions [10] are $a = 1.34$ nm, $b = 2.68$ nm and $c = 0.528$ nm. This clay appears in the form of talc-like sheets, arranged quincuncially and forming rectangular channels (1.34×0.67 nm^2) parallel to the axis of the fibres.

The adsorptives used (of N48 and N55 quality, from Alphagaz, Air Liquide) were of two types: those which give rise to only dispersion–repulsion forces, such as argon and methane, and those, such as nitrogen and carbon monoxide, which can additionally give rise to electrostatic type interactions.

RESULTS AND DISCUSSION

Thermal analysis

The CRTA results are shown in Fig. 2.

At first sight, these curves appear very different; for $AlPO_4$-5, a continuous dehydration is observed up to 1000°C, whereas in the case of sepiolite three dehydration steps are distinguishable. Nevertheless, a similarity between the two curves can be seen up to point A, around 80°C, where the loss of physisorbed water occurs. This phenomenon has already been noted in the case of Palygorskites (attapulgite and sepiolite) by Barrer [11]. The dehydroxylation of the two samples begins at about 80°C. The relative weight losses obtained between 80 and 1000°C were 3.2% for $AlPO_4$-5 and 7.4% for sepiolite.

The dehydroxylation follows three distinct steps in the case of sepiolite. The region I corresponds to the loss of physisorbed water (9.7% of the initial sample weight). The regions II and III correspond to the loss of water bound to the magnesium atoms at the edge of the sheets. The loss of water in the region II, between 80 and 300°C, is reversible and represents 2.7% of the initial weight. Loss of the rest of the water, taking place in the region III between 300 and 600°C, is irreversible and accompanied by a breakdown of the microporosity [12]. The final weight loss increment of 2.4% above 650°C is due to a dehydroxylation of the mineral itself.

The results obtained by differential scanning calorimetry with liquid nitrogen cooling (Fig. 3) are consistent with those of CRTA.

The peak observed for $AlPO_4$-5 and the first peak observed for sepiolite may be attributed to the loss of physisorbed water. The second peak observed for sepiolite corresponds to the first loss of water bound to the magnesium (region II of the CRTA).

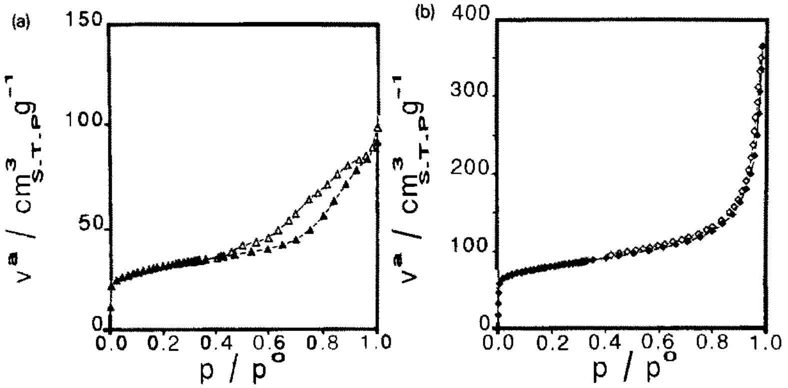

Fig. 4. Adsorption isotherms of nitrogen at 77 K on (a) $AlPO_4$-5 and (b) sepiolite obtained by static volumetry.

Adsorption of argon, methane, nitrogen and carbon monoxide at 77 K

The adsorption isotherms of nitrogen obtained by static volumetry are shown in Fig. 4. Both of them contain a plateau region as well as a hysteresis loop in the region above a relative pressure of 0.4. However, for sepiolite the hysteresis loop is not at all distinguishable, thus indicating that this clay contains no (or few) mesopores ($2 < d < 50$ nm) [3] and that it has a large external surface [2,13]. The $AlPO_4$-5 sample (Fig. 4a) has large individual crystals but nevertheless produces a significant hysteresis loop. The B.J.H. Method [14] applied to the desorption curve gives a mesopore distribution spread between 2 and 20 nm with a predominance of pores with an opening of 10 nm.

