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Characterization of the microporosity of pillared clays by nitrogen adsorption – application of the Horvath–Kawazoe approach

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The microporosity of aluminium pillared montmorillonite has been investigated by nitrogen adsorption, X-ray diffraction and electron microscopy. Control of the preparation conditions allowed the synthesis of solids with two types of micropores. Comparison of XRD measurements and Horvath–Kawazoe analysis of very low-pressure nitrogen adsorption have shown a new promising way to increase the micropore characterization. Disagreement between data from different techniques could be related to the different experimental conditions during measurements and to uncertain values of the interaction parameter in the Horvath–Kawazoe analysis.

1. Introduction

Important efforts have been devoted in recent years to the synthesis and characterization of pillared clays [1, 2]. This new kind of nano-composite is prepared by intercalating metal complex cations between the silicate layers of clays. Pillared oxides, formed after calcination, are capable of preventing the collapse of the interlayer spaces, generating therefore a microporous structure and a high specific surface area.

Pillared clays offer promise as new shape selective catalysts for reactions involving large molecules and as molecular adsorbents [3, 6]. Their usefulness is related to the micropore structure, which is not easy to characterize. X-ray diffraction is normally used to evaluate the interlayer spacing [7], but the pore size of pillared clays is determinated by both the interlayer distance and the lateral distance between pillars. More interesting information has been obtained using adsorption of probe molecules of known kinetic size [4, 8–14]. Recently, Horvath and Kawazoe have proposed a new method to determine the micropore volume distribution based on the adsorption isotherm data obtained at very low relative pressure (e.g. from $P/P_0 = 10^{-7}$–10^{-1} for nitrogen adsorption at 77 K) [15]. The Horvath–Kawazoe equation used in this analysis includes an interaction parameter dependent on the nature of both the adsorbent and the adsorbate. Reliable values for this parameter have been proposed only for active carbon [15] and zeolites [16]. As a first approach, based on the chemical similarity between zeolites and clays, the interaction parameter value derived for zeolites may be used to study pillared clays. Nevertheless, the validity of this approach should be checked by comparison with different characterization techniques.

In this work we studied three pillared clays and the starting material. Preparation conditions were chosen in order to obtain samples with different microporosity. Conventional nitrogen adsorption measurements, X-ray diffraction and electron microscopy have been used to characterize samples and these results are compared with the micropore size distribution obtained using the Horvath–Kawazoe equation to analyse low-pressure nitrogen adsorption data.

2. Experimental procedure

The starting material used in this work was montmorillonite (Kunipia F), kindly supplied by Kunimine Co. This commercial product is available in the sodium-exchanged form with a size less than 2 μm. Sodium montmorillonite was dispersed in water and aged for at least 2 months. It was then washed by dialysis until the conductivity of the surrounding water was less than 1.5 μS. The solid content of the dialysed clay dispersion was 7–10 g l^{-1}. The montmorillonite treated in this way and dried at 393 K for 16 h is referred to as (S-1).

Aluminium polycations were prepared by slow titration of 0.2 M $AlCl_3$ solution with 0.2 M NaOH under vigorous stirring [17, 18]. The sample referred to as (S-2), was prepared with an OH/Al mole ratio equal to 1 and aged at room temperature for two days (pH = 3.8). That referred to as (S-3) was prepared with an OH/Al mole ratio equal to 2 and aged at 363 K for 4 h (pH = 3.9) [19].

Both (S-2) and (S-3) pillared clays were obtained by dropping the aqueous montmorillonite suspension into the respective polycation solution with vigorous stirring (preparation ratio 30 mM Al/g clay), ageing at room temperature for 24 h, washing by centrifugation and drying at 393 K for 16 h. The sample referred to as (S-4) was obtained by calcination of sample (S-3) at 673 K for 4 h.

Aluminium-27 (78.2 MHz) nuclear magnetic resonance (^{27}Al NMR) spectra of the polycation solutions were obtained on a Varian VXR-300 spectrometer at room temperature using an 8 mm probe containing a capillary tube with $Al(OH)_4^-$ as aluminium reference (80 p.p.m. [20]) and D_2O as an external field-frequency lock. The Al_{13} (Keggin cation) presence in the aluminium solutions was evaluated by the 62.5 p.p.m. line corresponding to the central aluminium in tetrahedral coordination [21, 22].

