

## PREPARATION AND CHARACTERIZATION OF MONTMORILLONITES PILLARED BY CATIONIC SILICON SPECIES

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**Abstract**—The hydrolysis of 2-(2-trichlorosilylethyl)pyridine (TCSEP) or 3-aminopropyltrimethoxysilane (APTMS) yields a complex mixture of oligomers, the composition of which is a function of time. <sup>29</sup>Si NMR measurements show that the same oligosilsesquioxanes can be obtained from both compounds after prolonged hydrolysis. Ion exchange by montmorillonite with the pillaring solution obtained from TCSEP results in partial intercalation, with a noticeable fraction of the clay exchange sites occupied by protons not by the Si cationic species. Calcination of this pillared clay results in a mixture of phases showing 1.86 or 1.56 nm basal spacings. Pillaring of the same montmorillonite by the solution obtained by partial hydrolysis of APTMS results in a homogeneous solid with a basal spacing of 2 nm, which reduces to 1.65 nm upon calcination above 773 K. The microporous volume (pores <1 nm) of these Si-clays, determined after calcination at 773 K, 0.15 ml/g for the PILC obtained from TCSEP, and 0.186 ml/g for the PILC obtained from APTMS is comparable to that measured for Al or Zr pillared clays. A better thermal stability is observed for the clay pillared by APTMS, which retains a large microporosity (0.167 ml/g) up to 973 K in air. These Si-pillared clays show a small number of weakly acidic sites and some strongly acidic sites retaining ammonia up to 723 K, which are most likely localized on the clay layers.

**Key Words**—Cationic silicon complexes, Intercalation, Microporosity, Montmorillonite, Oligosilsesquioxanes, Pillared clays, Thermal stability.

### INTRODUCTION

Pillaring of smectites by complex inorganic cations yields porous solids that possess some of the properties of zeolites, strong acidity and regular porosity, since the size of the micropores is determined by the size of the pillars (Vaughan *et al.*, 1979, 1981; Burch, 1988; Figueras, 1988). Well-defined pore structures in the range 1–2 nm can be obtained. A great variety of catalysts have, thus, been prepared that are active for cracking (Vaughan *et al.*, 1979, 1981), alkylation (Occelli *et al.*, 1985; Matsuda *et al.*, 1986), dehydrogenation (Pinnavaia *et al.*, 1988), or epoxidation (Choudary *et al.*, 1990a, 1990b), according to the nature of the pillars.

The intercalation of Si compounds is attractive to prepare pillared clays of high thermal stability, which could be hydrophobic. Moreover, Si pillars should not introduce acidity, and this type of pillared clay could be interesting as a model compound for the study of the acidity. Si pillaring was first attempted by Endo *et al.* (1980) and Pinnavaia *et al.* (1983) using ion exchange of montmorillonite and hectorite with Si acetylacetonate. The product showed a 001 spacing of 1.26 nm after calcination at 773 K, corresponding to a single SiO<sub>2</sub> layer. The interlayer pore size of 0.3 nm thus obtained was too low for practical use in catalysis.

Farfan Torres *et al.* (1988) tried a different approach by using a positively charged silica sol obtained by acid hydrolysis of Si(OEt)<sub>4</sub>. They obtained 001 spacings of 1.49 nm after intercalation at room temperature, which decreased to 1 nm upon calcination at 873 K. The intercalation of montmorillonite by a positively charged silica sol has also been described by Moini and Pinnavaia (1988) who obtained pore sizes of 2.3 nm, with an unspecified thermal stability.

Johnson *et al.* (1988) and Pinnavaia (1992) reported the intercalation of smectites by a tubular microporous silicate, imogolite. This procedure yields a composite with a high microporosity 0.205 ml/g, stable up to 723 K.

A very attractive approach is due to Lewis *et al.* (1985) who proposed the use of 3-dimensional cationic silicon compounds known as oligosilsesquioxanes (Voronkov and Laurentyev, 1982) resulting from controlled hydrolysis of alkylchlorosilane precursors. Examples are given in their patent of the intercalation of the oligosilsesquioxanes derived from trichlorosilylethylpyridine. After calcination at 823 K in air, the pillared clay (PILC) obtained shows a 001 spacing of about 1.92 nm and a good thermal stability in steam up to 1023 K. This procedure has been applied with success to magadiite and yielded a solid with a specific surface area of about 150 m<sup>2</sup>/g stable to 923 K (Sprung *et al.*, 1990).

As previously reported (Fetter *et al.*, 1990), the bulky

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Si polycations obtained by partial hydrolysis of trichlorosilylethylpyridine (TCSEP) diffuse slowly into the clay particles and produce a heterogeneous distribution of the pillars. This results in some loss of surface area and thermal stability. It should be interesting to study in more detail the preparation and properties of these Si-PILCs and some results obtained by changing the structure of the starting silane material are presented here. We attempted to use 3-aminopropyltrimethoxysilane (APTMS) as starting material because 1) the oligosilsesquioxane expected from this compound should have a smaller size than that obtained from TCSEP and 2) APTMS is a common silane prepared at the industrial scale. The resulting oligosilsesquioxane should also show a different behavior because the basicity of the amine is different.

