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Porosity and thermal stability of PILCs prepared with clays from different origins and different metal–polyhydroxycationic species of Al and Al/Ce

João Pires,* Manuel Machado and M. Brotas de Carvalho

Faculdade de Ciências de Lisboa—Dep. de Química e Bioquímica, R. Ernesto Vasconcelos, Ed. C1, 5° piso, Campo Grande, 1700 Lisboa, Portugal

Montmorillonites from different origins have been pillared with polyhydroxycations of Al and Al/Ce in order to preferentially obtain pillared clays with large pores and good thermal stability. The precursors of the stable materials, *i.e.* the intercalating species, and the intercalated but not calcined samples, were studied by differential scanning calorimetry. The textural properties of the materials obtained with different pillaring solutions, and calcined at 500 and 700 °C, were studied by nitrogen adsorption. It is shown that depending predominantly on the oligomer composition and much less on the type of parent material, solids with different meso- and microporous volumes can be obtained with structures that, in some cases, present specific surface areas higher than 300 $m^2 g^{-1}$ at 700 °C.

Introduction

Materials which can present a variety of pore dimensions but that are mainly microporous, *i.e.* with pores less than 20 Å in diameter, can be obtained by intercalation of swelling clays, usually montmorillonites, with bulky inorganic polyhydroxycations. After calcination at a selected temperature, normally 350 °C but preferentially at higher temperatures in order to achieve a structure with good thermal stability, the intercalated polyhydroxycations can be transformed into rigid oxide pillars and a pillared clay (PILC) is, therefore, obtained.

PILCs were initially prepared[1] bearing in mind their use as cracking catalysts, since materials with pore openings larger than zeolite Y, the base of these catalysts, could in principle be obtained. Also, for this reason, polymeric cations of aluminium were selected since after calcination, in addition to suitable porosity, they could also provide acid sites[2] which have a major role in cracking catalysis. Besides adequate porosity and acidity, thermal stability is also an important property if the material is to be used in acid catalysis and this is still a drawback of PILCs. Although the industrial application of pillared clays has not yet been achieved, studies have already been carried out for the production on a pilot scale.[3]

In order to enhance the thermal stability of PILCs the intercalation of polymeric aluminium species together with rare-earth cations, particularly cerium, was tried.[4–9] Data in the literature concerning intercalation with mixed cations of aluminium and cerium are somewhat contradictory. For instance, specific surface areas and basal spacing values ranging from 165 $m^2 g^{-1}$ and 13.2 Å[6] to 500 $m^2 g^{-1}$ and 25 Å[8] are reported. In fact, in some cases no noticeable effect of cerium was detected in the thermal or textural properties of Al/Ce PILCs,[9] but other authors have reported a positive effect of this rare-earth cation, even for Al/Ce ratios as low as 1/52.[4] In some cases, the positive effect of cerium is noticed not only in the improvement of thermal stability but also because it allows the preparation of PILCs with larger micropores than when only aluminium is used.[8]

The possibility of increasing the pore dimensions is an additional factor of interest in the intercalation with mixed cations of Al and Ce. In fact, the search for materials which are in the transition from microporous to mesoporous solids has been gaining increased importance.[10] A last, but not least, aspect that motivated the research into new cerium containing materials, although not usually referred to in literature in the context of PILCs, is the important application of cerium in the form of cerium oxide in the formulation of catalysts for automotive exhaust gas treatment.[11]

The present work aims at the use of mixed cations of aluminium and cerium for preparing pillared clays with higher basal spacing and specific areas than those obtained when only aluminium is used. In this case, values of 19 Å and 250 $m^2 g^{-1}$ are normally found as upper limits for basal spacing and specific surface areas, respectively, of the samples after calcination at 500 °C. Clays from different origins, which present distinct chemical compositions, were used as parent materials. A systematic study of the textural properties of the obtained materials was made.

