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Alumina-pillared montmorillonite: effect of thermal and hydrothermal treatment on the accessible micropore volume

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In the search for materials having larger pores than zeolites, the concept of pillared clays gradually emerged. The substitution of zeolite-based commercial catalysts by pillared clays requires the improvement of the thermal and hydrothermal stability of the latter. Characterization of pillared clays has essentially consisted of nitrogen BET specific surface area and X-ray diffraction powder measurements. The study of the texture of pillared smectites really requires the assessment of their microporosity. However, little detailed information is available on the evolution of microporosity with thermal and hydrothermal treatments of these materials. The aim of this work was to supply such information on an alumina-pillared montmorillonite. The effect of La(III) addition was also studied. Up to now the thermal stability of the pillars has been over-estimated from measurement of the basal spacing. However, it has been found that the accessible volume decreases with increasing calcination temperature at a much greater rate than does the basal spacing. Therefore, the generally accepted conclusion that alumina pillars are stable at temperatures even higher than 500 °C may give a misleading picture of pore structure evolution with calcination temperature. Lanthanum appears to exert a small positive effect on the thermal and hydrothermal stability of the pillared montmorillonite.

1. Introduction

Zeolites, the traditional fluid-cracking catalysts, contain relatively small pores. The large amount of non-selective pre-cracking that would have to take place before the large residual molecules were reduced to a size capable of diffusing into a small-pored catalyst is an inherent problem. In the search for materials having larger pores, the concept of pillared clays gradually emerged.

The insertion of molecules into clay minerals to prop apart the aluminosilicate sheets was first done by Barrer and McLeod [1]. Pillars of hydroxy aluminium and other cations capable of being dehydrated to oxide pillars and thereafter supporting temperatures higher than 500 °C without structural collapse were first reported by Brindley and Sempels [2].

The cracking activity of pillared smectite is initially similar to that of zeolite-based commercial fluid-cracking catalysts. Selectivity to light cycle gas-oil (furnace oil) production is attributed to their micropore structure which is accessible to C_5–C_{10} *n*-paraffins and branched aromatics [3]. However, the substitution of zeolite-based commercial catalysts by pillared clays requires the improvement of the thermal and hydrothermal stability of the latter. The catalytic activity of cross-linked smectites decreases dramatically with thermal treatments [4].

Characterization of pillared clays usually consists of nitrogen BET specific surface area, *S*(BET), and X-ray diffraction powder patterns. The adsorption capacity for a series of adsorbates has also been carried out, although a proper differentiation is not usual between the amount taken up into the interlamellar spacing and that on the external surface, such as multilayer and condensed in meso- and macropores. Based on *S*(BET) and basal spacing measurements it has been concluded that a series of pillared smectites is stable after heating at temperatures higher than 500 °C [5], which is not consistent with the above-mentioned catalytic activity results.

The characterization of the texture of pillared smectites really requires the assessment of microporosity. However, little detailed information is available on the evolution of microporosity with thermal and hydrothermal treatments of these materials. The aim of the present work is to supply such information on an alumina-pillared montmorillonite. The effect of La(III) addition has also been studied.

2. Experimental procedure

X-ray powder diffraction diagrams were obtained with a Siemens Kristaloflex D-500 instrument, using CuK_α radiation and a nickel filter, 36 kV and 26 mA.

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The energy-dispersive X-ray (EDX) microanalysis was performed using a Kevec analyser, model 8000.

Nitrogen adsorption isotherms were carried out with a Micromeritic system, model 2200 A, at 77.35 K.

3. Results and discussion

3.1. Materials

A Trancos smectite mineral from Gador, Almería (Spain), was used [6]. The < 2 μm fraction was collected, corresponding to montmorillonite with a charge deficit per unit cell of 0.87 (0.36 + 0.51) [7].