## EXPERIMENTAL METHODS

### *Preparation of the pillaring solution*

The two silanes used are 2-(trichlorosilylethyl)pyridine (TCSEP, Petrarch) and 3-aminopropyltrimethoxysilane (APTMS from ABCR, Germany). The procedures for the hydrolysis of silanes and characterization of the pillaring solutions were obtained from the reports by Voronkov and Laurentyev (1982).

For TCSEP, to 175 ml of methanol at 273 K were added dropwise first 24 g of silane, then 10.5 ml of demineralized water. The solution was stirred for 1 hr. The final pH was  $-0.72$ . After aging for 3 days in the dark, the pH was 1.09.

For APTMS, to 60 ml of methanol at room temperature were added first 20 g of silane, then 6 ml of an aqueous solution of HCl (16%). The solution was stirred for 27 hr. 300 ml of acetone were added and the solution heated to reflux for 1 hr, then cooled to room temperature while stirring for 3 hr. The final pH was 9.7. The solution was stored in the dark.

### *Preparation of the pillared clay (PILC)*

The initial material used for intercalation was a Vol-clay montmorillonite, sedimented by CECA (Honfleur, France) and composed of particles smaller than 0.5  $\mu\text{m}$ . XRD patterns showed no contamination by other phases. The chemical composition (wt. % on a dry basis) of this clay was:

SiO<sub>2</sub>:66.5%; Al<sub>2</sub>O<sub>3</sub>:20.6%; Fe<sub>2</sub>O<sub>3</sub>:4.6%;  
MgO:2.8%; Na<sub>2</sub>O:4.5%; K<sub>2</sub>O:0.23%;  
and CaO:0.32%.

In a typical preparation of a clay pillared with TCSEP, 5 g of clay in the Na form were suspended in 1670 ml of deionized water and stirred for 1 hr. The required amount of pillaring solution was diluted in 90 ml of water (pH of the solution thus obtained was 0.3) and added dropwise (30 min) to the clay slurry. The final

pH of 1.76 was adjusted to 5.8 by addition of NH<sub>4</sub>OH, and the suspension was stirred for 17 hr at room temperature. The samples prepared from this precursor will be referred to as P samples.

The procedure was identical for the intercalation of APTMS, with the noticeable difference that the final pH of the slurry was 10.3. The samples obtained from APTMS will be referred to as A samples. In all the cases, the PILC was filtered and dried at room temperature in a thin bed (<1 mm).

The chemical analyses were done by atomic absorption spectroscopy after dissolution of the sample. The amount of silica fixed by intercalation was obtained from the chemical composition of the PILC, calculated for the same Al<sub>2</sub>O<sub>3</sub> content as the original clay.

### *Thermal treatments*

The PILCs were calcined in air at different temperatures in the range 373 K–1023 K to anchor the pillars to the clay sheet and remove the organic moiety of the pillars. A thin bed of clay was introduced to a horizontal furnace swept by an air flow of about 100 ml/min. The heating rate was 50°/hr and the selected temperature was maintained for 5 hr. A fresh sample was used for each calcination temperature.

### *Characterization techniques*

The solids were characterized by their basal spacings, surface areas, and microporosities. Basal spacings were determined from XRD patterns recorded on a CGR Theta 60 instrument using Cu K $\alpha$ 1 radiation. The XRD data were obtained from oriented samples at different steps of intercalation and from powders after calcination. The precision of d(001) measurement was estimated to  $\pm 0.05$  nm. Surface areas and micropore volumes (pores <1 nm) were obtained from the adsorption isotherms determined for N<sub>2</sub> at liquid nitrogen temperature, using the BET and Dubinin equations. Since the original clay shows no microporosity, the micropore volume is a good estimation of the extent of pillaring.

A few PILCs were analyzed by transmission electron microscopy using samples prepared by inclusion in a resin. NMR spectra of <sup>29</sup>Si were taken on the pillaring solution using a Bruker 250 instrument and on the pillared clay using a high-resolution solid state Bruker AM 300 instrument. All the chemical shifts reported are relative to TMS.

The distribution of the acid strengths was determined by stepwise thermal desorption of ammonia (STD). In this procedure, the catalyst is first activated, then saturated with NH<sub>3</sub> at 373 K, and the excess of base is eliminated in vacuum (10<sup>2</sup> Pa) at 373 K. Thereafter, the reactor is swept by nitrogen and the temperature increased (1 K/min) in steps of 50 K, with the duration of each step being 40 min. The ammonia evolved was trapped in a HCl solution and continu-