Experimental

Parent materials

Three smectites were used as parent materials: one from Wyoming (WYO) and two of Portuguese origin, from Benavila (BEN) and Porto Santo (PTS). These clays, after purification by sedimentation and decarbonation, were extensively characterised regarding their chemical and textural properties in previous works[12–14] where details can be found. The structural formulae of each parent material are: for PTS, $(Si_{3.70}Al_{0.30})^{IV}(Al_{1.16}Fe_{0.51}Mg_{0.45})^{VI}(1/2Ca,K,Na)_{0.39}$; for BEN, $(Si_{3.77}Al_{0.23})^{IV}(Al_{1.13}Fe_{0.47}Mg_{0.50})^{VI}(1/2Ca,K,Na)_{0.46}$; and for WYO, $(Si_{3.91}Al_{0.09})^{IV}(Al_{1.51}Fe_{0.18}Mg_{0.26})^{VI}(1/2Ca,K,Na)_{0.49}$. The A_{BET} are 142, 49 and 67 $m^2 g^{-1}$ respectively for PTS, BEN and WYO. The micropore volumes are 0.034 $cm^3 g^{-1}$ for PTS and 0.009 $cm^3 g^{-1}$ for BEN and WYO.[12]

Synthesis procedure

The source of Al was aluminium chlorohydrate (Locron L Hoechst) and the Ce source was cerium trichloride heptahydrate (Aldrich, 99%). The preparation of the intercalating polyhydroxycations, *i.e.* the oligomer solution, was based on that reported in the literature.[6,8] Hydrothermal conditions were adopted for ageing the oligomer solutions which were kept overnight in a Teflon lined stainless steel autoclave, at 150 °C. The total [Al]+[Ce] concentration used in the preparation of the pillaring solutions varied between 0.42 and 2.9 M, keeping the molar Al/Ce ratio equal to 5. (The products obtained from these solutions are identified hereafter by Al or

Al/Ce, followed by the total concentration of the pillaring solution. For instance Al-2.5 and Al/Ce-2.5 indicate two PILCs that were obtained from solutions, which contained aluminium, or aluminium and cerium, respectively, at a total concentration of 2.5 M.) The Al/clay ratio was always 20 mmol of Al per g of clay. The oligomer solution was added to the clay dispersion under stirring which was maintained for 45 min after the addition was completed. The mixture was then stored overnight at 25 °C. After centrifugation the solid phase was washed by dialysis until the conductivity of the water was less than 1 mS m^{-1}, then centrifuged, partially dried in a rotary evaporator, lyophilised and, in some cases, calcined at different temperatures. The composition and the total concentration of the pillaring solutions prepared in an autoclave were the main parameters considered in order to try to conclude, in a systematic way, their influence on the thermal stability and textural properties of the final products. However, some other samples were also obtained without autoclave treatment: for these, the oligomer solutions (Al/Ce = 5) were prepared by refluxing through a procedure previously optimised in this laboratory for the preparation of Al-PILCs.[13]

During the calcination, the samples were maintained at a final temperature (350, 500 or 700 °C) for 2 h after a ramp rate of 1 °C min^{-1} and under a flux of dry air.

DSC

Differential scanning calorimetry (DSC) results were obtained using a Setaram TG-DSC 111 under a flow of helium (99.995%). The temperature range studied was from ambient to 600 °C with a rate of 10 °C min^{-1}. The data were obtained for the oligomer solutions, after drying at ambient temperature, and for the intercalated materials before calcination.

X-Ray diffraction

Diffractograms were obtained using a Philips Phillips PX 1820 instrument, using Cu-Kα radiation with oriented mounts.

Adsorption measurements

Textural properties, such as specific surface area (A_{BET}) and porous volumes, were evaluated from nitrogen adsorption isotherms at −196 °C. About 50 mg of PILC was outgassed at 300 °C for 2 h after a ramp rate of 10 °C min^{-1} under a dynamic vacuum $>10^{-2}$ Pa. Nitrogen was 99.995% pure and the data were collected, either in a manual Pyrex apparatus where pressure readings were made with a previously calibrated Baratron transducer, or in an automated instrument from Omnisorp, model 100Cx.

Results and Discussion

Oligomer species and intercalated materials

When studying the preparation of pillared clays, particularly with mixed pillars of Al and Ce, little attention is usually paid to the nature of the intercalating species and the intercalated but not calcined materials which are, in fact, the precursors of the stable materials. There are reasons for this: due to the complexity and lability of species in oligomer solutions, few techniques can give useful information. We believe that an effort should be made in this sense in order to better understand the formation of PILCs, making it less empirical and trial-and-error in nature. A relatively simple and widely available technique which can give some information on this subject is DSC.[13]

