SINTERING OF MONTOMORILLONITES PILLARED BY HYDROXY-ALUMINUM SPECIES

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Abstract—The sintering of montmorillonites pillared by hydroxy-Al species was investigated by several techniques. The change of the microporosity of the pillared interlayer clay with temperature shows that sintering was mainly due to the loss of microporosity. On calcination of the parent clay at 760°C, the X-ray powder diffraction pattern did not change; the 060 line shifted only slightly from 8.988 to 9.017 Å. The infrared (IR) spectrum suggested some dehydroxylation, but the structure appears to have been preserved. On calcination of the pillared clay at >700°C, the intensity of the 001 line decreased steadily, the 060 line broadened, and the b parameter decreased slightly from 8.988 to 8.928 Å. Fe^{3+} ions apparently occupied only one site after calcination at 300°C and two sites after calcination at 700°C. Smaller isomer shifts and higher quadrupole splittings in the Mössbauer spectra suggest that calcination produced more covalent bonding of Fe^{3+} and a highly distorted structure. The IR spectrum was significantly modified by calcination of the sample, and the 935- and 1125-cm^{-1} bands disappeared and the 1035-cm^{-1} band broadened. These results suggest that at <700°C the pillars sintered and that the clay progressively decomposed at >750°C. The pillaring-induced decrease of thermal stability of the clay was likely due to the introduction of protons during the first step of the preparation. The thermal stability of these Al-pillared interlayer complexes is comparable to that reported for hydroxy-silicoaluminum montmorillonites and fluorhectorites.

Key Words—Calcination, Hydroxy-Al, Infrared spectroscopy, Montmorillonite, Mössbauer spectroscopy, Pillared interlayer complex, Thermal stability.

Résumé—Le frittage de montmorillonites pontées par des polycations aluminiques a été étudié par différentes techniques. Les variations de la porosité de l'argile pontée en fonction de la température de calcination sous air sec montrent que le frittage est principalement dû à la disparition de la microporosité. Le spectre de rayons X de l'argile initiale est préservé après calcination à 760°C, la seule modification notable étant un léger déplacement de la raie 060 de 8,988 à 9,017 Å; le spectre infrarouge révèle un début de deshydroxylation, mais la structure reste intacte. La calcination de l'argile pontée provoque une diminution régulière de l'intensité de la raie 001 et un élargissement de la raie 060 au dessus de 700°C, avec une légère contraction du paramètre b de 8,988 à 8,928 Å. Les ions Fe^{3+} occupent un seul type de site après calcination à 300°C et deux sites différents après calcination à 700°C. Après calcination, le déplacement chimique relatif à ces ions diminue et l'écartement quadrupolaire augmente, ce qui suggère des liaisons plus covalentes avec le réseau et une structure très désordonnée. Le spectre IR est également fortement modifié par la calcination avec la disparition des bandes de vibration à 935 et 1125 cm^{-1} et l'élargissement de la bande à 1035 cm^{-1}. Ces résultats sont interprétés par un frittage des piliers aluminiques pour T <700°C et une destruction progressive du feuillet de l'argile au dessus de 750°C. La baisse de stabilité thermique de l'argile induite par le pontage est attribuée à l'introduction de protons au cours de la première étape de la préparation. La stabilité thermique de ces argiles pontées par des polycations aluminium est comparable à celle des montmorillonites et des fluorhectorites pontées par des silico-aluminates.

INTRODUCTION

Recently, several methods have been reported for preparing pillared forms of swelling clay minerals (PILCs). These methods involve the introduction of complex inorganic polycations into the interlayer space of these minerals, thereby producing a regular porous structure having pore apertures controlled by the size of the pillaring species. Montmorillonites pillared by

aluminum (Lahav *et al.*, 1978; Vaughan *et al.*, 1979; Occeli and Tindwa, 1983), zirconium (Yamanaka and Brindley, 1978), titanium (Jacobs *et al.*, 1982; Sterte, 1986; Yamanaka *et al.*, 1986), chromium (Shabtai *et al.*, 1980a; Pinnavaia *et al.*, 1985b), hydroxy cations or cationic organo-silicon compounds (Lewis *et al.*, 1985) have been described. Shabtai *et al.* (1980b) reported that pillared clays are more active than Y-type zeolites for the cracking of bulky molecules; therefore, clays could be attractive catalysts for converting heavy petroleum fractions. If these clays are to be used as cracking catalysts, they must be thermally and hydrothermally stable.