The basal spacing of the samples was measured by X-ray diffraction (XRD) of a thin layer of the clays on glass slides using a Philips PW 1710 difractometer with nickel filtered CuK_α radiation.

Nitrogen adsorption measurements at 77 K were carried out on a Micromeritics ASAP 2000 micropore analyser equipped with a molecular drag pump (ultimate vacuum 10^{-8} bar). The samples were previously degassed at 393 K for 24 h. Surface areas, S_{Lang} ($0.01 \leq P/P_0 \leq 0.05$) were calculated using the Langmuir equation for monolayers which is more suitable for microporous solids than the BET equation for multilayers [5, 11, 23–26]. Total pore volumes, V_p, were estimated at a relative pressure of 0.99. Micropore volumes and size distribution were obtained using Horvath–Kawazoe (H–K) analysis [15]. The interaction parameter value used in this analysis was 3.49×10^{-43} erg cm^4 mol^{-1}, suggested for zeolites [16]. Micropore volumes, $V_{\mu p}$, were calculated for pores with diameter less than 2 nm [27]. Mesopore volumes, V_{mp}, were calculated by subtracting the micropore volume from the total pore volume.

Electron microscopy observations were carried out in a Jeol 4000 EX ($C_s = 1.00$ mm) and a Hitachi 7000 FA. Samples were ground in an agate mortar and then dispersed in isopropyl alcohol in an ultrasonic bath for several minutes. Some drops of this suspension were deposited on a standard copper grid previously covered with a holey carbon film.

3. Results

Fig. 1 shows the ^{27}Al NMR spectra of aluminium solutions used to prepare (S-2) and (S-3). The fraction of aluminium in the form Al_{13} polycation (Keggin ion) is related to the signal ratio between the line at 62.5 p.p.m. and 0 p.p.m., corresponding to tetrahedral and octahedral aluminium, respectively. It can be seen that the conditions used to prepare the solution for (S-2) (OH/Al = 1, aged 2 days at room temperature) produced a significantly lower amount of Al_{13} ion than those used for (S-3). (OH/Al = 2, aged 4 h at 363 K.)

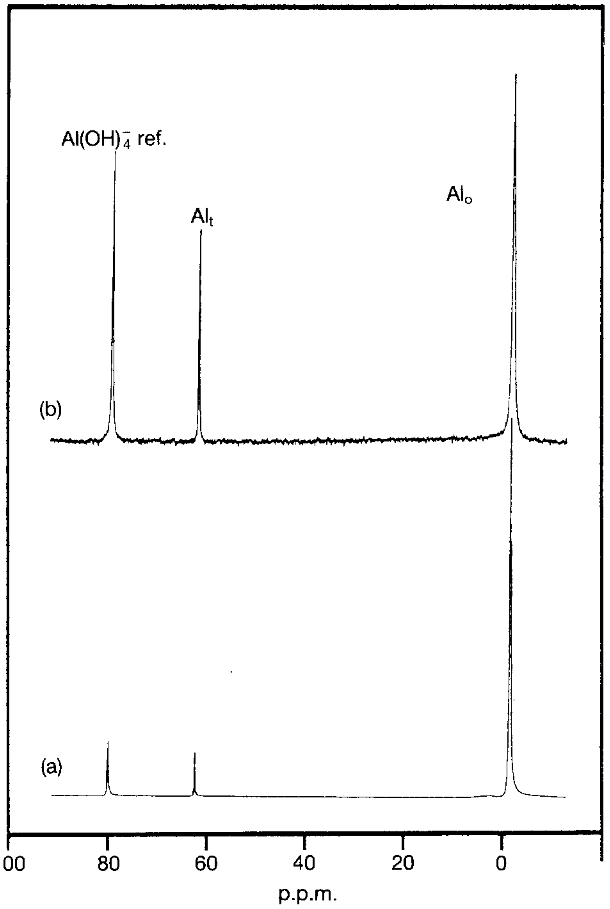

Figure 1 ^{27}Al NMR spectra of aluminium solutions used to prepare (a) (S-2) and (b) (S-3). (a) OH/Al mole ratio equal to 1 and aged at room temperature for 2 days. (b) OH/Al mole ratio equal to 2 and aged at 363 K for 4 h.