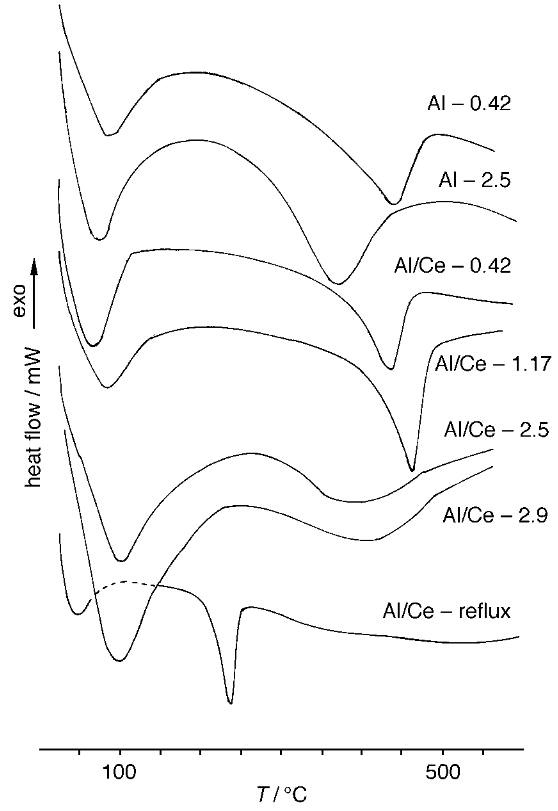

Fig. 1 Heat-flow (DSC) curves for the intercalated but not calcined clays

In Fig. 1 heat-flow *vs.* temperature curves are displayed for several intercalated but not calcined products. It can be seen that after a first broad peak around 100 °C, which is mainly due to the loss of physisorbed water, a higher temperature peak exists, near 400 °C (or 250 °C in the case of the refluxed solution) that can be identified with the transformation of the intercalating species into oxide pillars.[13] Briefly, one can conclude that the oligomers prepared with and without autoclave must be different, since the latter decompose at a temperature which is, on average, 150 °C lower. In fact, the DSC curve for the clay intercalated with the Al/Ce oligomer solution prepared by reflux shows a peak near 250 °C. This pattern is quite similar to that previously obtained with the more usual form of Al-PILCs,[13] where the intercalating species are believed to be the well known Keggin ions $[Al_{13}O_4(OH)_{(24+x)}(H_2O)_{(12-x)}]^{(7-x)+}$. Another feature in the DSC curves is the sharpness of the peak around 400 °C. In fact, sharper peaks are observed for the samples treated with less concentrated solutions both with and without cerium.

Table 1 gives the temperatures for the minimum in the heat-flow curves of the oligomers (curves not shown) and for the intercalated materials. Only one column is given for PILCs since, in the heating curves, no significant effect of different parent materials was noticed. It can be seen that when the total concentration increases the stability of the oligomer complex decreases, with the exception of Al/Ce-1.7. Additionally, for equivalent concentrations the presence of cerium does not modify the stability of the intercalating

Table 1 Temperatures at which the minimum occurs in the heat-flow curve (DSC) for several oligomers and intercalated clays (not calcined)

	T/°C	
sample	oligomer	uncalcined PILC
Al-0.42	430	440
Al-2.5	400	370
Al/Ce-0.42	440	440
Al/Ce-1.7	460	460
Al/Ce-2.5	400	400
Al/Ce-2.9	380	400
Al/Ce-reflux	not determined	250

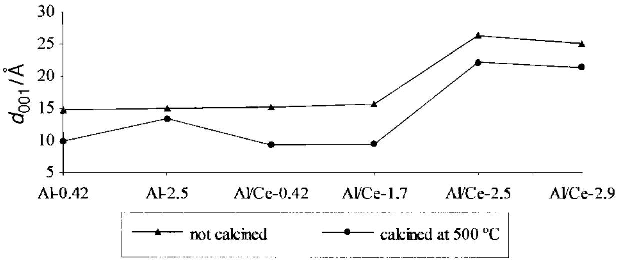

Fig. 2 Relation between the basal spacing (d_{001}) of the intercalated materials, before and after calcination, and the concentration of the pillaring solutions

oligomers. On the other hand, the intercalation does not seem to greatly change the stability of the oligomers.