The thermal properties of pillared clays, however, have been scarcely described. In the open literature, Occelli and Tindwa (1983) reported poor hydrothermal stability at 650°C for an Al-PILC. Bartley and Burch (1985) observed a similar behavior for Zr-PILCs and a severe loss of surface area at 730°C. Similar stabilities were described by Sterte (1986) for Ti-PILCs, which show a twofold decrease of surface area between 700° and 800°C. Surprisingly, the steam-treated samples showed a more gradual decrease in surface area with increasing temperature and retained a surface area of about 170 m²/g at 800°C, compared with 100 m²/g for a sample calcined in dry air at 800°C. In the patent literature, Vaughan *et al.* (1979) reported a substantial improvement of the hydrothermal stability by pillaring smectites with mixed oligocations containing Al in combination with Si. The surface area reached 165 m²/g after steaming at 760°C. Lewis *et al.* (1985) pillared montmorillonites with polyhedral oligosilsesquioxane compounds which, upon calcination, gave rise to two-layer silica structures between the layers. A pillared product, having d(001) values of 16.1–19.7 Å and surface areas of 150–400 m²/g was obtained and retained 85% of the intensity of its initial 001 XRD line after steaming for 1 hr at 750°C, and 40% after steaming at 800°C.

Many authors have pointed out the importance of the stability of the chemical bond linking the pillars to the clay. Plee *et al.* (1985) investigated the process of pillaring using high-resolution, solid-state nuclear magnetic resonance (MAS-NMR) of ^{29}Si and ^{27}Al. They obtained direct spectroscopic evidence that $(Al_{13}O_4 \cdot (OH)_{24}(H_2O)_{12})^{7+}$ was the pillaring species. In uncalcined pillared products, only electrostatic bonding exists between the negatively charged layers and the pillaring oligocations. For clays containing no tetrahedral substitution, e.g., hectorite or Laponite, calcining the pillared material did not change the MAS-NMR spectra. Therefore, no reaction was apparent between the pillaring cation and the clay layer. For beidellite, which contains substitutions in the tetrahedral layer, the MAS-NMR data suggest that calcination induces a reaction between the Al polymer and the Al-substituted tetra-

hedral layer, resulting in a strong covalent bond. Plee *et al.* (1985) described the formation of these new Al–O–Al bonds by a reaction between inverted Al tetrahedra in the clay tetrahedral layer and Al–OH groups of hydroxy-Al cations.

Pinnavaia *et al.* (1985b) suggested two mechanisms for the pillaring of smectites. Although calcined alumina-pillared montmorillonite and Laponite exhibited no evidence for layer reaction, MAS-NMR data showed the occurrence of significant structural changes in fluorhectorite. The model proposed by Plee *et al.* (1985) was adapted to fluorhectorite, assuming that SiO_4 units could be inverted and linked to hydroxy-Al cations. The higher reactivity of fluorhectorite was ascribed to the presence of F atoms, which labilize the Si–O bonds.

Sterte and Shabtai (1987) reported a high stability for montmorillonites and fluorhectorites pillared by hydroxy-silico-aluminum species. After calcination in air at 700°C, the surface area was 220 m²/g for montmorillonite and 150 m²/g for fluorhectorite, compared to 320 m²/g and 230 m²/g at 300°C. The remarkable stability of Si-Al-fluorhectorite was attributed to, following the proposals of Pinnavaia *et al.* (1985b), the formation of a covalent bond between inverted SiO_4 units of the clay tetrahedral layer and the hydroxy oligocations. The formation of these bonds may therefore be an important factor for the thermal properties of pillared clays, and most workers agree (e.g., Plee *et al.*, 1985; Pinnavaia *et al.*, 1985a) on the absence of such bonds in Al-montmorillonites, the stability of which was correlated by Tichit *et al.* (1985) and Tokarz and Shabtai (1985) with the density of the pillars.