Fig. 2 shows the adsorption–desorption isotherm for nitrogen on (S-1). The adsorption isotherm is type I in the Brunauer, Deming, Dewing and Teller (BDDT) classification [27] at low pressures (microporous solids). The hysteresis loop (B type in the Boer classification [28]) indicates the presence of mesoporosity. Mesoporosity of this type of sample can be related to "house-card" structures [29]. The general aspect of the isotherm did not change after the pillaring process, showing only a significant increase in the amount of nitrogen adsorbed.

Table I presents the values of surface area, S_{Lang}, total pore volume, V_p, microporous volume, $V_{\mu p}$, and mesoporous volume, V_{mp}. All these parameters increased for (S-2) with respect to (S-1), but the increases were more important for (S-3). Calcination treatment of (S-3), yielding (S-4), produced an additional slight increase in all the parameters.

XRD patterns of the four samples are presented in Fig. 3. Basal spacings of the significant peaks are shown on the same figure. (S-1) shows a sharp peak at 1.23 nm corresponding to 0.27 nm interlayer distance, after subtracting the montmorillonite layer thickness 0.96 nm. (S-2) presents a double peak with maxima corresponding to interlayer distances of 0.9 and 0.36 nm. (S-3) shows an asymmetric peak with an important tail at higher angles, with a maximum corresponding to an interlayer distance of 0.86 nm. (S-4) shows a peak with the same shape and maxima position as (S-3), but showing a slightly more disordered material.

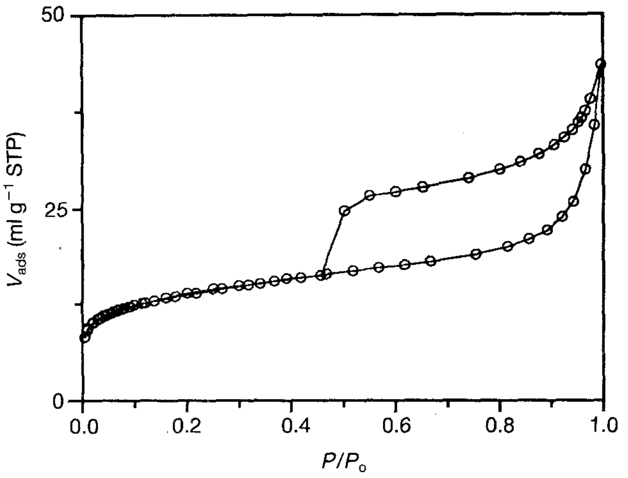

Figure 2 Nitrogen adsorption–desorption isotherm of (S-1).

The micropore volume distributions using the Horvath–Kawazoe equation, shown in Fig. 4 (S-1) did not show microporosity accessible to the nitrogen molecule in significant amounts. (S-2) shows an increase of the microporosity with two features. The first one with a sharp maximum at 0.5 nm and the second one, broader, mainly between 0.6 and 1 nm. (S-3) also shows two zones but the one corresponding to higher pore diameter presents an important increase. Finally, (S-4) shows an increase in both the micropore volume and the pore size.

Conventional transmission electron microscopy did not reveal significant variations in the morphology of samples. Dark elongated zones, which might be the laminar configurations in a perpendicular orientation were commonly observed. High-resolution electron microscopy (HREM) observations were carried out specially in the elongated zones with the darker contrast. Lattice resolution was not easily obtained due to technical and experimental difficulties related to the nature of the samples, showing low stability. Nevertheless, after a long evacuation time and several attempts, lattice images were obtained in all cases.

Fig. 5 shows HREM micrographs of the samples studied, showing lattice images of the clay sheets. Lattice *d*-spacing measurements were carried out directly from the negative film images. Variations in *d*-spacing in each sample were detected even in the same zone under study; also structural alternations, for example dislocation planes, were observed in all the samples. Table II presents *d*-spacing measurements for the four samples.