The montmorillonite pillared with alumina, Al-CLM, as well as that containing alumina and lanthanum, Al(La)-CLM, was prepared according to the method described by Brindley and Yamanaka [8]. Hydroxyaluminium solutions of composition ratio OH/Al = 1.84 were prepared by adding a 0.01M NaOH solution to one of 0.1M $Al(NO_3)_3$. In the case of Al(La)-CLM, the precursor solution of Al(III) contained 4% La(III). The final pH values were 4.32 and 4.77, respectively. These solutions were aged at reflux temperature (85–95 °C) for 10 h, which appears to have a beneficial effect on the subsequent pillaring process in accordance with data reported by Tokarz and Shabtai [9].

The evolution of the experimental potentiometric titration curves of the 0.1M Al(III) and 0.1M Al(III)–2×10^{-2}M La(III) solutions showed no differences [10].

Separate 300 mg samples of the sodium-saturated montmorillonite, Na-M, were weighed into 50 ml centrifuge tubes and 25 ml aliquots of the aged Al(III)–Al(III)/La(III) solutions were added. Dispersion was helped by ultrasonic radiation. The suspensions were stirred and allowed to react for 3 h, after which they were centrifuged and another 25 ml solution added. The above procedure was repeated four times. The Al-CLM and Al(La)-CLM thus synthesized were air dried at 100 °C. The samples were heated in nitrogen at 300 °C for 5 h to transform the hydroxycations into oxide pillars.

Air drying was used in order to obtain a well-ordered pillared montmorillonite, because the study of the microporosity is the real aim of this work. Freeze-dried products show meso- and macro-porous structure and only one or two orders of 0 0 1 reflection.

The study of the thermal stability of the pillared montmorillonite was carried out on samples air-heated for 6 h at 300, 500 and 700 °C. The hydrothermal pretreatment consisted of heating at 300 °C and an H_2O pressure of 1×10^7 Pa.

3.2. X-ray powder diffraction (XRD) analysis

The expansion of the montmorillonite basal spacing by exchange of hydroxy-aluminium and hydroxy-aluminium/lanthanum ions and the subsequent collapse by heat treatment were followed by X-ray diffraction.

Fig. 1 shows XRD patterns of the pillared samples air-preheated at 300, 500 and 700 °C. Na-M has been included as a reference sample. The pillared clays heated at 300 °C showed a basal spacing above 1.8 nm. Upon heating at 500 °C, the products still showed a spacing of 1.72 nm (Al-CLM) and 1.62 nm (Al(La)-CLM), although the intensities of the peaks decreased as usual. Calcination first induced a contraction of the spacing, then a decrease in intensity of the (0 0 1) line, apparently due to the loss of the long-range ordering along the *c*-axis. After heating at 700 °C these samples showed weak, broad and unclear basal spacing of about 1.55 nm, indicating that heating had induced more structure irregularities.

XRD patterns for the hydrothermally treated samples are recorded in Fig. 2. The pillared samples retained a basal spacing of 1.54 nm (Al-CLM) and 1.47 nm (Al(La)-CLM). The broadening of the diffraction could be due to a greater variability in pillar height.

3.3. Energy-dispersive X-ray (EDX) microanalysis

The elemental content of microvolumes (roughly 1 μm^3) of the polycrystalline samples was analysed by EDX. The minimum detection limits were below 1%.

Fig. 3 shows the X-ray emission lines of Na-M, Al-CLM and Al(La)-CLM polycrystalline samples air heated at 300 °C. The number of counts in the spectral peaks associated with each element in the sample reflects the concentration of the elements. However, the relationship between net peak counts and elemental concentration is neither simple nor straightforward. Quantitative calculations require the so-called ZAF corrections, but the net peak count ratio of two elements is expected to be roughly equivalent to the ratio of the corresponding concentrations.

The shape of the traces in Fig. 3 remains constant; because the observed particles of each sample and the ratio between the net peak counts of silicon and aluminium roughly agrees with that between the atomic concentrations measured by atomic absorption.