The maximum temperature at which these pillared clays can be used still cannot be predicted. The thermal stability of the clay itself has been shown to depend on the chemical composition of the layer and on the nature of the interlayer cations (Ames and Sand, 1958). Trioctahedral clays are generally more stable than dioctahedral clays; stability is markedly less for the H forms. Ames and Sand (1958) reported a maximum hydrothermal stability of 750°C for trioctahedral clays, using very severe conditions, i.e., 1000 atm H_2O for 2 days. The present work was undertaken to gain insight into the different processes involved in the collapse of PILCs. The original clays contained Fe^{3+} substituting for Al^{3+} in the octahedral layer. Mössbauer spectrometry was used to determine the local environment of these Fe^{3+} cations, which is believed to reflect the deformations of the clay sheets upon thermal treatments.

EXPERIMENTAL

Preparation of the pillared clays

The procedure for preparing the pillared clays was described by Lahav *et al.* (1978). The starting material was a natural montmorillonite from Greece, furnished

Table 1. Chemical composition (anhydrous) (mole %) of original and intercalated clays.

	Montmorillonite	Al-PILC[1]
SiO_2	61.74	61.74
Al_2O_3	20.13	39.71
Fe_2O_3	7.39	6.58
CaO	1.98	0.09
MgO	3.86	4.98
Na_2O	0.24	0.11
K_2O	3.58	1.66
TiO_2	0.87	n.d.
d(001) (Å)[2]	12.6	18.6
Specific[2] area (m^2/g)	70	350

n.d. = not determined.

[1] Chemical composition of the pillared interlayer complex (PILC) is referred to the initial silica content of the clay.

[2] d(001) values determined on samples dried at room temperature and specific areas on samples evacuated at 300°C.

by Expansia (Aramon, France). A solution containing the pillaring agent, the hydroxy-Al oligomer $(Al_{13}O_4 \cdot (OH)_{24}(H_2O)_{12})^{7+}$, was prepared by mixing 0.2 M solutions of $AlCl_3 \cdot 6H_2O$ and NaOH. The desired volume of intercalating agent was added dropwise at room temperature to the clay previously dispersed in deionized water.

After intercalation, the clay slurry was stirred for 3 hr at 80°C, filtered, washed several times in hot deionized water, and dried at 60°C in air.

Thermal treatment of the pillared clays

The pillared clays were calcined in a shallow bed in a horizontal furnace swept by an air flow of 100 ml/min. The heating rate was 50°C/hr, and the desired temperature was maintained for 5 hr. A fresh sample was used for each calcination temperature.

Characterization studies

Several techniques were used to define the basal spacings, specific surface, pore-size distribution, and structure of the PILCs. The position of the 001 X-ray powder diffraction (XRD) peak defined the interlayer distance. Its symmetry and intensity were also indicative of the ordering along the axis. The 060 peak gave similar information about the b parameter. XRD patterns were recorded on a CGR Theta 60 instrument using monochromatized CuKα radiation.

Surface areas were obtained from N_2 adsorption isotherms using BET methods. The analysis of the desorption branch of the isotherm by the method described by Barrett *et al.* (1951) allowed pore-size distributions to be obtained, assuming a cylindrical shape for the pores.

Infrared (IR) spectra were recorded between 1200 and 600 cm^{-1} with a Beckman Microlab 600 computing spectrometer. The samples were crushed, mixed with KBr powder, and pressed into wafers. A typical wafer concentration was 3 mg of pillared clay in 300 mg KBr.