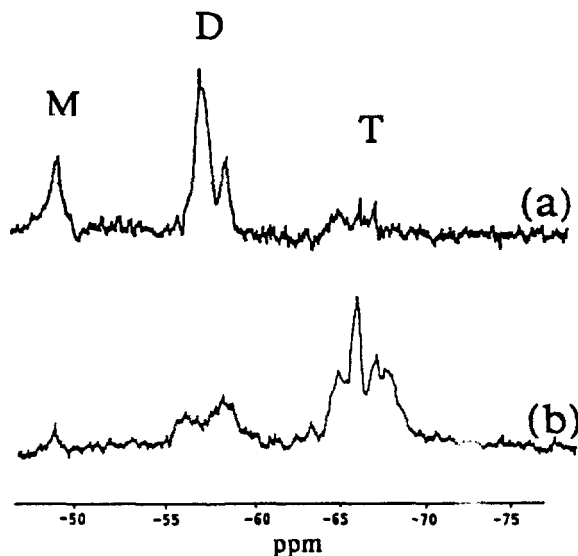


Figure 1.  $^{29}\text{Si}$  NMR spectra of the pillaring solutions prepared from trichlorosilylethylpyridine a) after 1 hr of reaction and b) after 3 days.

ously titrated by conductimetry. This method provides a good estimation of strong acidities.

## RESULTS AND DISCUSSION

### Nature of the pillaring solution

The  $^{29}\text{Si}$  spectrum of the solution of TCSEP hydrolyzed for 100 min shows several resonance lines: a line at  $-50$  ppm decreasing with time, assigned to the TCSEP reactant, and several lines between  $-57$  and  $-69$  ppm increasing with time, attributed to the hydrolysis products (Figure 1). The resonance line at  $-55$  to  $-60$  ppm is expected for disubstituted  $\text{Si}(\text{R})_2\text{O}_2$  species and the line at  $-67$  ppm for tri-substituted  $\text{R-SiO}_3$  species (Kintzinger and Marsmann, 1981). This last species would be representative of the tridimensional oligosilsquioxane postulated by Lewis *et al.* (1985). The presence of other species, however, suggests that the hydrolysis of TCSEP is a complex and slow process giving a mixture of compounds. These may include the protonated monomer, the partially hydrolyzed species, and dimeric or trimeric species. The slow step of the reaction is the polycondensation of the hydroxylated species formed by hydrolysis of  $\text{Si-Cl}$  or  $\text{Si-OR}$  bonds. Both solutions of TCSEP aged for three days and the solution of APTMS, which has been heated to reflux contain mainly  $\text{R-SiO}_3$  tri-substituted species the detailed structure of which cannot be determined.

### Intercalation with the TCSEP solution

Since Si-NMR showed the presence of different species at different times of hydrolysis of the pillaring solution, the fresh solution of TCSEP aged for about

Table 1. Amount of silicon retained by the clay in different conditions of intercalation, using the solution prepared by hydrolysis of trichlorosilylethylpyridine.

Sample	Temperature K	Si/clay g/g	$\text{NH}_4^+/\text{Si}$	wt. % $\text{SiO}_2$ retained	d 001 <sup>1</sup> nm
Fresh solution					
P8	298	0.2	0	20.2	2.64
P6	298	0.08	5	12.8	2.6
P5	353	0.08	0	10.8	2.62
Solution aged 3 days					
P3	298	0.08	0	8.1	2.18
P2	298	0.08	10	7.2	2.21
P7	353	0.08	0	12.9	2.54
P1	298	0.05	0	2.8	2.04
Solution aged 4 months					
P4	298	0.08	0	9.8	2.24

<sup>1</sup> d 001 of the product dried at room temperature.

1 hr and the solution aged for 3 days were both used. The amount of Si exchanged by the clay is reported in Table 1 as a function of the conditions of intercalation. This amount can be varied between 2.8 and 20 wt. %, which allows the investigation of the influence of Si loading on the surface area and micropore volume. After the solution has aged for several days and reached a steady state of hydrolysis, the degree of exchange increases with the amount of Si in the solution and the temperature of intercalation. The addition of ammonium ions to the solution, in order to perform competitive ion exchange, has a negligible effect on the degree of exchange. This suggests a strong interaction between the silicon compounds and the clay.

The use of either the fresh or aged solution of TCSEP yield XRD pattern, reported in Figures 2c and 2e shows the presence of two intense 001 peaks: a line at about 2.6 nm when the pillaring solution is fresh (2.2 nm when the solution has been aged) and a second one at 1.3 nm for the fresh solution (1.2 nm for the aged solution).

The higher spacing undoubtedly represents the intercalation of the clay by polymeric species as evidenced by their Si-NMR lines at about 67 ppm, which appear to be strongly held by the solid since the spectrum is little affected by repeated washings. The line at 1.2–1.3 nm can be assigned either to the 002 harmonic of the line at 2.6 nm, or more probably to the 001 line of the non intercalated clay.

The expansion of the clay by the intercalation of the silicon compound can also be evidenced by direct examination of the lattice fringe image spacings by electron microscopy, as illustrated in Figures 3a and 3b. To some extent, electron microscopy also suggests a heterogeneity in the samples, since different distances can be measured in different zones of good crystallinity.