The hydrothermal treatment at 300 °C exerts different effects on Na-M, on the one hand, and the pillared montmorillonites, on the other. Na-M exhibits a homogeneous composition and the Si/Al net peak count ratio approaches that of the untreated sample. However, the hydrothermally treated Al-CLM and Al(La)-CLM samples show a composition which changes greatly for some particles, Fig. 4. It denotes a partial decomposition of the pillared montmorillonites.

3.4. Nitrogen adsorption isotherms

Pillared smectites are essentially characterized by basal spacing and BET specific surface area measurements. Frequently a simple relationship has been assumed between both magnitudes. Table I shows *S*(BET) and *d*(0 0 1) values obtained for the present samples after the thermal treatments indicated. The surface area of Na-M calcined at 300 °C agrees with that of Li-M preheated at the same temperature, with their layers irreversibly collapsed (Hofmann–Klemen effect [11]). This proves that the nitrogen molecules

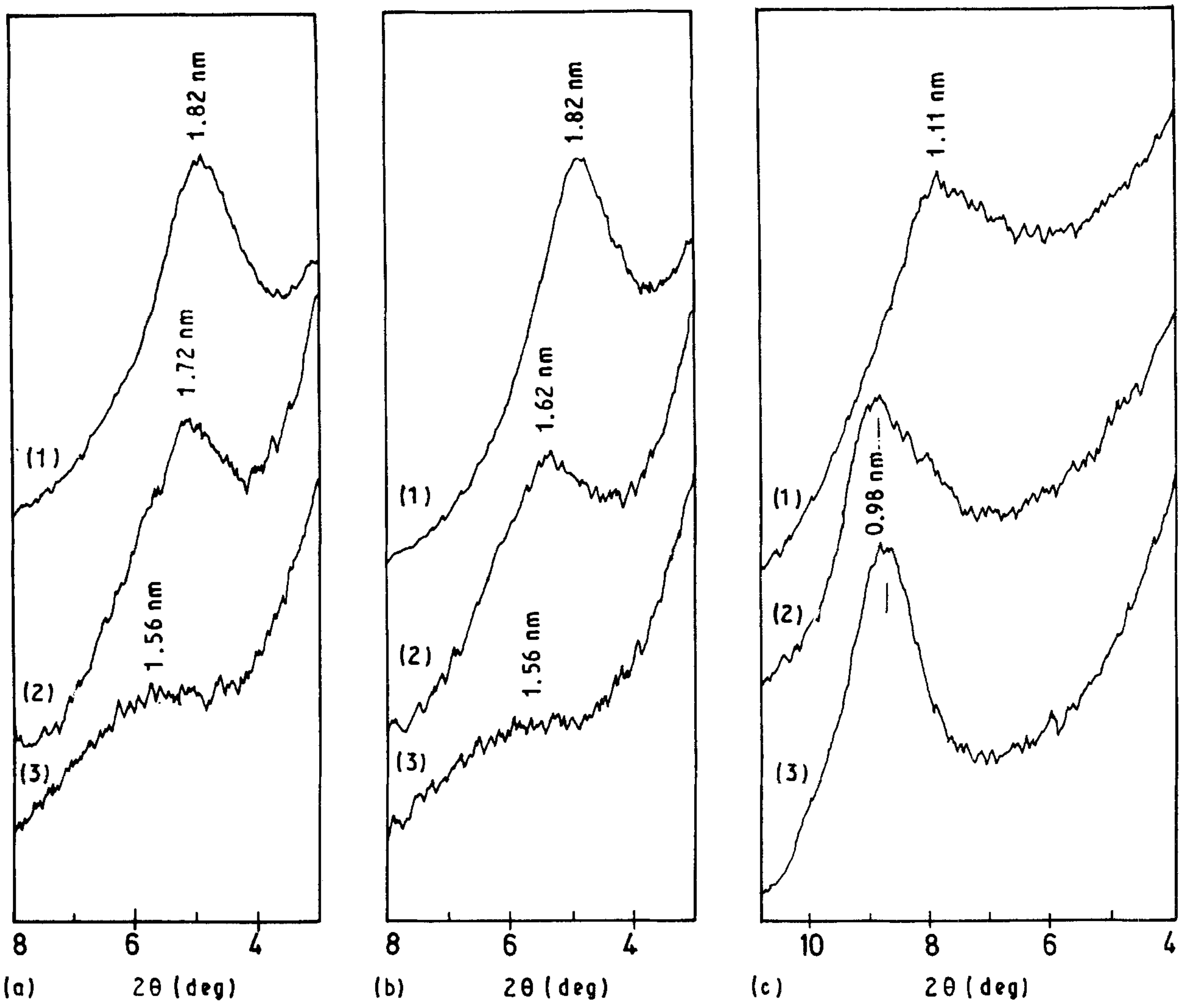

Figure 1 (0 0 1) XRD spacings for (a) Al-CLM, (b) Al(La)-CLM and (c) Na-M after preheating 6 h in air at (1) 300 °C, (2) 500 °C, and (3) 700 °C.

do not enter the interlamellar spacing of sodium montmorillonite and only the external surface area is estimated from the adsorption isotherms. A sintering effect was observed for Na-M, which was especially important at 700 °C. The pillared samples showed S(BET) values in the usual range, decreasing with d(0 0 1). However, the extent of the change for both magnitudes does not show any simple relationship, although a linear relation had previously been claimed to exist for hydroxy-chromium montmorillonites [12].

Data can be collected from the literature which are inconsistent with a significant relationship. It was observed by Yamanaka and Hattori [13] that the surface area for an iron oxide pillared montmorillonite increases with increasing preheating temperature up to about 350 °C, and then decreases gradually, while the basal spacing decreases with increasing temperature up to a nearly constant value at 250 °C.