Mössbauer spectra were recorded at room temperature on a Elscint MFD4 spectrometer driven by a Promeda multichannel analyzer. The samples contained 10–15 mg Fe/cm^2; the ^{57}Co source was 20 mCi. The spectra were computer fitted using the program GMFP of Ruebenbauer and Birchall (1979) using Lorentzian approximation. Between 10^7 and 2×10^7 counts per channel were accumulated. The maximum absorbance was about 5%. Isomer shifts (IS) are given with respect to metallic iron with a precision of 0.01 mm/s. The accuracies on quadrupole splittings (QS) and linewidths are 0.05 mm/s.

RESULTS

Characterization of the intercalated clay

The chemical compositions of the natural montmorillonite used in this study and those of the clay exchanged with $(Al_{13}O_4(OH)_{24}(H_2O)_{12})^{7+}$ cations are listed in Table 1. The exchange was responsible for the decrease in the concentrations of K$^+$, Na$^+$, and Ca^{2+}. In montmorillonites, Mg^{2+} and Fe^{3+} replace some Al^{3+} in the octahedral layer; hence, only a small quantity of these cations was exchangeable.

The intercalation of $(Al_{13}O_4(OH)_{24}(H_2O)_{12})^{7+}$ cations was accompanied by a shift of the 001 spacing from 12.60 to 18.60 Å (Figure 1a). Simultaneously, the specific area increased from 70 m^2/g for the initial clay to 350 m^2/g for the intercalated sample outgassed at 300°C under secondary vacuum. More information about these specific areas was deduced from the application of the Barrett-Joyner-Halenda (1951) method to the N_2 adsorption isotherm. For the initial montmorillonite, all the surface (70 m^2/g) was in pores in the size range 20–200 Å, defined as mesopores. In contrast, for the Al$_{13}$-exchanged montmorillonite, calcined at 300°C, 70% of the specific area, i.e., 245 m^2/g, was in pores <20 Å in diameter, defined as micropores. On intercalation, the surface area contained in the mesopores increased only by about 30 m^2/g compared with the initial clay. Consequently, the pillaring process produced an important microporosity, but only a small amount of mesopores in these air-dried samples. The b cristallographic parameter of the aluminosilicate structure was not changed by the Al$_{13}$ exchange, as evidenced by the unchanged position of the 060 XRD line (Figure 1b).

Mössbauer parameters of Fe^{3+} ions remained unchanged (Figure 2, Table 2), showing that the environment of iron did not change by intercalation. Thus, the structure of the clay sheet appears to have been unaffected by the process.

The 001 XRD peaks and specific areas of samples calcined as high as 800°C are shown in Figure 3. Basal XRD spacings were reduced to 17.60 Å at 300°C and
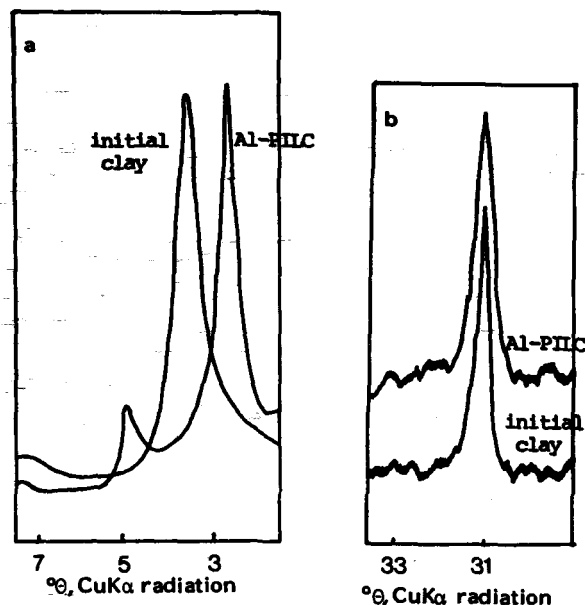
Figure 1. (a) 001 and (b) 060 X-ray powder diffraction spacings for original Greek montmorillonite and Al-pillared interlayer complex.

then remained constant at higher temperatures. The intensity of this XRD peak decreased with the treatment temperature, apparently due to the loss of long-range ordering along the c axis. The surface area measured on the samples calcined at 500°C was 340 m^2/g; however, at higher temperatures a uniform decrease was observed to 140 m^2/g at 800°C.