In order to continue the discussion, it is useful to have a first measure of the degree of success of the intercalation process for each sample. This can be made by analysing the basal spacing (d_{001}) obtained from the X-ray diffractograms, presented in Fig. 2 for BEN-PILCs (either uncalcined or calcined at 500 °C) which illustrates the general pattern obtained with the different parent materials. Fig. 2 also shows that some expansion is always observed with all the oligomers used. Moreover, only those samples prepared with oligomer solutions that contain both Al and Ce with total concentrations equal to or higher than 2.5 M exhibit a permanent expansion after calcination at 500 °C, *i.e.* after the transformations which are associated with the high temperature peak in the heat flow curve are completed. Therefore, from the XRD and DSC results, we conclude that the most stable materials of the studied series are obtained from oligomers that dehydroxylate at lower temperatures. Also, and assuming that the increased sharpness of the DSC peaks can be related with the fact that the OH groups in the intercalating species have a similar environment, a more flattened DSC curve is probably due to a wider range of hydroxyl groups, giving rise to a more progressive dehydroxylation and to the formation of more thermally stable materials.

Textural properties of PILCs

The features of the texture of PILCs, the specific surface area and porosity, were evaluated from nitrogen adsorption isotherms determined at 77 K. The reproducibility of the intercalation process can be verified from Fig. 3, which displays the isotherms obtained with two different samples prepared from the same parent material (PTS) but through two distinct runs with oligomer solutions of the type Al/Ce-2.5. The curves are not exactly superimposed but, bearing in mind that the parent materials are natural products and that the preparation of PILCs involves a number of unitary operations, the obtained reproducibility of the process seems to be acceptable.

In Fig. 4 a set of isotherms, determined for samples prepared from the Wyoming clay and calcined at 500 °C, exemplifies the different types of isotherm shape obtained with the samples prepared with different concentrations of aluminium and cerium. For clarity, the desorption points are not shown but hysteresis was present, in distinct degrees, in all samples. These isotherms vary from types I and II,[15] hence the materials have, to different extents, characteristics of microporous (width <20 Å) and mesoporous materials (20 Å<width<500 Å). It is clear from Fig. 4 that isotherms with increased type I character, corresponding to materials with a large proportion of micropores, are obtained from solutions of high concentrations of Al and Ce. Conversely, type II isotherms were obtained with samples prepared with the less concentrated solutions. From these data, A_{BET} values were calculated for each sample, at relative pressures lower than 0.15, and these are presented in Table 2 where the respective d_{001} values are also included.

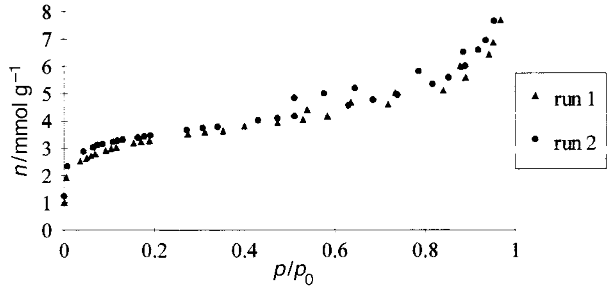

Fig. 3 Test of reproducibility of the synthesis method, by nitrogen adsorption at 77 K, in PILCs obtained from the PTS parent material

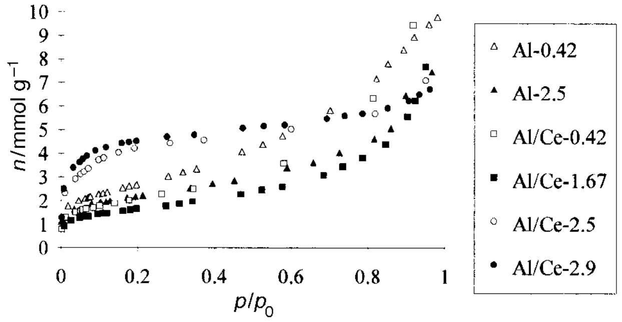

Fig. 4 Nitrogen adsorption isotherms in the samples prepared from the WYO parent material with the indicated oligomer solutions, calcined at 500 °C

For the evaluation of the microporosity, different methods can be used, each with its own advantages and drawbacks.[15] Particularly in the cases when high external areas or mesoporosity are also present, comparison plots with an appropriate reference isotherm are quite suitable. In this work a nitrogen isotherm obtained in Wyoming clay calcined at 850 °C[13] was used as the reference, in order to construct the comparison plots. Some of these are depicted in Fig. 5, where the adsorbed amounts in the synthesised products (ordinates) are plotted against the amounts in the reference isotherm at the same relative pressures (abscissae). The micropore volumes, estimated from the intercept of the intermediate linear range,[16] are given for the various samples in Table 2. Particularly curious in Fig. 5 are the results corresponding to the product prepared with the Al-0.42 oligomer solution and a similar situation occurs with the Al/Ce-0.42 sample. In fact, while the intercept of the linear part of the Al-0.42 curve has the lowest value of the samples plotted in Fig. 5, indicating the lower development of microporosity, the upward deviation from the intermediate linear branch towards higher n is quite accentuated, thus indicating the presence of pronounced mesoporosity.