The MAS-NMR  $^{29}\text{Si}$  spectra of the clay pillared with the fresh or the aged solution are nearly identical (Fig-

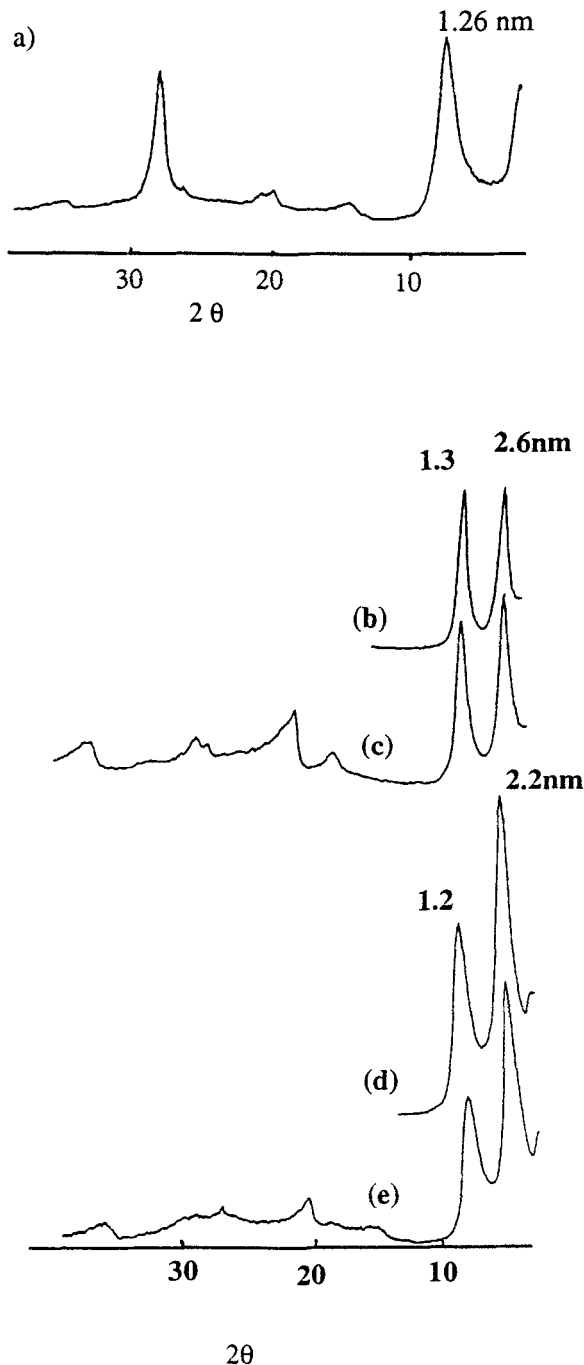


Figure 2. X-Ray diffraction pattern of the original clay a) after intercalation by the fresh solution obtained from trichlorosilylethylpyridine; b) just after ion exchange and c) after several washings, or intercalation with the solution aged several days; and d) just after ion exchange and e) after three washings.

ure 4) and contain two intense lines at  $-92.1$  (Si in the clay layer) and  $-67.5$  ppm (Si in the pillars, corresponding to the tri-substituted species in the solution). The PILC obtained from the fresh solution contains



Figure 3. Electron micrograph of the pillared clays prepared from both types of silicon compounds: a and b) different zones of a sample prepared from trichlorosilylethylpyridine; and c) sample prepared from aminopropyltrimethoxysilane.

an additional line at  $-60.5$  ppm, which corresponds to the resonance of monomeric TCSEP in solution. This line is weaker on the PILC obtained from the solution aged for several days.

It, thus, appears that the interactions with the clay of the monomer and the products of hydrolysis are strong. Both types of cations are observed on the pillared clay; and from the XRD and TEM data, some evidence exists that the intercalated clay is a mixture of phases with different intercalates.

*Intercalation with the APTMS solution*

The main results are summarized in Table 2, in which the reproducibility of the experiment is illustrated by samples A1 and A8 and A3 and A4, prepared under the same conditions. The amount of silica exchanged under similar conditions of intercalation is lower with the solution of APTMS. The Si cations can be removed from the clay by extensive washing, and the addition of ammonia decreases the degree of exchange (com-