The specific areas contained in micropores and mesopores for each calcined sample are listed in Figure 4. The loss of specific area was essentially related to the disappearance of the micropores, the mesopores remaining unchanged (~100 m^2/g). In both the original clay and the Al-PILC the surface contained in mesopores was constant, regardless of the calcination temperature.

Influence of thermal treatment and pillaring on structure of aluminosilicate clay layer

Thermal treatment of the initial clay. The structural evolution of the aluminosilicate layer was characterized by IR spectrometry. The main IR absorption bands of montmorillonite in the range 600–1200 cm^{-1} were assigned by Stubican and Roy (1961a, 1961b). The shoulder at 1125 cm^{-1} (Figure 5a) was attributed to the Si–O stretching vibration of the apical oxygens of the tetrahedral layer. The large band centered at 1035 cm^{-1} was attributed to the combined stretching and bending vibrations of the Si–O bonds related to the basal oxygens. The band at 935 cm^{-1} is due to an OH group bonded to Al atoms. Bands in the range 600–
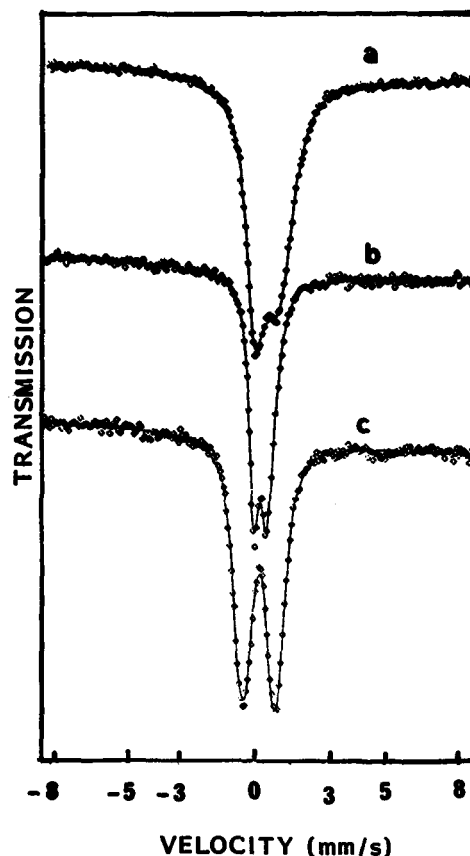

Figure 2. Mössbauer spectrum of (a) original Greek montmorillonite, (b) unheated Al-pillared interlayer complex (PILC), (c) Al-PILC heated at 680°C.

900 cm^{-1} are related to different Si–O and Si–O–Al^{VI} vibrations and have not been assigned precisely.

Figures 5a and 5b compare the IR spectra obtained on uncalcined and calcined (760°C in dry air) samples of the Greek montmorillonite, respectively. For the calcined sample, the band at 935 cm^{-1} is absent, and the shoulder at about 1125 cm^{-1} is sharper than for the untreated sample. Between 700 and 900 cm^{-1} the bands initially at 850, 800, and 710 cm^{-1} for the uncalcinated sample are more intense. The band at 800 cm^{-1} has not shifted, but the two other bands have shifted to 875 and 734 cm^{-1}. The absence of a band at 935 cm^{-1} may be attributed to dehydroxylation.

The increase in intensity of the 1125-cm^{-1} shoulder and the shifts of the bands at 850 and 710 cm^{-1} suggest modifications in the bonding of the apical oxygens and distorsions of the Si–O–Al bonds, reflecting structural changes occurring in the clay sheet. From the XRD data, the b parameter increased from 8.988 to 9.017 Å, in line with the IR results. Thus, a dilatation of the sheet on calcination appears to have taken place, but the structural integrity of the original clay sheet was still preserved at 760°C.
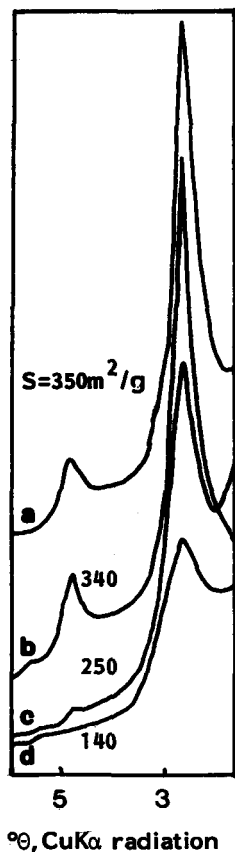
Figure 3.   001 X-ray powder diffraction spacings and specific areas of Al-PILC, (a) unheated and heated at (b) 500°C, (c) 700°C, and (d) 800°C.