The total porous volume is sometimes taken from the adsorption at high relative pressures, *e.g.* 0.95.[17] By subtracting from these values those corresponding to the micropore volumes (Table 2) the mesoporous volumes were obtained. In Fig. 6 the effect of the different types of oligomer on the relative amounts of micro- and mesopores is shown. It is clear that the same general pattern is observed for the products obtained from the three parent materials. In addition, it can be seen in this figure that mesoporosity clearly predominates until the total concentration of aluminium and cerium is 2.5 M. For the PILCs obtained with the Al/Ce-2.5 and Al/Ce-2.9 oligomer solutions a considerable amount of microporosity is developed but mesoporosity still contributes appreciably to the total porous volume. It is noticeable that this microporosity is higher than that present in samples without cerium obtained by optimised procedures and calcined at the same temperature.[13]

Table 2 Basal spacings (d_{001}/Å), specific surface areas (A_{BET}/m^2 g^{-1}) and microporous volumes (V_{micro}/cm^3 g^{-1}) for the different products calcined at 500 °C

	BEN			PTS			WYO		
sample	d_{001}	A_{BET}	V_{micro}	d_{001}	A_{BET}	V_{micro}	d_{001}	A_{BET}	V_{micro}
Al-0.42	9.9	190	0.047	9.6	221	0.058	9.9	212	0.055
Al-2.5	13.5	184	0.067	13.1	198	0.070	12.9	177	0.061
Al/Ce-0.42	9.4	159	0.035	9.7	195	0.035	9.6	163	0.047
Al/Ce-1.7	9.5	142	0.045	10.2	165	0.061	9.7	133	0.042
Al/Ce-2.5	22.2	370	0.177	22.2	286	0.124	21.9	370	0.171
Al/Ce-2.9	21.4	346	0.161	14.6	337	0.153	21.8	375	0.182
Al/Ce-reflux	15.3	195	0.094	16.9	219	0.079	—	—	—
Al/Ce-2.5[a]	21	246	0.120	—	122	0.048	21.2	346	0.162

[a] Calcined at 700 °C.

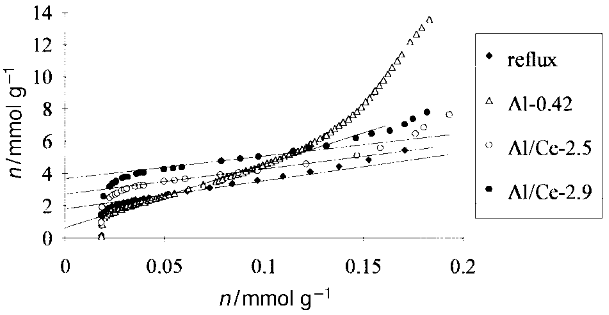

Fig. 5 Comparison plots of nitrogen adsorption at 77 K for the solids prepared from the PTS parent material treated with the indicated oligomers (y-axis: adsorbed N_2 in synthesised product; x-axis: adsorbed N_2 in the reference isotherm at the same relative pressure)

In the case of PILCs prepared from total (Al+Ce) concentrations of 2.5 and 2.9 M, calcined at 500 °C, which present high values of A_{BET} and micropore volumes, the samples prepared from BEN and PTS parent materials present values comparable to those obtained in the PILCs derived from the WYO clay. For a calcination temperature of 700 °C the textural parameters are lower for the PILCs obtained from the Portuguese parent materials, revealing a lower thermal stability. This situation can be appreciated in Table 2 and in Fig. 7 where adsorption isotherms in BEN-PILCs, obtained with the Al/Ce-2.5 oligomer solution, calcined at different temperatures, are presented. For products calcined at 350 °C the adsorbed amounts are low, in accordance with the findings presented in the previous section; at this temperature the intercalated species are not transformed into oxide pillars. The adsorbed amounts are at a maximum at 500 °C and decrease at a calcination temperature of 700 °C. However, comparing the PILCs cal-