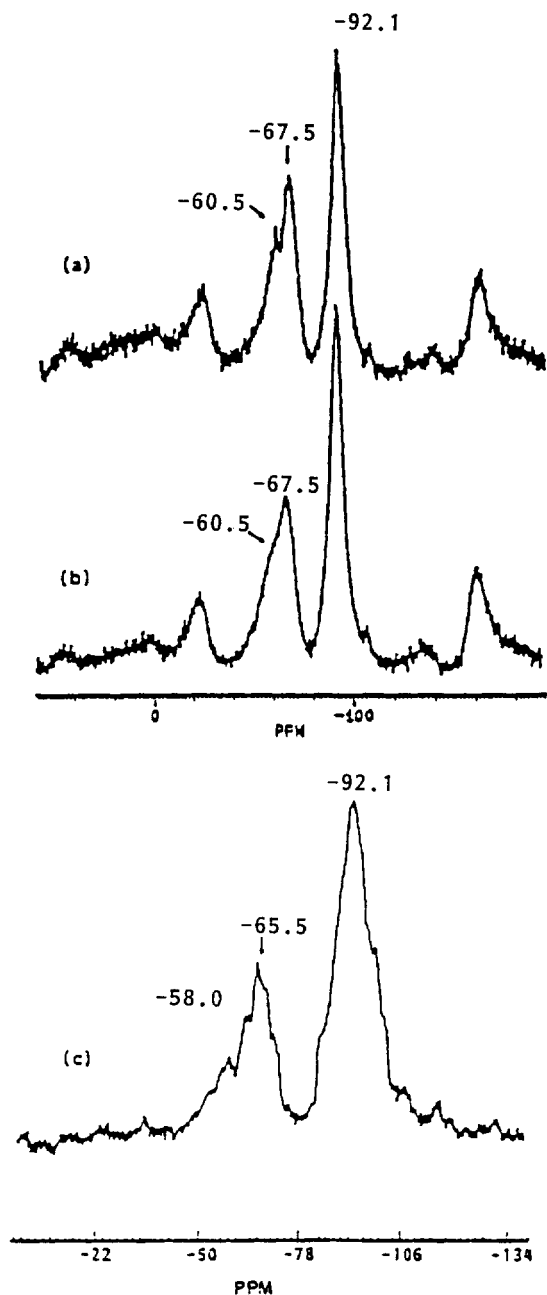


Figure 4.  $^{29}\text{Si}$  MAS-NMR spectra of the clay after pillaring with a) a fresh solution of tri-chlorosilylethylpyridine, b) an aged solution of tri-chlorosilylethylpyridine, and c) a solution of aminopropyltri-methoxysilane.

parison of A4 and A2). These observations suggest a lower selectivity for the cationic species formed from APTMS.

The XRD patterns of the products obtained at different steps of the process of intercalation are reported in Figure 5. The spectrum *a* contains two peaks at 2 and 2.5 nm characterizing an expansion of the clay with two types of cationic species. Repeated washing

Table 2. Amount of  $\text{SiO}_2$  fixed by the clay when the solution of 3-aminopropyltrimethoxysilane is used for the intercalation.

Sample	Temp K	Dilution g clay/liter water	Si/clay g/g	$\text{NH}_4/\text{Si}$	wt. % $\text{SiO}_2$ retained	d 001 <sup>1</sup> nm
A6	298	1	0.6	0	13.7	1.85
A3	298	3.3	0.2	0	5.6	1.96
A7	298	3.3	0.1	0	5.2	1.87
A4	298	3.3	0.2	0	6.2	2.0
A2	298	3.3	0.2	10	3.5	1.93
A1	353	5	0.15	0	2.5	1.76
A8	353	5	0.15	0	3.5	1.8

<sup>1</sup> d 001 of the product dried at room temperature.

eliminates the higher d-peak, and the clay appears as a rather homogeneous solid, with a narrow XRD peak at 2 nm. This corresponds approximately to an inter-layer distance of 1.1 nm, smaller than the 1.2 or 1.6 nm reached with the TCSEP solution. This agrees with the smaller size of the oligosilsesquioxane obtained in the case of APTMS. In this case, TEM provides further evidence for an increased homogeneity of the sample (Figure 3c).

The MAS-NMR  $^{29}\text{Si}$  spectrum of the clay pillared by the APTMS solution (Figure 4c) is not very different from that obtained with the other Si compound. The relatively broad band contains both signals at -65.5 and -58 ppm attributed to di- and tri-substituted Si compounds, but the resolution of MAS-NMR is not sufficient to characterize them further.

The observation that the cationic Si species introduced from the APTMS solution can be washed out of the clay is indicative of a lower selectivity of the clay for these cations. This lower interaction with the cationic sites is probably due to the basic pH, at which only a small fraction of the silicon oligomer can be protonated. This weaker charge on the complex would reduce the electrostatic interactions with the clay sheets and favor diffusion within the particles, thus creating a homogeneous distribution of the pillars and a better ordered structure.

#### Calcination of the pillared clays

Upon calcination of both types of samples above 773 K, the organic moiety of the cationic Si complex is burned off. In the MAS-NMR spectrum a new line appears at -106 ppm and the resonance line of the initial Si cation at -67.5 ppm disappears (Figure 6). Si in the pillars then has the environment of Si in silica (Lippmaa *et al.*, 1980; Kintzinger and Marsmann, 1981), thus showing the presence of siloxane species.