The adsorption isotherms of argon, methane, nitrogen and carbon monoxide at 77 K obtained by quasi-equilibrium volumetry in the relative pressure region below 0.2 and the curves of the corresponding derived enthalpies are given in Figs. 5 and 6. Putting aside the case of methane, all the isotherms are similar for $AlPO_4$-5 but quite dissimilar for sepiolite. The fact that the same number of molecules are adsorbed per unit cell independent of the adsorptive introduced can be interpreted as an adsorption by site, i.e. on sites of highest energy, on the inner surface of the aluminophosphate micropore. This is confirmed elsewhere by the calculation of the potential energy distribution using the Lennard-Jones approximation from the position of the oxygen atoms, which leads to a theoretical maximum loading of four argon atoms adsorbed per unit cell (u.c.) [15].

The curves of the derived enthalpies for $AlPO_4$-5 (Fig. 6a) indicate increasing intermolecular interactions in the adsorbed phase (adsorbate–adsorbate interactions) such that $\Delta_{ads}\dot{h}$ continually rises from $\theta = 0.2$ to $\theta = 0.8$ (θ is equal to the ratio of the amount adsorbed at a given point to

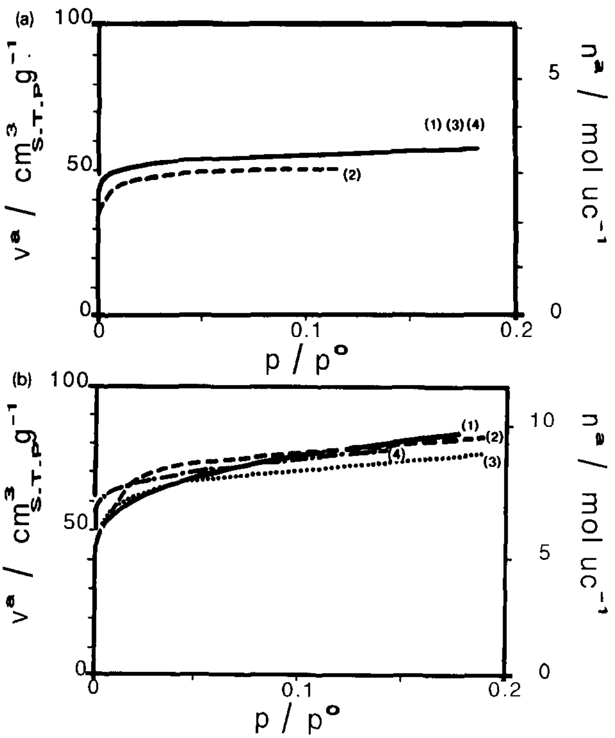

Fig. 5. Adsorption isotherms (1, argon; 2, methane; 3, nitrogen; 4, carbon monoxide) obtained by quasi-equilibrium volumetry for (a) $AlPO_4$-5 and (b) sepiolite.

the amount adsorbed on the plateau region of the isotherm). The molecules adsorbed on the sites of highest energy still possess a certain mobility. The behaviour of methane is unique in respect to its isotherm (an adsorption of

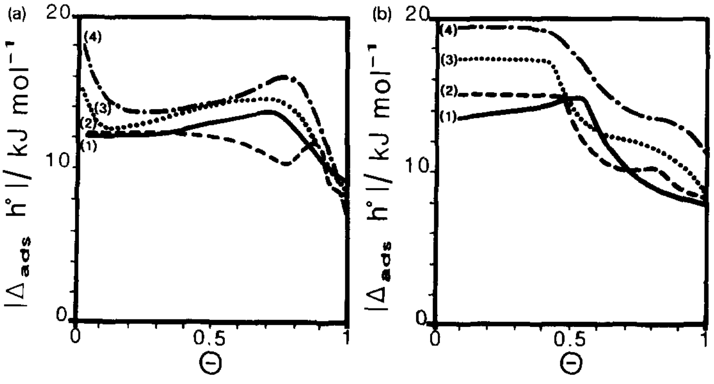

Fig. 6. Curves of the derived enthalphy of adsorption at 77 K (1, argon; 2, methane; 3, nitrogen; 4, carbon monoxide) on (a) $AlPO_4$-5 and (b) sepiolite; $\theta = v^a / v^a_m$ where v^a_m is the amount adsorbed on the plateau region of the isotherm.