Shabtai *et al.* [14] reported that lithium fluorohectorites cross-linked with hydroxy-aluminium oligomers showed a constant basal spacing after preheating from 250 °C to 400 °C, 1.85 nm, but a surface area which decreased from 373 $m^2 g^{-1}$ to 278 $m^2 g^{-1}$. As a last example, it can be mentioned [15] that S(BET) decreased for an alumina montmorillonite with the calcination temperature from 340 $m^2 g^{-1}$ to 125.6 $m^2 g^{-1}$, the basal spacing decreasing simultaneously by less than 3%, from 1.810 nm to 1.770 nm.

The BET method has become the most widely used standard procedure for the determination of the surface area of finely divided materials. However, if this method is to be used, it should be established that multilayer formation is operative and is not accompanied by micropore filling, according to IUPAC recommendations [16]. The BET analysis does not take into account the possibility of micropore filling.

The pillaring of smectites gives rise to the formation of slit-shaped pores in the region of micropores, with a width not exceeding 2 nm. Therefore, the surface area calculated by the BET method is incorrect and loses its meaning.

On other occasions, the total pore volume, V_p, has been used to characterize the pillared smectites. It is derived from the amount of vapour adsorbed at a relative pressure close to unity, by assuming that the pores are then filled with condensed adsorptive in the normal liquid state. Again, micropore filling can make the calculated total pore volume incorrect. Sterte *et al.* [17] report that changes in pore structure after thermal and hydrothermal treatments of three different alumina-pillared montmorillonites have been studied. It is worth mentioning that the greatest pore volume

