Water adsorption in aluminium pillared clays and zeolites

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Adsorption of water at 298 K has been studied in aluminium pillared clays (PILCs) and in zeolite types A, Y and ZSM-20, and kinetic and equilibrium results obtained. PILCs were prepared by two methods, which differ only in the OH/Al ratio of the oligomer solution, and by using three different parent clay materials. These methods led to PILCs that, when calcined at 623 K, present BET areas ranging from 250 to 350 $m^2 g^{-1}$ and basal spacings from 1.6 to 1.8 nm. For Y and ZSM-20 zeolites, the sodium and protonated forms were studied. The equilibrium results were compared with literature data corresponding to an ideal isotherm for use in dehumidification and discussed in terms of textural and chemical properties, namely the Si/Al ratio of zeolites and PILCs. For these latter materials an effect of the parent clay on water adsorption was studied, which seems to be related to the degree of substitution in the tetrahedral sheets.

When characterising the adsorption properties of microporous solids, characteristics such as BET surface area, together with micropore volume and dimensions, are among the first investigated. However, and depending on the possible uses of a particular material, hydrophobic properties, besides textural properties, can also be important.

Amongst the different types of microporous materials, activated carbons and zeolites are the most studied and also have wider applications, chiefly in adsorption. Activated carbons are essentially hydrophobic,[1] whereas, zeolites show varying behaviour towards water adsorption. Therefore, highly hydrophobic materials, for example silicalite,[2] are completely opposite to, for example, zeolite 4A which is routinely used as a dessicant. These opposite behaviours are not due to structural differences, the pore apertures in silicalite being only 1–1.5 Å larger than in zeolite 4A. Rather, water adsorption in zeolites with similar structures depends upon the chemical composition of the framework. For instance, Chen[3] reported results of water adsorption in zeolite mordenite with various SiO_2/Al_2O_3 ratios. It was concluded that when this ratio was <20 (higher aluminium content) adsorbed volumes of water and hydrocarbons were comparable but, when this ratio was >40 (lower aluminium content) the amounts of adsorbed water decreased to almost zero. Hydrocarbon uptakes, by contrast, do not show appreciable dependence on the SiO_2/Al_2O_3 ratios between 40 and 90. Other authors have reported an almost inverse relationship between the framework Si/Al ratio and water uptake in dealuminated faujasite type zeolites.[4]

Another class of microporous materials are pillared clays (PILCs). Although much less studied than activated carbons or zeolites, they have potential interest as adsorbents[5,6] and catalysts[7] or catalysts supports.[8] PILCs are obtained through the intercalation between clay sheets of large polyhydroxycations, usually composed of aluminium or zirconium, and subsequent thermal decomposition that transforms these voluminous cations into rigid oxide pillars.[9] The materials thus obtained are mainly microporous and normally present micropore dimensions larger than those found in zeolites, particularly when one has in mind solids which are obtained with comparable experimental complexity as, for example, A or Y zeolites. Although adsorption properties of PILCs have not been widely studied, some attention has, however, been paid to the water adsorption,[10–12] since desiccation is an important field in the application of adsorbent materials, primarily in gas-fired dehumidification and cooling applications.

The objective of this work was to study the adsorption of water in aluminium pillared clays, in particular to reveal the effect of parent materials and intercalation methods on the affinity of the resulting samples towards water, and also to relate this to the behaviour found in zeolites.

Experimental

Materials

Two Portuguese clays, one from Benavila, Alentejo (BEN) and another from Porto Santo, Madeira archipelago (PTS), as well as a clay from Wyoming (WYO), were used as starting materials to obtain PILCs. The characterisation of these parent clays was extensively carried out in previous work,[13] detailing their synthesis, chemical analysis, stucture, textural properties and affinity for water. The clays were mainly montmorillonites with similar cation exchange capacities (*ca.* 120 mequiv./100 g). They have different degrees of tetrahedral substitution[14] and the PTS sample showed some characteristics of beidellite.[13]

Three types of zeolites were also used. ZSM-20 zeolite, an intergrowth of the EMT and FAU structures, was obtained as has been described previously.[15] A detailed characterisation of structural[15] and textural properties of this material can be found elsewhere.[16] NaY zeolite was from Union Carbide and zeolite 4A from Merck.

Protonated forms, HY and HZSM-20, were obtained, as usual, by ion exchange with aqueous 2 M NH_4NO_3 (Y), with three exchanges at ambient temperature and two at 373 K, or aqueous 1 M NH_4Cl (ZSM-20), with three exchanges at ambient temperature and calcination at 673 K.