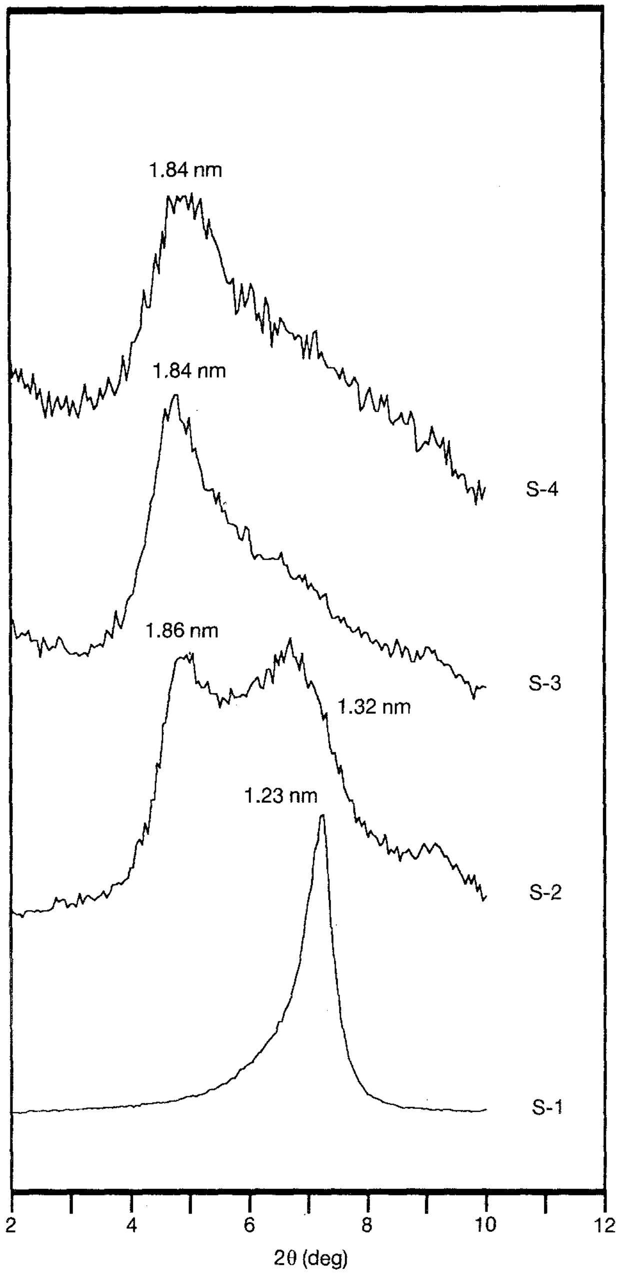

Figure 3 X-ray diffraction of the four samples.

4. Discussion

Surface area and pore volume increases (S-2) to (S-4) with respect to (S-1) confirms that aluminium species used during preparation had entered between the clay layers, increasing the nitrogen accessibility. Changes are mainly related to microporosity, whilst mesoporosity remains relatively constant. (S-3) and its

TABLE I Langmuir surface areas and pore volumes of the samples

Samples	S_{Lang}(m^2 g^{-1})[a]	V_p(ml g^{-1})[b]	$V_{\mu p}$(ml g^{-1})[c]	V_{mp}(ml g^{-1})[d]
S-1	52 ($C = 355$)	0.067	0.018	0.049
S-2	87 ($C = 542$)	0.083	0.030	0.053
S-3	263 ($C = 652$)	0.155	0.095	0.060
S-4	311 ($C = 483$)	0.186	0.111	0.075

[a] $0.01 \leqslant P/P_0 \leqslant 0.05$ interval of P/P_0.
[b] Total pore volume at $P/P_0 = 0.99$.
[c] From H–K analyses ($d_p \leqslant 2$ nm).
[d] $V_{mp} = V_p - V_{\mu p}$.