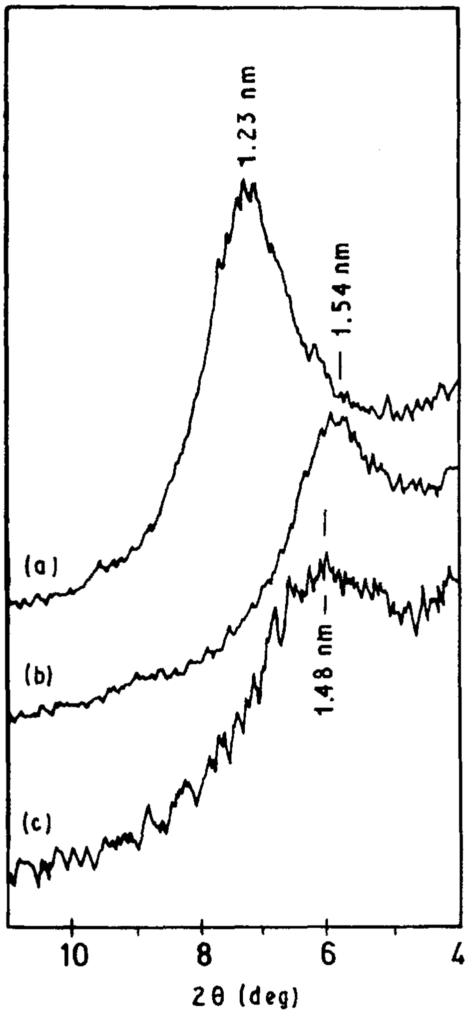

Figure 2 (0 0 1) XRD spacings for (a) Na-M, (b) Al-CLM and (c) Al(La)-CLM after hydrothermal treatment for 24 h at 300 °C and 1×10^7 Pa.

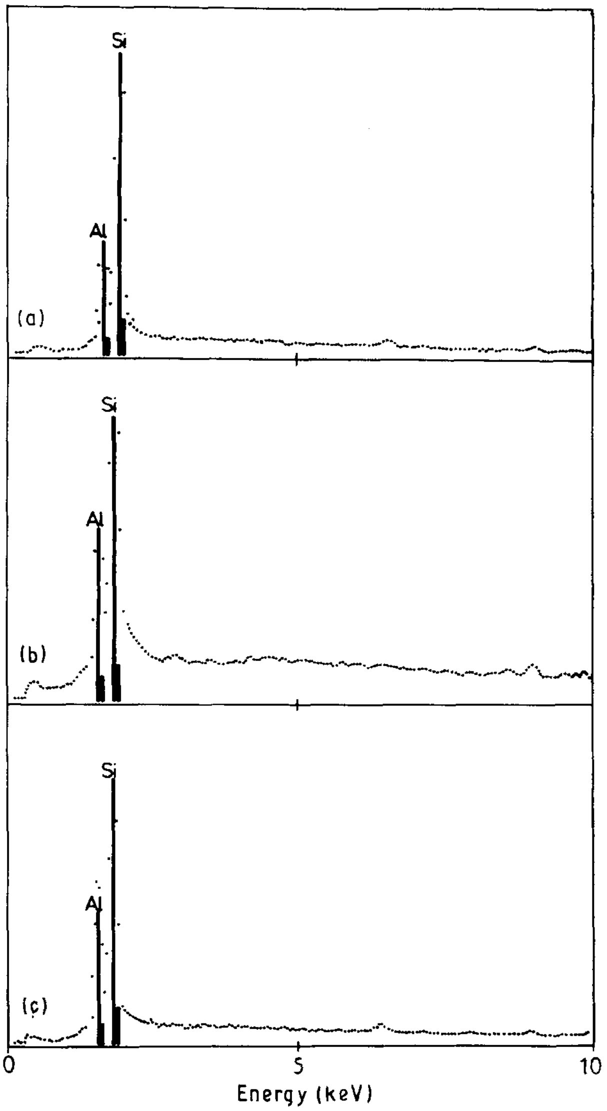

Figure 3 X-ray emission lines of (a) Na-M, (b) Al-CLM and (c) Al(La)-CLM air heated at 300 °C.