Pillaring

The intercalation process, detailed in the literature,[17,18] has been described previously.[14] Two kinds of PILCs, designated A and B, were obtained with each of the parent clays. Samples A and B differed with respect to the method of preparation of the polyoxy cation (oligomer) solution. The initial OH/Al ratio in this solution was 0.8 (A) or 2 (B). After mixing NaOH and $AlCl_3$ solutions, and ageing for 2 h at 333 K, the pH was increased to 6 in both cases. The oligomer solution was then added dropwise to the clay solution at 353 K under stirring, refluxed for 3 h and kept at 298 K overnight. After centrifugation, the solid was washed in a dialysis tube until a of conductivity of <1 mS m^{-1} was observed in the washings. The samples were then freeze-dried and calcined at 623 K. Properties of the obtained PILCs are listed in Table 1.

Table 1 A_{BET} and microporous volumes (w) from nitrogen adsorption at 77 K and basal spacing (d_{001}) for the several PILCs

	BEN		PTS		WYO	
	A	B	A	B	A	B
A_{BET}/m^2 g^{-1}	302	350	250	307	270	350
w/cm^3 g^{-1}	0.118	0.130	0.078	0.084	0.106	0.130
d_{001}/nm	1.73	1.79	1.63	1.81	1.83	1.83

Water adsorption isotherms

Water adsorption was performed in a gravimetric apparatus, using a C.I. Electronics balance. The millipore water was purified *in situ* by freeze–vacuum–thaw cycles. The temperature at which adsorption was carried out was maintained at 298±0.1 K with a water-bath. To measure adsorption at equilibrium, the times varied from 16 h for the first point to 2 or 1 h for the following points of the isotherms.

Outgassing of the pillared clays was achieved using a combination of rotary/oil diffusion pumps, which produced a vacuum better than 10^{-2} Pa (10^{-4} Torr), heating from ambient temperature to 573 K at 5 K min^{-1} and maintaining this temperature for 2 h. For zeolites, a higher temperature (623 K) and a longer time (4 h) were used.

Results and Discussion

Kinetic data

Fig. 1 shows relative amounts of adsorbed water, obtained at 298 K, and near the saturation pressure, as a function of the time for 4A zeolite and PILCs obtained by method A. As expected, the initial branch of the curve for 4A zeolite is very steep and >90% of the total uptake is complete in the first 10 min, reflecting the high affinity of water for this zeolite. Water adsorption in PILCs is slower with 90% of the uptake being completed within 2 h.

For PILCs, we fitted the equations obtained for isothermal adsorption when diffusion within the microparticles is rate controlling, assuming two geometrical forms for clay particles.[19] If uniform spheres are considered, values of D/r^2, where D is the diffusion coefficient and r an equivalent radius, are of the order of 10^{-3} min^{-1}, whereas in the case of slabs, probably a more reliable hypothesis given the structure of clays, values of D/l^2 ($2l$ being the slab thickness) of *ca.* 10^{-2} min^{-1} are found.

Data on the kinetics of adsorption of water in PILCs are, to our knowledge, not present in the literature. Therefore, we attempted to compare our results with values of diffusivities (D/r^2) found for other materials. For zeolite A, for instance, values of D/r^2 near 60 min^{-1} have been obtained with particles of size *ca.* 5 μm.[20] The fact that the particle size distributions of the parent materials used in the present study present a maximum at about 5 μm, gave us the opportunity to make, at least to a first approximation, a direct comparison between D values. From our results it seems that the diffusion coefficients of water in pillared clays prepared as previously described are likely to be three or four orders of magnitude lower than in zeolite 4A.

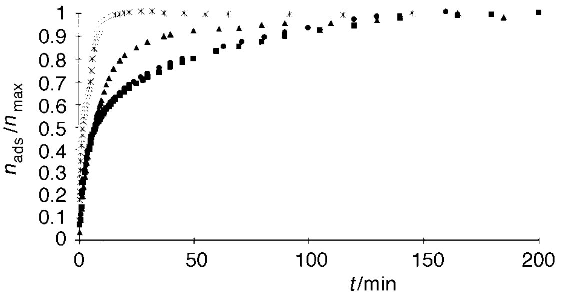

Fig. 1 Relation between the quantities of adsorbed water as a function of time, at 298 K, and the respective maximum adsorbed amounts for 4A zeolite and PILCs obtained by method A (∗, 4A; ●, PTS-A; ▲, BEN-A; ■, WYO-A)

Equilibrium data

Fig. 2 shows isotherms obtained with two sub-samples of WYO-A. Different points in the initial part of the isotherm were measured after keeping the systems overnight and it can be seen that the determined data for the two samples define the same curve within experimental uncertainty. Although the isotherm is mainly of type I,[21] it is much less rectangular than the corresponding nitrogen isotherm.[13,14] The slight inflexion seen at relative pressures around 0.2 has also been reported in the literature for pillared clays[10–12] and for other families of solids,[22] and can be related to the process of micropore filling.