Figure 4.   Specific surface areas contained in micropores and mesopores of the heated Al-pillared interlayer complexes.

Influence of pillaring and thermal treatment. The IR spectra of the montmorillonite pillared with $(Al_{13}O_4(OH)_{24}(H_2O)_{12})^{7+}$ cations as prepared and calcined at various temperatures to 760°C are reported in Figure 6. Ion exchange did not affect the bands at 1125 and 1035 cm^{-1}, and only a shift to 735 cm^{-1} of the band initially at 710 cm^{-1} was noticed. The tetrahedral layer was therefore not modified. These data confirm the results obtained by XRD and Mössbauer spectroscopy, which showed that the intercalation did not affect the structure of the clay layer.

After calcination, the IR spectrum changed as follows: (1) The dehydroxylation process was evidenced by the disappearance of the band at 935 cm^{-1} at calcination temperatures of 300°C. (2) For higher temperatures, the shoulder at 1125 cm^{-1} decreased progressively, accompanied by a broadening of the band centered at 1035 cm^{-1}. (3) The bands initially at 800 and 735 cm^{-1} shifted to 775 and 700 cm^{-1}, respectively, at 300°C and were no longer detectable at about 700°C.

Simultaneously, the *b* parameter decreased from 8.988 to 8.928 Å after the sample was calcined at 300°C.
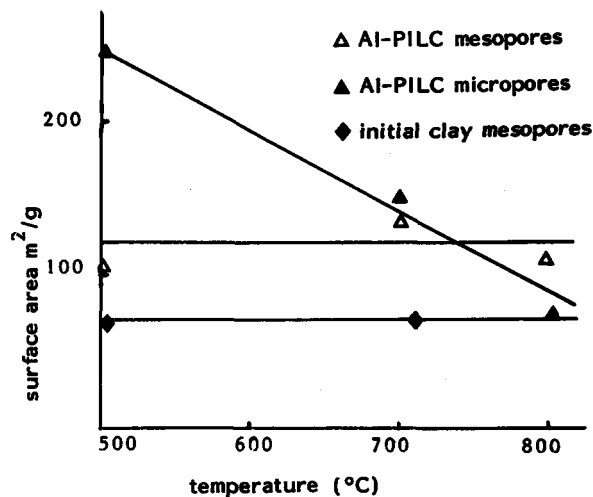
It then remained constant, but the 060 peak became broader, indicating a decrease of the short-range ordering of the layer structure. The Mössbauer parameters for example, on a sample calcined at 680°C (Table 2, Figure 2b) suggest a distorsion of the environment of iron. The Fe^{3+} ions were coordinated differently, and two types of sites were defined having different numbers of OH groups in their environment. QS values were also enhanced compared with those found for the initial clay, and the values of IS decreased, probably because of the development of more covalent bonds between iron and its neighbors (Rozenson and Heller-Kallai, 1977). According to these authors, higher QS values suggest distorsion of the environment of Fe^{3+}. Assuming that this cation is a label atom reflecting the structure of the clay sheet, the clay sheet of the PILC was probably progressively destroyed on calcination. This process began at slightly less than 700°C and produced a completely distorted state at 750°–780°C.