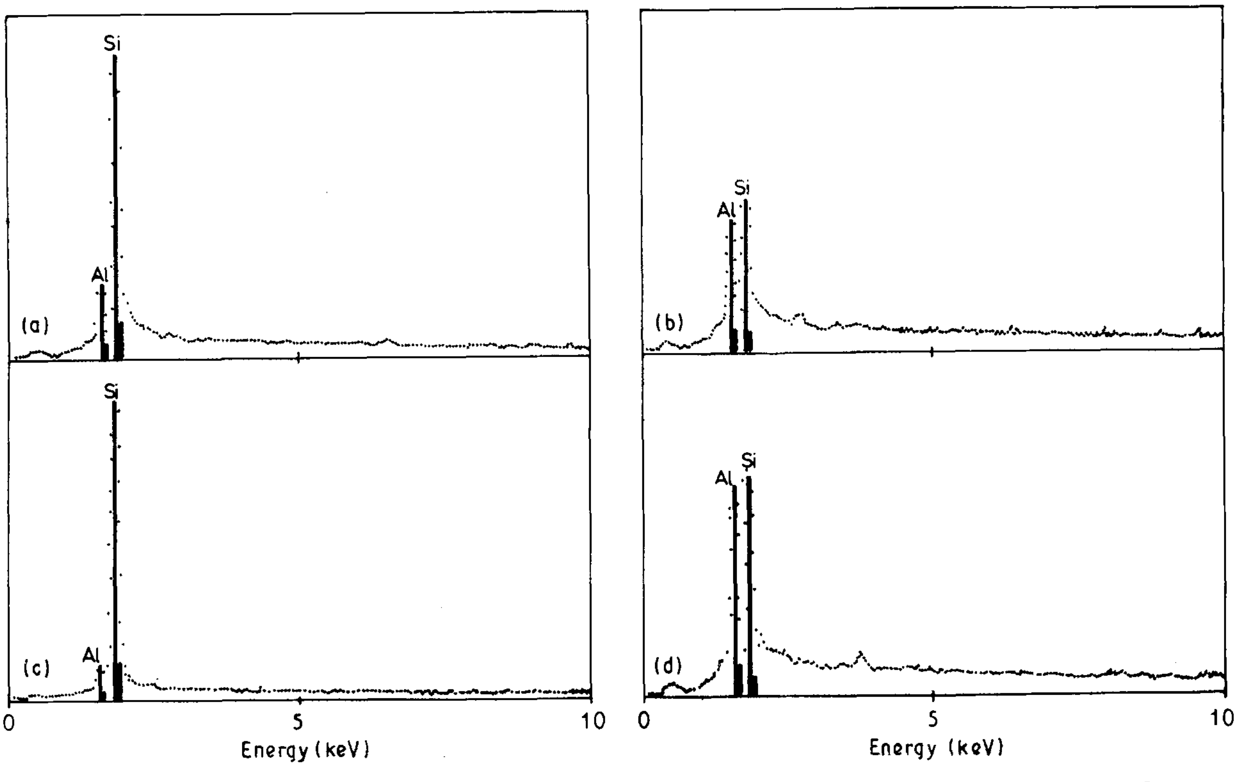

Figure 4 X-ray emission lines of (a, b) Al-CLM and (c, d) Al(La)-CLM hydrothermal treatment for 24 h at 300 °C and 1×10^7 Pa.

TABLE I BET specific surface area and basal spacing

Sample	Temperature (°C)	S (BET) (m^2 g^{-1})	d (0 0 1) (nm)
Li-M	300	109	0.95
Na-M	300	108	1.26
Na-M	500	85	1.26
Na-M	700	38	0.99
Al-CLM	300	276	1.82
Al-CLM	500	160	1.72
Al-CLM	700	121	1.55[a]
Al(La)-CLM	300	225	1.84
Al(La)-CLM	500	198	1.62
Al(La)-CLM	700	129	1.55[a]
Na-M	300 (HT)	100	1.23
Al-CLM	300 (HT)	99	1.54
Al(La)-CLM	300 (HT)	115	1.47

[a] Very broad band.

(0.26 cm^{3}g^{-1}) corresponds to the sample with the smallest surface area (143 cm^{3}g^{-1}).

The filling of micropores also falsifies the calculation of pore-size distribution by methods based on the application of the Kelvin equation. This is the case of the BJH procedure used in [15].

The use of S(BET), V_p or pore-size distribution can give rise to a misleading picture of the thermal stability of pillared smectite with respect to accessible volume.