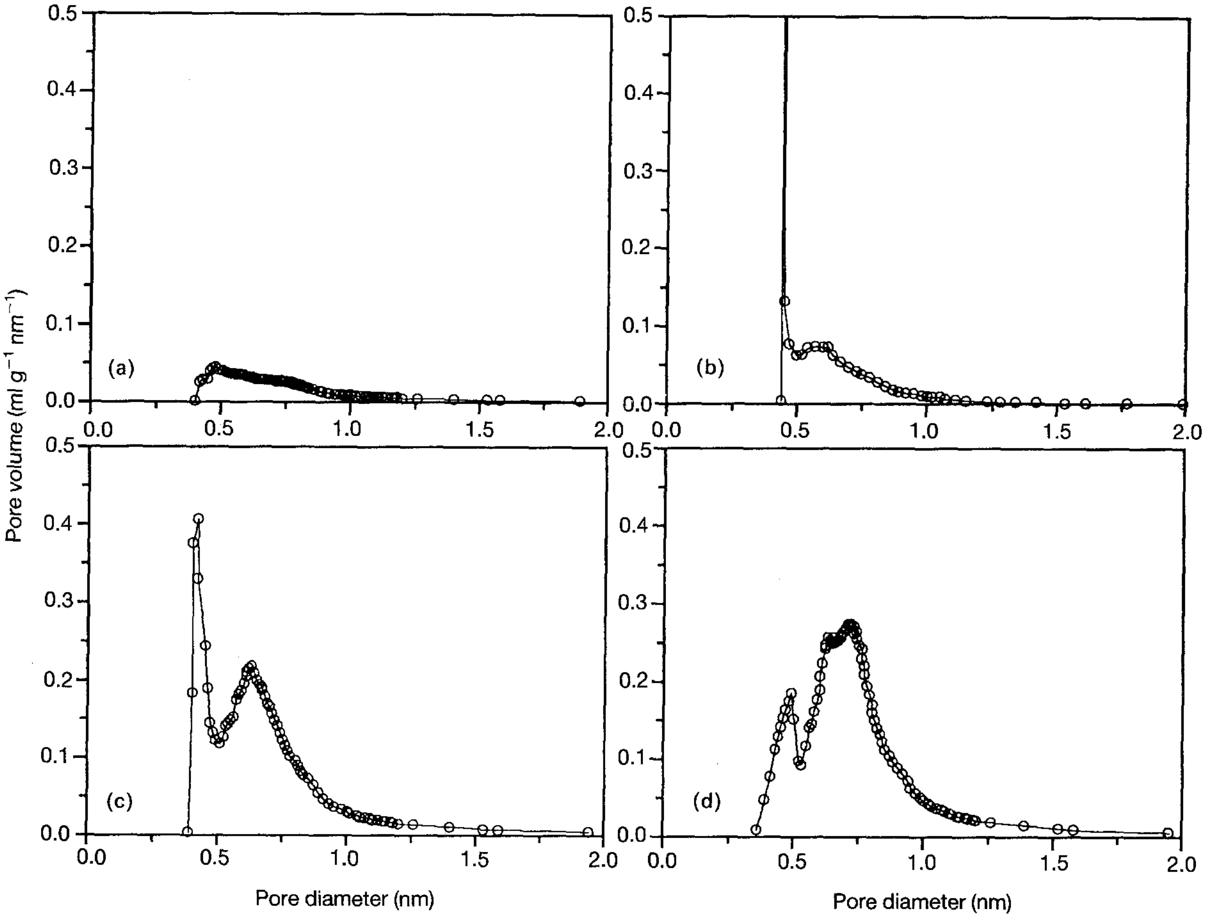

Figure 4 Micropore volume distributions for samples using the Horvath–Kawazoe analysis. (a) S-1, (b) S-2, (c) S-3, (d) S-4.

calcinated form, (S-4), show more important textural changes than (S-2), due to differences in the preparation conditions. The distance between the silicate layers after the intercalation process depends on the nature of the aluminium species present in the solution used. The maximum distance can be obtained with Al_{13} (Keggin ion) [1, 30] but other species can be produced by hydrolysis of aluminium solutions with concentrations higher than 10^{-4} M [22, 31–33]. The OH/Al ratio and the ageing conditions control the amount of Al_{13} produced [17–19]. ^{27}Al NMR spectra confirm that the conditions chosen to prepare the aluminium solution for (S-3) produced a large amount of Al_{13} than that used for (S-2) and in agreement, surface area and pore volume increases in (S-3) and (S-4) are also greater than in (S-2).