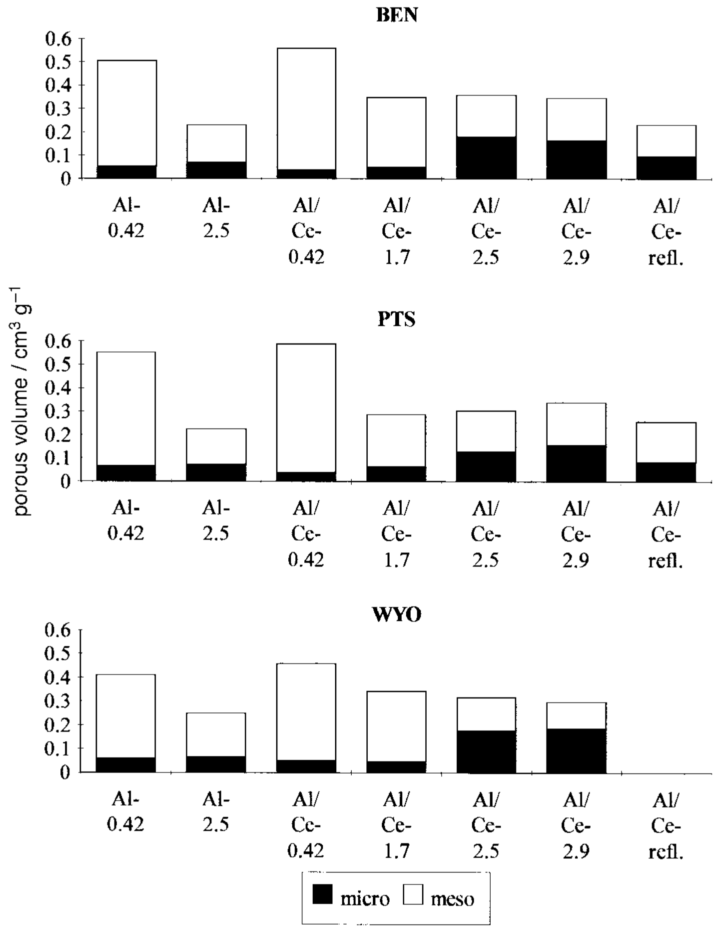

Fig. 6 Porosity of samples obtained from different parent materials, treated with different oligomers and calcined at 500 °C

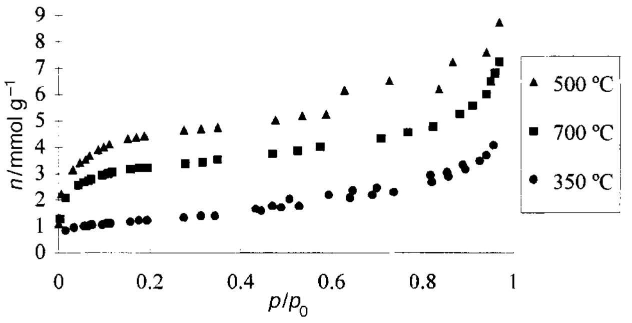

Fig. 7 Thermal stability of PILCs prepared from the BEN parent material with the oligomer solution Al/Ce-2.5

cined at 700 °C, the A_{BET} and microporous volumes are about three times higher than the values obtained in the samples with aluminium and cerium (*ca.* 100 m^2 g^{-1} and 0.04 cm^3 g^{-1}), or aluminium only, but made by reflux. These findings confirm the positive effect on the thermal stability of PILCs resulting from the use of both aluminium and cerium in an autoclave, under precise hydrothermal conditions, for the preparation of oligomers.

Conclusions

The intercalation of clays with oligomers prepared from the hydrothermal treatment of solutions containing aluminium and cerium is a route for the preparation of materials with high thermal stability and an appropriate range of pore dimensions. In fact, by changing the total metal concentration of the oligomer solution, materials were obtained where either mesoporosity or microporosity predominates. When microporosity is dominant, the pore sizes are in the transition range between micro- and mesopores as indicated by the high basal spacing. In addition it has been proved that the differences between the starting materials are not too evident in the characteristics of the porosity of these PILCs. On the contrary, the chemical compositions of the parent materials, namely the extent of octahedral substitution, (which in our study is higher in the Portuguese clays than in the Wyoming clay) appear to influence thermal stability. In line with the present study application (*e.g.* as adsorbents) of these materials with their wide range of large pores, synthesised from naturally occurring clays, deserves further systematic research.

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