Characterization of the texture of pillared smectites requires the assessment of microporosity. The close proximity of the pore walls gives rise to an increase in the strength of the adsorbent–adsorbate interactions and the micropores are filled at very low relative pressures. The t-method assesses microporosity by comparing the shape of a given isotherm with that of a standard on a non-porous solid. This has been selected here according to the IUPAC recommendation [16], rather than a Type II isotherm which happens to have the same C value as the isotherm on the particular microporous solid. Figs 5–8 exhibit the t-curves for the pillared and reference montmorillonites. The microvolume, V_m, has been obtained from the intercepts of the linear traces extrapolated back to the Y-axis and the external surface, S_t, from their slope.

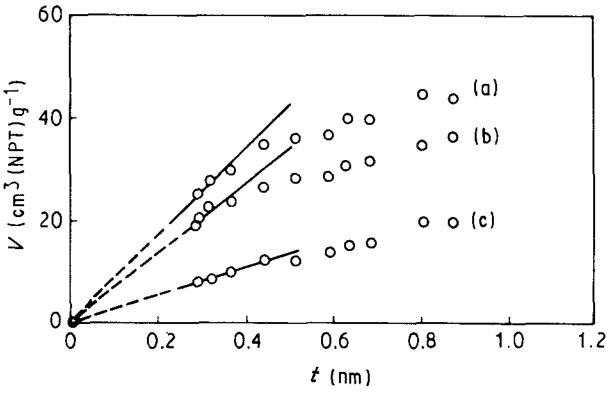

Figure 5 t-plots for nitrogen adsorption at 77.35 K upon Na-M after air-preheating 6 h at (a) 300 °C, (b) 500 °C and (c) 700 °C.

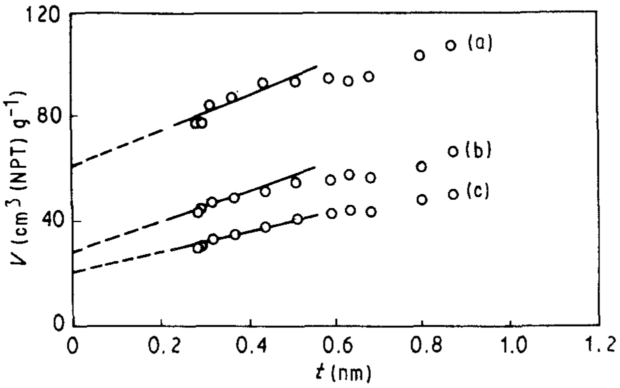

Figure 6 t-plots for nitrogen adsorption at 77.35 K upon Al-CLM after air-preheating 6 h at (a) 300 °C, (b) 500 °C and (c) 700 °C.

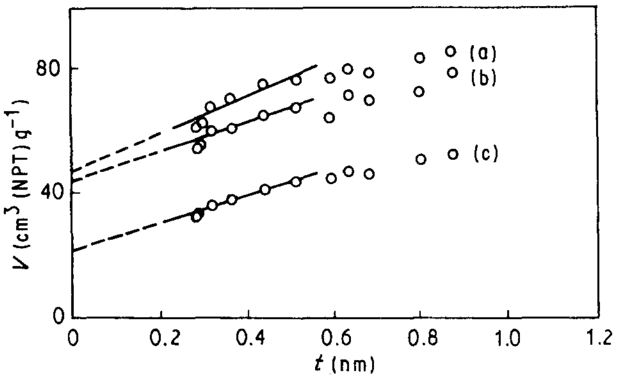

Figure 7 t-plots for nitrogen adsorption at 77.35 K upon Al(La)-CLM after air-preheating 6 h at (a) 300 °C, (b) 500 °C, and (c) 700 °C.