The XRD patterns of the PILC prepared from the TCSEP solution are reported in Figure 7. For the samples calcined at 773 K, the patterns show a single broad peak centered at 1.8–1.9 nm. In some cases, this peak appears as a doublet and can then be interpreted to

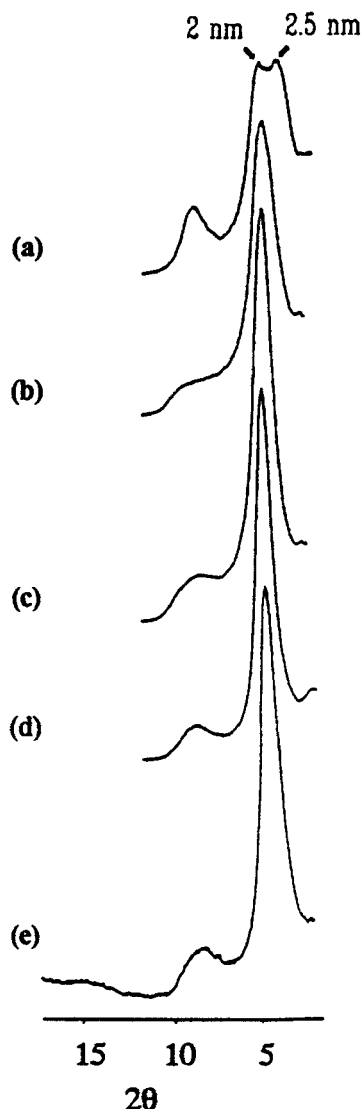


Figure 5. 001 XRD pattern of montmorillonite pillared by aminopropyltrimethoxysilane, a) just after ion exchange, b) washed once, c) washed twice, d) washed three times, and e) final product (washed five times).

represent the formation of two pillared clays with different 001 spacings: a phase with an interlayer separation of about 0.65 nm and a second one with a separation of about 0.9–1 nm. After calcination, the 001 line of the residual non intercalated material at 1.2 nm almost disappears, with the concomitant appearance of a background characteristic of an amorphous phase. At the acidic pH used for the intercalation, some of the Na cations of the original clay are substituted by protons. The protonic clay shows a low thermal stability above 773 K (Tichit *et al.*, 1988) and is most likely transformed into an amorphous phase during calcination.

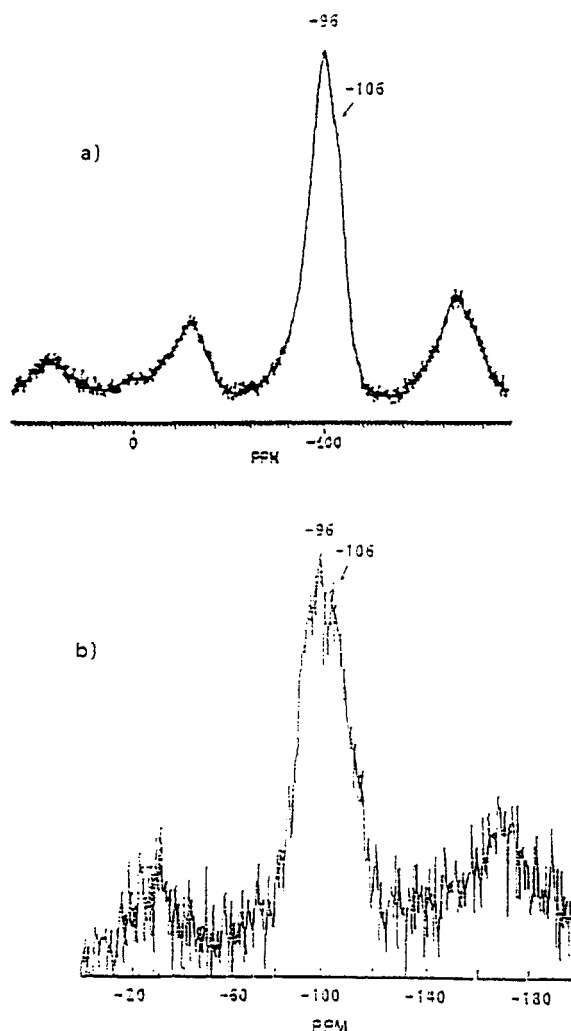


Figure 6.  $^{29}\text{Si}$  MAS-NMR spectra of the pillared clays obtained from a) trichlorosilylethylpyridine and b) aminopropyltrimethoxysilane after calcination at 873 K.

Upon calcination, the PILC obtained from the APTMS solution shows the XRD patterns reported in Figure 8. Calcination induces a contraction of the 001 spacing, expected by the loss of the organic moiety, and progressively increases disorder in the sample. The basal spacing is smaller in that case, 1.6 nm as compared with 1.8 nm for the sample ex-TCSEP. This interlayer spacing of 0.65 nm corresponds to a silicate species containing two layers of Si atoms. This structure is very stable and is still observed at 973 K in the case of APTMS, whereas the samples obtained from TCSEP have almost totally collapsed.