3 molecules per unit cell at $p/p^0 = 0.1$ compared with 3.5 for the other adsorbates) and the unique evolution of its derived enthalpy of adsorption, which is interpreted as a probable variation of the mobility or density in the adsorbed phase and thus ultimately justifies a more careful investigation by neutron diffraction.

The decrease of the derived enthalphy of adsorption of nitrogen and carbon monoxide as θ increases from 0 to 0.2 is interpreted as the existence of specific interactions between the molecules and the hydroxylated sites found at defects in the aluminophosphate structure (the adsorption of argon is not sensitive to the hydroxyl population [16]). Thamm et al. [17] detected a similar phenomenon for the adsorption of benzene (permanent quadrupole moment $= -29.7 \times 10^{-4}$C m^2). The curves in Fig. 6a allow an estimation of the contribution of these hydroxyl sites to the adsorption, 10% of the B.E.T. "monolayer" [18] for nitrogen and 15% for carbon monoxide. Microcalorimetry also gives an indication that these sites are heterogeneous with a continuous energy variation.

The case of sepiolite is more complex (Fig. 6b). The first part of the curves of the derived enthalphy of adsorption corresponds to adsorption on homogeneous sites ($-Mg(OH_2)_2$), which are situated parallel and aligned to the axis of the structural micropores and on which the specific interactions with N_2 and CO take place. These sites also probably induce a moment in the argon atom, as the value of the derived enthalphy is high. On the other hand, in the region where θ ranges between 0 and 0.5, the derived enthalphy of adsorption remains constant for N_2, CO and CH_4, the last-named molecule being highly polarizable (2.6×10^{-3} nm^3). The fact that adsorption occurs on highly polarized sites suggests that the mobility on the surface of the adsorbent decreases, thus limiting the extent of the adsorbate–adsorbate interactions. On the other hand, for argon, which has no permanent moment and a lower polarizability (1.63×10^{-3} nm^3) than that of methane, an increase of these interactions is observed during the course of the adsorption in the micropores. In the region of $\theta = 0.4$, the adsorption on the high energy sites is completed in the structural micropores of the clay. At this point 3.2–4 molecules are adsorbed per unit cell. The derived enthalpy of adsorption is then seen to decrease rapidly until about $\theta = 0.7$; this behaviour is attributed to adsorption in volume, by filling (cooperative adsorption [13]) of the interfibral heterogeneous microporosity [19] as the value of the derived enthalpy of the adsorption tends to that of the enthalpy of liquefaction [20]. It should be noted that, in the region of θ up to 0.5, the values of the derived enthalpies of adsorption of the four adsorptives are greater for sepiolite than for $AlPO_4$-5. This is due to the larger specific interactions between the adsorbate molecules and the polar sites of sepiolite. In effect, if the adsorption resulted only from textural effect ("London dispersion" forces), the results would be reversed, since the micropores of $AlPO_4$-5 are approximately twice as narrow as those of the clay (cross-sections are 0.42 nm^2 for $AlPO_4$-5 and 0.89 nm^2 for sepiolite).

CONCLUSION

The comparison by calorimetry of the physisorption of various gases, either with or without a permanent dipole/quadrupole moment, in the primary micropores of $AlPO_4$-5 and sepiolite shows that the adsorption occurs "by site". In the aluminophosphate $AlPO_4$-5, with an electrically neutral framework, the molecules are sufficiently mobile and close enough to give rise to adsorbate–adsorbate type interactions. In the structural micropores of the sepiolite clay the adsorption sites are strongly polar, and so the adsorbed molecules are less mobile, thus hindering any adsorbate–adsorbate interaction. The "volumic" adsorption resulting from cooperative effects appears only in the larger and more heterogeneous interfibral micropores of the sepiolite. Microcalorimetry allows a straightforward detection of the completion of the adsorption by site in the structural channels of the clay. This technique also shows that, for the aluminophosphate, an average of four molecules are adsorbed per unit cell.

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