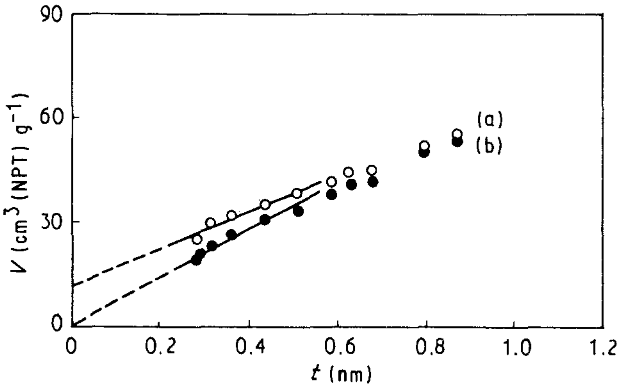

Figure 8 t-plots for nitrogen adsorption at 77.35 K upon (a) Al-CLM and (b) Al(La)-CLM after hydrothermal treatment for 24 h at 300 °C and 1 × 10^7 Pa.

The theoretical interlayer volume, V_t, has been calculated from the basal spacing, after subtracting the volume occupied by the pillars (Table II). The actual accessible volume, V_m for the pillared montmorillonites preheated at 300 °C is only about 30% of expectation from d(0 0 1). There are very few papers in the literature assessing microporosity, but from them [18, 19] and the data shown in Table II, the maximum micropore volume for alumina-pillared montmorillonites is in the region of 0.1 cm^3 g^{-1}.

Up to now the thermal stability of the pillars has been over-estimated from measurement of the basal spacing. However, Table II shows that the accessible volume decreases with increasing calcination temperature at a much greater rate than the basal spacing.

TABLE II S_t and micropore volume

Sample	Temperature (°C)	S_t (m^2 g^{-1})	V_m (cm^3 g^{-1})	V_t (cm^3 g^{-1})
Na-M	300	100	0.01	0.00
Na-M	500	87	0.00	0.00
Na-M	700	42	0.00	0.00
Al-CLM	300	100	0.09	0.27
Al-CLM	500	90	0.04	0.23
Al-CLM	700	59	0.03	0.20
Al(La)-CLM	300	95	0.07	0.28
Al(La)-CLM	500	73	0.06	0.20
Al(La)-CLM	700	69	0.03	–
Al-CLM	300 (HT)	90	0.00	0.17
Al(La)-CLM	300 (HT)	83	0.02	0.14

Therefore, the generally accepted conclusion that alumina pillars are stable at temperatures even above 500 °C may give a misleading picture of the pore structure evolution with calcination temperature.

Hydrothermal treatment at 300 °C cancelled out the interlayer accessible volume for Al-CLM, although a broad band can still be appreciated in its XRD diagram, centred around a value corresponding to a basal spacing of about 1.5 nm.

Lanthanum appears to exert a small positive effect towards the thermal and hydrothermal stability of the pillared montmorillonite.

By comparing data in both Tables I and II, a good agreement is observed between S_t for the pillared samples and S(BET) for Na-M after calcination at 300, 500 and 700 °C. The values of S(BET) for the pillared microporous montmorillonites lack any clear meaning.

4. Conclusions

From the literature and the present results, the maximum micropore volume accessible for alumina-pillared montmorillonite is shown to be about 0.1 cm^{3}g^{-1}.

The accessible microvolume decreases with increasing calcination temperature at a much greater rate than the basal spacing. Therefore, the generally accepted conclusion, from basal spacing measurements, that alumina pillars are stable at temperatures higher than 500 °C may give a misleading picture of their pore structure evolution with calcination temperature.

Hydrothermal treatment at 300 °C and 1×10^7 Pa cancels out the interlayer accessible volume for Al-CLM, although a broad band can still be appreciated in its XRD diagram, centred around a value corresponding to a basal spacing of about 1.5 nm.

Hydrothermal treatment at 300 °C and 1×10^7 Pa exerts different effects on Na-M and the pillared montmorillonites, according to EDR microanalysis. Sodium montmorillonite exhibits a homogeneous composition after hydrothermal treatment, and an Si/Al atomic ratio approaching that of untreated sample. The pillared montmorillonite shows a partial decomposition.

Lanthanum appears to exert a very small positive effect on the thermal and hydrothermal stability of the pillared montmorillonite studied.

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