For the sake of clarity, adsorption isotherms are shown separately for each type of material in Fig. 3 for zeolites and Fig. 4 and 5 for PILCs A and B, respectively. Adsorbed amounts are normalised to 100% using the adsorption capacity values at $p/p^0=0.8$ which are listed in Table 2. This type of presentation allows a reference isotherm corresponding to an ideal adsorbent for use in dehumidification equipment, with a separation factor of 0.1, to be included.[10,23]

For the zeolites, the adsorbed amounts obtained in Y and 4A zeolites (Table 2) are of the magnitude of the values found in the literature.[24] As can be seen in Fig. 3, zeolite 4A presents a higher initial slope in the isotherm, that is, high adsorbed amounts are observed at low pressures, in relation to the other zeolites. These slopes, which can be interpreted as a measure of the affinity for water adsorption, are in the sequence 4A > Y > ZSM-20 which is the reverse order of the free dimension of the supercages, as well as the Si/Al ratios of these

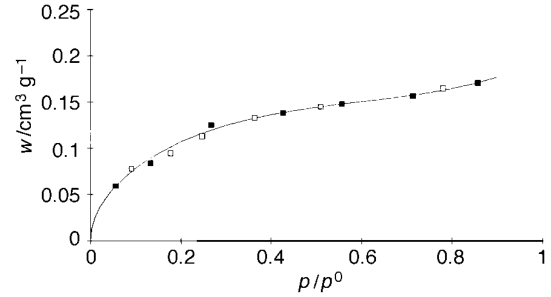

Fig. 2 Water adsorption isotherm for the WYO-A pillared clay. The data were obtained in two sub-samples represented by closed and open symbols, respectively.

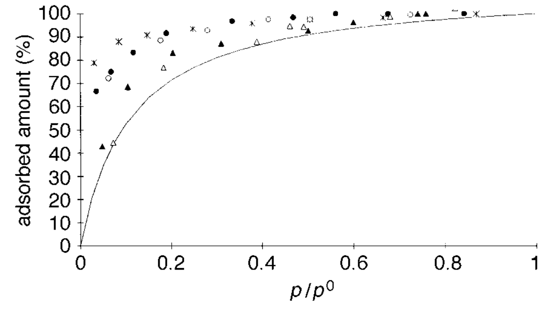

Fig. 3 Water adsorption isotherms at 298 K, with the uptakes expressed in percentage (taking as 100% the value at $p/p^0=0.8$) for the indicated zeolites. The solid curve represents an ideal isotherm for use in dehumidification equipment with a separation factor of 0.1 (∗, 4A; ●, NaY; ○, HY; ▲, NAZSM-20; △, HZSM-20; ——, ideal).

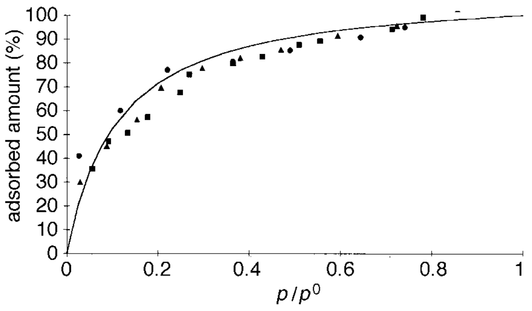

Fig. 4 Water adsorption isotherms at 298 K, with the uptakes expressed in percentage (taking as 100% the value at $p/p^o = 0.8$) for PILCs obtained by method A from the different parent clays. The solid curve represents an ideal isotherm for use in dehumidification equipment with a separation factor of 0.1 (●; PTS-A; ▲, BEN-A; ■, WYO-A; ——, ideal).

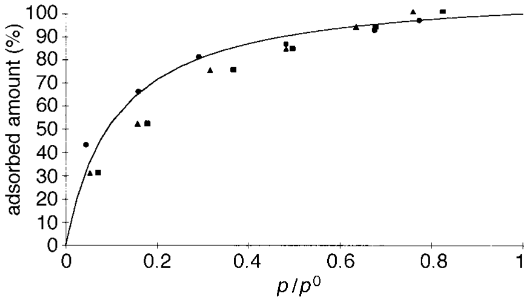

Fig. 5 Water adsorption isotherms at 298 K, with the uptakes expressed in percentage (taking as 100% the value at $p/p^o = 0.8$) for PILCs obtained by method B from the different parent clays. The solid curve represents an ideal isotherm for use in dehumidification equipment with a separation factor of 0.1 (●, PTS-B; ▲, BEN-B, ■, WYO-B, ——, ideal).