The samples calcined below 773 K show a very small surface area (Table 3). The internal porosity of the material is occluded by the pillars and not accessible even to nitrogen. It was previously reported (Tichit *et al.*, 1988) that the structure of the clay was destroyed

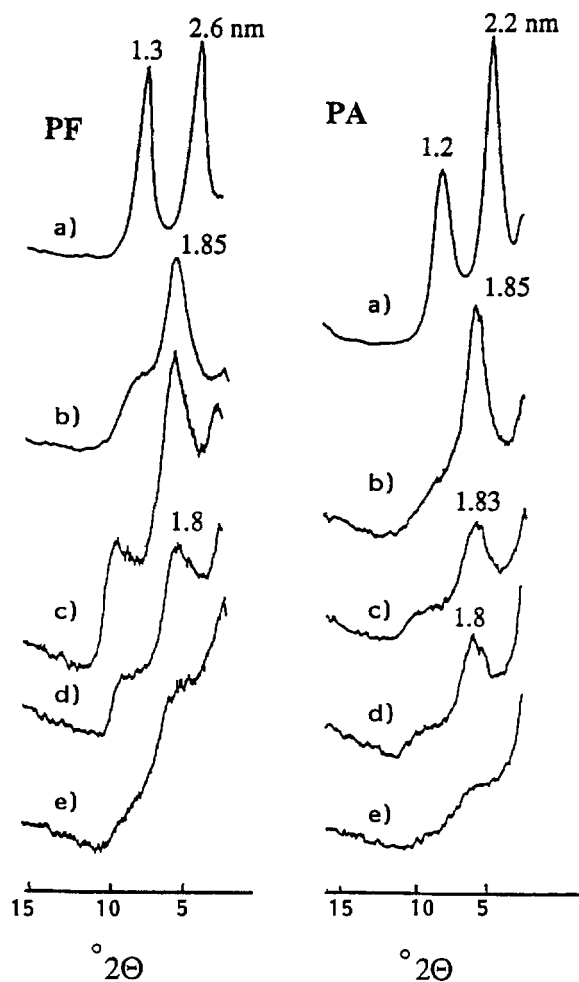


Figure 7. 001 XRD patterns of the Si-pillared clays obtained with a) noncalcined trichlorosilylethylpyridine and calcined at b) 773 K, c) 873 K, d) 973 K, and e) 1073 K. The pillared clays, PF, are obtained using the fresh solution and, PA, the solution aged for several days.

by calcination above 1023 K, and this probably represents the higher temperature limit of PILC stability. The microporous volumes measured on the Si-PILCs are comparable to those determined on Al-(Plee *et al.*, 1987) or Zr-PILC (Figueras *et al.*, 1989). It is also interesting to compare our results on the samples prepared from TCSEP with those reported by Lewis *et al.* (1985): The characteristics reported by these authors are identical to ours within experimental error for surface area (250 m<sup>2</sup>/g), 001 spacing (1.9 nm) and total pore volume (0.25–0.3 ml/g) and, hence, it can be assumed that both series of solids are similar.

The two types of Si-PILCs are compared in Table 3. In both cases, the surface area and micropore volume go through a maximum after calcination at 773 or 873 K. Both surface areas and micropore volumes are larger for the sample prepared from the APTMS solution in

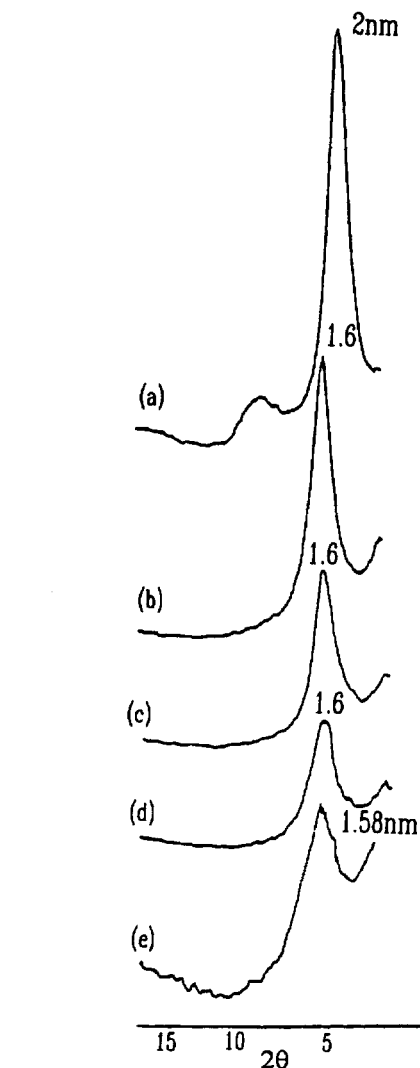


Figure 8. 001 XRD patterns of the Si-pillared clays obtained with a) noncalcined aminopropyltrimethoxysilane and calcined at b) 773 K, c) 873 K, d) 973 K, and e) 1073 K.

spite of the lower degree of exchange by Si-polycations. This behavior can be accounted for, as proposed earlier, by the hindered diffusion of the Si cationic species obtained from TCSEP in acidic medium due to their larger size and higher exchange selectivity. In contrast, the pillars are better distributed in the case of APTMS, which explains their higher porosity (better quality of the pillaring process) and better stability.