Interplanar spacings of the samples measured by HREM confirm the separation produced by the pillaring process. Despite the large variation in the interplanar spacing in each sample the mean value appeared to be constantly 0.3–0.5 nm smaller than those observed by XRD measurements. This discrepancy has been attributed to the dehydration of specimens in the vacuum chamber of the microscope [29]. Atomic resolution images of pillared and neighbouring zones (see the arrow on Fig. 5c) were also obtained but image interpretation is currently in progress. These kind of observations have been related to different oxides of the pillaring cation out of the interlayered space of the clay [29, 34].

Additional information about microporosity can be obtained by comparing XRD measurements and the H–K micropore volume distribution obtained by means of nitrogen adsorption. Comparison between results must be carried out carefully, taking into account differences and similarities between the measured parameters and experimental conditions used in each technique. Interplanar spacing, d_{001}, were obtained by means of XRD. Measurements were carried out in air using oriented samples on glass slides at room temperature. In contrast nitrogen adsorption experiments to obtain microporosity information must be carried out at very low pressures (beginning from $P/P_0 = 10^{-7}$) demanding first a vigorous degassing treatment (493 K; 24 h; ultimate vacuum 2×10^{-8} bar) of the samples. Horvath–Kawazoe calculations, used to obtain the micropore volume distribution, depend on the interaction parameter value used [15]. There are no literature values for this parameter when clays are analysed and the value suggested for zeolites [16] has been used. The main

TABLE II Basal spacings of the samples from HREM

Samples	d(nm)
S-1	$1.20 < d < 1.26$
S-2	$1.16 < d < 1.49$
S-3	$1.50 < d < 1.90$
S-4	$1.50 < d < 1.75$