DISCUSSION

Pillaring increased the specific surface area of the original montmorillonite from 70 to 350 m²/g essentially by the creation of micropores <20 Å in diameter. This increase in surface area is consistent with the expansion of the structure observed by XRD. Upon calcination in dry air at >500°C, the surface area decreased steadily, essentially due to the disappearance of the micropores without the creation of mesopores. As shown by XRD results, the structure became less and less defined along the *c* axis. These results reflect the progressive degradation of the pillars. At about 700°C, the clay layer became distorted, as evidenced by a broadening of the 060 line and changes in the IR and Mössbauer spectra. Consequently, for the samples studied here, the thermal stability of the clay layer itself

Figure 5. Infrared spectra of the original Greek montmorillonite (a) unheated and (b) heated at 760°C.

was not the limiting factor for the thermal stability of the PILC at 700°C. Indeed, the parent montmorillonite appeared to be stable as high as 760°C. Therefore, the pillaring process appears to have decreased the thermal stability of the aluminosilicate layer, as is suggested by the XRD and IR data.

The reason for this effect can be found in the influence of ion exchange on the thermal stability (Tichit *et al.,* 1988). Intercalation in an acid medium corresponds to an exchange of the initial cations partly by Al_{13} oligomers and partly by protons. It is well known that the thermal stability of the H form of the clay is less than that of the initial clay (Ames and Sand, 1958). Moreover, the dehydroxylation of the pillars produces water, and the local partial pressure of water in the structure was probably high enough to induce hydrolysis in the PILC. According to Occelli (1983), steam markedly decreases the thermal stability of the clay. Both effects probably were important.

Our results are compared in Table 3 with those reported by Shabtai and coworkers using different methods of preparation. For this comparison, the samples presenting the higher thermal stabilities were selected.

Figure 6. Infrared spectra of the Al-pillared interlayer complex (a) unheated and heated at (b) 300°C, (c) 700°C, (d) 760°C.

All these different samples have similar basal spacings. The intercalation of La-exchanged montmorillonites by hydroxy-Al species, using a ratio Al/clay = 2, yields LaAl-CLM having a basal spacing of 16.8 Å (Tokarz and Shabtai, 1985). The intercalation of montmorillonite and fluorhectorite, by a silico-aluminum complex (ratio Si/Al in the complex = 1.04), gives pillared clays having 001 XRD peaks at 17.1 Å for SiAl-CLM and 18.3 Å for SiAl-CLFH (Sterte and Shabtai, 1987), compared to 17.6 Å for Al-PILC (present work).

The differences in surface area of the samples treated at low temperature are noteworthy. After calcination at 700°C, these differences are rather marginal. Therefore, a superior efficiency of hydroxy-SiAl oligocations as pillars is not clearly demonstrated for montmorillonites. The decrease of the surface area between 500° and 700°C is about 30% for pillared fluorhectorite and Al-PILCS. This decrease of surface area probably reflects the strength of the bond linking the pillars to the clay layer. Thus, the strength of this bond appears to be comparable in Al-montmorillonites and SiAl-fluorhectorites.

Table 2. Mössbauer spectroscopic data for parent clay, Al-PILC dried at room temperature, and an Al-PILC calcined at 680°C.

Sample (number of sites)	IS (mm/s)	QS (mm/s)	Γ (mm/s)	Misfit (%)	χ^2	Percentage of spectrum
Parent clay (1)	0.31	0.53	0.68	0.08	1.62	100
Al-PILC (1)	0.32	0.54	0.59	0.09	1.52	100
Al-PILC calcined at 680°C (2)						
Site 1	0.28	0.97	0.46	0.08	1.48	45
Site 2	0.26	1.58	0.70			55

Table 3. Thermal stabilities of pillared montmorillonites obtained by different preparation methods.

Sample	Surface area (m²/g)		
	250°C	500°C	700°C
Al-PILC (this work)	350	340	240
La-Al CLM	497	394	248
SiAl-CLM	325	273	227
SiAl-CLFH	230	230	150

From these results the thermal stability of the intercalated montmorillonites appears to be controlled mainly by the sintering of the pillars and secondarily by the density and distribution of the pillars. At temperatures >760°C, the stability of the clay sheet itself is questionable; this temperature probably represents the highest temperature at which such PILCs could be used.

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