#### *Influence of the Si content on the properties*

The microporous volume retained at 973 K changes with the amount of Si exchanged by the clay (Table 4). A maximum appears at about 6–8 wt. % SiO<sub>2</sub> fixed in both cases. The silicon compound props apart the layers of the clay and occupies part of the void space

Table 3. Specific surface areas and micropore volumes for two samples prepared from an aged solution of 2-(2-trichlorosilylethyl)pyridine (sample P, loaded to 12.2% SiO<sub>2</sub> by exchange) and a solution of 3-aminopropyltrimethoxysilane (sample A, loaded to 5.6% SiO<sub>2</sub> by exchange), calcined at different temperatures.

Calcination temperature (K)	Sample P		Sample A	
	Specific surf area (m <sup>2</sup> /g)	Micropore volume (ml/g)	Specific surf area (m <sup>2</sup> /g)	Micropore volume (ml/g)
573	19	0.01	55	0.03
773	310	0.147	331	0.16
873	246	0.113	396	0.186
973	243	0.11	360	0.167
1023	143	0.023	208	0.065

created by intercalation. Below 8 wt. %, the first process predominates; and above 10 wt. % SiO<sub>2</sub>, the increased ion exchange tends to fill the micropore volume with silica.

#### Acidity of the Si-pillared clays

The acidity of these Si-PILCs was evaluated by NH<sub>3</sub> desorption. The results are reported in Figure 9, to which an Al-pillared montmorillonite (BA1) prepared by competitive ion exchange of aluminium hydroxy cations and ammonia is added for comparison. It has been previously reported that these Al-PILCs exhibit a strong acidity, comparable to that of HY zeolites (Figueras *et al.*, 1990). The Si-clays also show a strong acidity as evidenced by the retention of ammonia at 723 K. The comparison of BA1 with P3 shows a comparable acidity for these two solids. Since silica is a weak acid, this strong acidity is most likely localized on the clay layers and connected to the exchange sites not occupied by Si cations but by protons. The PILC

Table 4. Influence of the amount of silica retained by the clay on the textural properties of the resulting PILC calcined at 973 K.

SiO <sub>2</sub> retained (wt. %)	d 001 (nm)	Specific surf area (m <sup>2</sup> /g)	Micropore volume (ml/g)
Sample P			
2.8	1.70	128	0.051
7.2	1.77	218	0.103
8.1	1.80	243	0.11
9.8	1.80	222	0.102
10.8	1.81	123	0.044
12.8	1.82	131	0.047
12.9	1.83	125	0.040
20.2	1.86	112	0.05
Sample A			
2.5	1.50	63	0.03
3.5	1.53	137	0.064
5.6	1.58	360	0.167
5.6	1.58	313	0.146
10.7	1.58	193	0.087
13.6	1.57	88	0.041

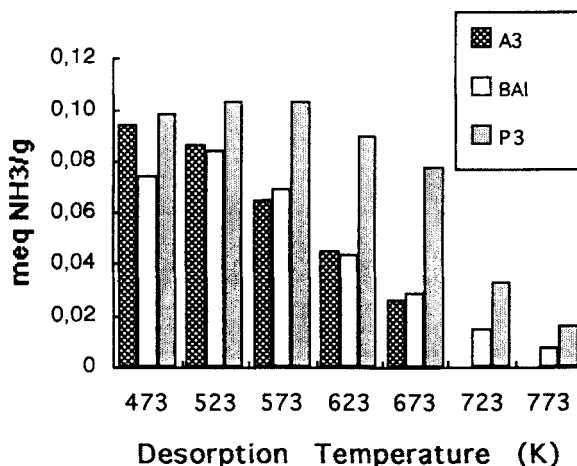


Figure 9. Distributions of the number of acid sites as a function of the desorption temperature for two Si-PILCs, A3 and P3, compared with a montmorillonite pillared by aluminium (BA1). All the samples have been calcined at 873 K.

obtained from TCSEP (P3) shows a lower number of acid sites when compared on a weight basis; but due to the larger surface area of the material obtained from APTMS, the density of sites is similar.

#### CONCLUSION

The intercalation of montmorillonite by the products of hydrolysis of 2-(2-trichlorosilylethyl)pyridine yields a mixture of several phases—the non intercalated clay, the clay intercalated by a polymer with an interlayer distance of 0.9–1 nm, or the clay intercalated by a dimeric species with an interlayer height of 0.6–0.7 nm. The formation of these mixtures can be accounted for by the different kinetics of intercalation. A faster exchange of the smaller mono or dimeric species could explain the results. The same process of intercalation of montmorillonite using a solution of 3-aminopropyltrimethoxysilane partially hydrolyzed yields a more homogeneous solid, with an interlayer separation of about 0.7 nm and larger surface area and micropore volume. This can be attributed to the smaller size of the oligosilcations produced in that case due to the smaller organic moiety of the pillars. These Si-PILCs lose their microporosity only above 973 K and appear as strong acids. The use of APTMS increases both stability and acidity.

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