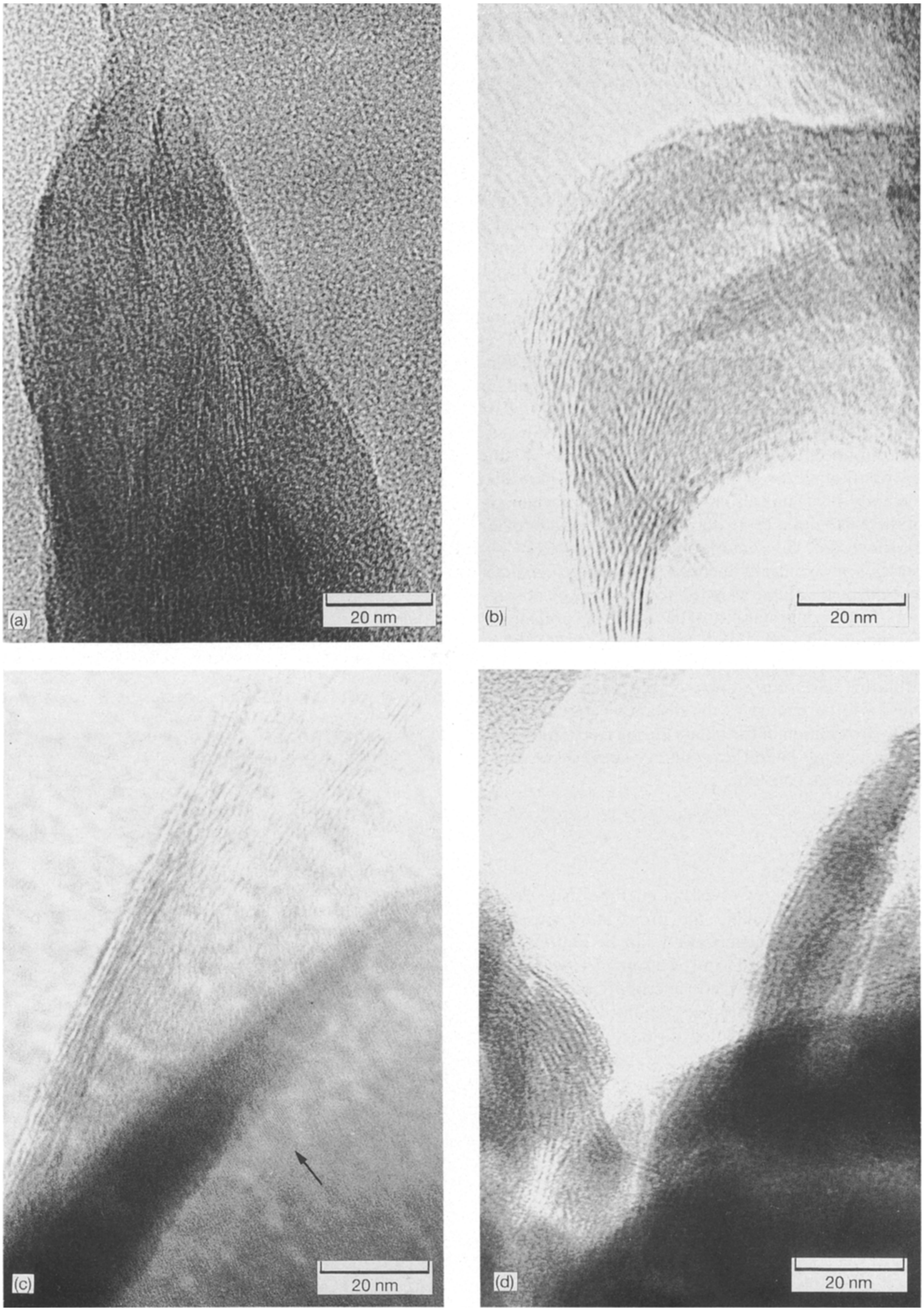

Figure 5 HREM micrographs of (a) (S-1), (b) (S-2), (c) (S-3) and (d) (S-4).

change produced by varying the interaction parameter is a shift in the pore volume distribution curve along the pore diameter axis whilst maintaining the general shape. The pore diameter obtained with this calculation is related to the nitrogen accessibility and for a pillared clay, the former is controlled by both the distance between the clay layers and the separation between pillars.

In consequence, differences shown between the results of these two techniques can be due to the degree of dehydration of the samples, the value of the interaction parameter used in the Horvath–Kawazoe equation, and the influence of the distance between pillars.

The interlayer distance for (S-1), measured by XRD, is so narrow that nitrogen adsorption does not show microporosity in a significant amount. (S-2) has been prepared with an aluminium solution where the Al_{13} ion has been only partially formed. As a consequence, two types of intercalation species will be produced: Keggin ion and aluminium hydroxide species [35]. Both XRD and nitrogen microporosity analyses confirmed this interpretation, showing two maxima. Preparation of (S-3) was made with an aluminium solution that had a higher Al_{13} content than that used for (S-2), producing mainly typical aluminium pillars (0.8–0.9 nm); this is reflected in XRD and nitrogen adsorption data. In addition, the micropore volume distribution shows some porosity at lower pore diameters (0.4–0.6 nm), also in agreement with asymmetry of the XRD peak. (S-4), obtained by calcination of (S-3), shows the same interlayer distance by XRD, but presents a significant increase in the pore diameter and the pore volume as measured by nitrogen adsorption. The thermal stability of basal spacing obtained in aluminium pillared clays is well known [9, 35, 36], as shown before. Therefore, the micropore volume distribution variation shown by nitrogen adsorption must also be related to the distance between pillars. Dehydroxylation of the pillars during calcination [37] could increase lateral accessibility keeping the interlayer distance constant.

5. Conclusions

Pillared clays with two types of microporosity can be prepared by controlling the preparation variables. Microporosity characterization can be improved by comparison of the XRD and electron microscopy data with the Horvath–Kawazoe micropore analysis. Disagreement between pore sizes obtained with different techniques could be related to differences in the experimental conditions and to the uncertain value of the interaction parameter used in the Horvath–Kawazoe analysis. Nevertheless, the H–K method appears to be a new promising way to improve the micropore characterization, but additional efforts should be devoted to the determination of a reliable value for the interaction parameter for different samples.

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