Table 2 Amounts of adsorbed water (w) at $p/p^0 = 0.8$ and 298 K in the different PILCs and zeolites studied

	BEN		PTS		WYO				
	A	B	A	B	A	B	YZSM-20	NaY	A
w/cm^3 g^{-1}	0.17	0.21	0.13	0.18	0.17	0.19	0.28	0.25	0.25

zeolites (Table 3). These are the two factors that mainly govern water adsorption which will be favoured by smaller pores and low Si/Al ratios. Upon removal of sodium ions from the zeolites and PILCs, which removes hydrophilic centres, only a small effect in water adsorption on Y and ZSM-20 zeolites (Fig. 3) was observed. This is an unexpected result, since adsorption in these zeolites of less polar molecules, such as hydrocarbons,[25] xenon[26] or carbon dioxide,[27] is significantly modified by the presence of cations.

In relation to the ideal adsorption (solid curve), Fig. 3 shows that, with partial exception for HZSM-20, zeolites give rise to isotherms of too high rectangular character. However for dehumidification and regeneration, materials with a moderate type I isotherm are preferred.[10,23] PILCs obtained by method A (Fig. 4), generally speaking, show adsorption isotherms somewehat lower than ideal. It should be emphasised that the initial slopes of the isotherms are in line with the previously proposed pore size distribution for these PILCs,[13] with the proportion of smaller pores increasing from WYO-A to PTS-A.

Table 3 Si/Al ratios of the parent clays, PILCs and zeolites studied

	BEN		PTS		WYO	
$Si/Al_{tetrahedral}{}^a$	16		12		43	
$Si/Al_{total}{}^a$	2.8		2.5		2.4	
PILC (method)	A	B	A	B	A	B
$Si/Al_{total}{}^b$	1.1	0.92	0.93	0.84	1.04	1.16
zeolite	A		Y		ZSM-20	
Si/Al	1[c]		2.3[c]		4.8[d]	

[a]Si by gravimetric analysis and Al by complexometry. [b]By inductively coupled plasma. [c]Values from supplier. [d]By atomic absorption spectroscopy.

For the clays pillared by method B (Fig. 5) the adsorption isotherms for BEN and WYO were less than ideal, but for the PTS PILC a reasonable agreement with the ideal case is obtained, there being only some deviation at relative pressures near 0.5.

In a previous work[13] when comparing the three parent clays, an enhanced adsorption of polar molecules, including water, was seen for the PTS clay. For instance the adsorbed amounts of water vary between a minimum of 0.205 g (g clay)$^{-1}$ and a maximum value of 0.317 g (g clay)$^{-1}$ respectively for WYO and PTS parent clays. However, this property is not particularly related to the efficiency of the intercalation process, when only the textural properties of the final products are considered. As can be seen in Table 1, PTS PILCs present, in general, minimum values of A_{BET}, micropore volumes and basal spacings. Conversely the parent materials can control other properties of PILCs, for instance, catalytic properties which, in some cases, are better in PILCs obtained from clays with high tetrahedral substitution.[7]

The features of water adsorption in PILCs, and particularly in PTS PILCs, are believed to be related to the nature of the parent clay, and an attempt to rationalise this fact was made considering the Si/Al ratios (Table 3). First, values of Si/Al_{total} for clays and PILCs (where Al_{total} represent Al from clay sheets and pillars) are not very different for several clays and, while the smallest values are seen for PTS PILCs, the Si/Al_{total} values do not clearly relate to any property. However, considering the relation between Si and $Al_{tetrahedral}$ in the parent materials, *i.e.* the aluminium in the tetrahedral sheets which is, according to the structure of clays, more exposed to adsorption, lower $Si/Al_{tetrahedral}$ is found for the PTS clay providing, together with textural characteristics, a possible explanation for the adsorption results.

Conclusions

We believe that the results obtained for water adsorption in PILCs, particularly with products prepared by method B and using as parent material a clay from Madeira archipelago (PTS clay), are quite promising. In fact, the more general pattern of results quoted in the literature involves PILCs in which water adsorption has been enhanced, in the whole range of relative pressures, with post-synthesis treatment, by exchange with various cations. Results that approach the performance of an ideal adsorbent for dehumidification have, to our knowledge, never been achieved prior to this work with as-synthesised PILCs.

The water adsorption in PILCs seems to be related to the chemical nature of the parent clay, in particular the Si/Al ratio of the tetrahedral sheets. This behaviour has some analogy to what happens in the case of zeolites, where water adsorption is more related with the Si/Al framework ratio than with the type of the positive species that balances the negative charge in the structure.

These aspects, which are not completely clarified in PILCs, nor even in the more studied zeolites, deserve further investigation. However, from this study it can be concluded that the chemical composition of the tetrahedral sheets is relevant for the adsorption of water in pillared clays.

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