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Al-PILLARED MONTMORILLONITE OBTAINED IN CONCENTRATED MEDIA. EFFECT OF THE ANIONS (NITRATE, SULFATE AND CHLORIDE) ASSOCIATED WITH THE Al SPECIES

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Abstract—Basic Al chloride, sulfate and nitrate were prepared by hydrolysis of Al chloride followed by precipitation with a Na sulfate solution, then re-dissolution in a Ba nitrate solution. The three laboratory-synthesized oligomers and solid, commercial chlorhydrol were characterized by X-ray diffraction, ^{27}Al nuclear magnetic resonance and scanning electron microscopy coupled with energy dispersion spectroscopy analysis. The results showed that basic Al chloride contained unknown crystalline Keggin species. In commercial chlorhydrol, Al_{13} species were present in small amounts aside from the monomeric species. Basic Al nitrate or sulfate contained exclusively Al_{13} species. Pillaring a raw montmorillonite with different Al complexes in very concentrated media using both the clay and the oligomer in the solid state led to different pillared structures. Characterization by transmission electron microscopy, nitrogen adsorption, and thermogravimetric analysis of the materials obtained shows that pillaring with sulfate or chloride oligomers gave very heterogeneous pillared clays. Although basic Al nitrate and commercial chlorhydrol give better ordered and well organized pillared clays, the stacking obtained with chlorhydrol is greater.

Key Words—Anions Effect, Commercial Chlorhydrol, Concentrated Media, PILC, Synthesized Al_{13} Oligomers.

INTRODUCTION

The use of pillared clays in many applications such as heterogeneous catalysis or adsorption has recently led to research their production on an industrial scale. Different authors have reported pillaring processes in concentrated media. Concentrations of clay up to 50% in water or in acetone were used (Storaro *et al.*, 1996, 1998; Fetter *et al.*, 1997; Salerno and Mendioroz, 2002) with chlorhydrol in solution or as powder. Some authors reported pillaring by use of the clay powder and the pillaring solution (Schoonheydt and Leeman, 1992; Frini *et al.*, 1997; Moreno *et al.*, 1997; Sanchez and Montes, 1998; Vicente and Lambert, 2003). In order to reduce the total water volume used in all these previous methods, Aouad *et al.* (2005) reported a new method in which the two reagents were both in the solid state. Pillaring of powder montmorillonite was performed using powdered synthesized solid Al oligomers and commercial chlorhydrol. The intercalation of the oligomer in the interlayer space of the clay was obtained by dialysis of the powder mixture in a membrane suspended in water.

In order to understand the nature of the pillaring oligomer, it is important to study the structure of the pillared material obtained. Many studies have been conducted on solutions obtained by hydrolysis of metallic salts with a base (Wang and Hsu, 1994), the best studied and oldest being Al_{13}, the so-called 'Keggin ion'. It was widely studied by different techniques, in solution and in the solid state, in order to determine the different hydroxy-aluminum species and their corresponding structure. Casey (2006) presents a very interesting updated review on the different large aqueous aluminum hydroxide molecules. That author reported the different structures of these clusters and their uses with environmental significance. He also reported different Al_{13} isomers identified as α, β, γ, δ and ε. In the α structure, the four trimeric groups of AlO_6 octahedra share corners with one another. By stepwise rotation, the number of these trimeric groups which share edges with one another increases from 1 for β to 4 for ε, which is the structure of the classical Keggin ion. Besides this ε-Al_{13}, which has been synthesized and structurally characterized by Johansson (1960a, 1960b), only the δ isomer of Al_{13} was studied by Fu *et al.* (1991). The α form has not yet been isolated but was detected in the mineral structure of zunyite.

The present work investigates the effect on clay pillaring in concentrated media, of the anions associated with the basic Al complexes. This work includes the characterization by X-ray diffraction (XRD), scanning electron microscopy (SEM) and nuclear magnetic resonance (NMR) of the initial synthesized Al solid complexes associated with different anions (chloride, sulfate or nitrate) and of the solid commercial chlorhy-

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drol used for the pillaring. Moreover, the nitrate and chloride pillaring oligomers in solution were studied by NMR (the synthetic solid sulfate and the commercial chlorhydrol which we used are available only as powders). To our knowledge, this is the first time that these solid oligomers (except for the sulfate) have been studied by SEM. It is also the first time that the laboratory-synthesized nitrate oligomer has been studied in the solid state by XRD and NMR. The resulting pillared clays (AlPMt) obtained in concentrated media were characterized by XRD, TEM, TGA and N_2 adsorption isotherms.

EXPERIMENTAL

Materials

The clay is a commercial Wyoming montmorillonite (Mt) obtained from Comptoir des Minéraux et Matières Premières (France), and used as received. Its cation exchange capacity (CEC), as determined by adsorption of copper ethylenediamine complex (Bergaya and Vayer, 1997), is 100 cmol(+)/kg of calcined clay, and its BET surface area is 29 m^2/g.

Solid chlorhydrol (aluminum chlorhydrate) from Reheis Co. was supplied by Quarréchim. Its empirical formula, given by the manufacturer, is $Al_2(OH)_5Cl.2H_2O$. The ratios Al/Cl, Al/H_2O and OH/Al of 2/1, 1/1 and 2.5/1, respectively, are in agreement with the formula of the Keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]$ if seven chloride anions are assumed to be present to neutralize the charge of the complex (Teagarden *et al.*, 1981).

The method generally used for the industrial preparation, based on the dissolution of Al metal by an acid (Bergaya, 1990) can be summarized by the simplified reaction

$$2Al + HCl + 7H_2O \rightarrow Al_2(OH)_5^+ + 3H_2\uparrow + Cl^- + 2H_2O \qquad (1)$$

The chemicals used in preparing the pillaring agents, namely $AlCl_3.6H_2O$ (Fluka), Na_2SO_4 (Prolabo), NaOH and $Ba(NO_3)_2$ (Aldrich Chemical Company) were used as received.

Laboratory synthesis of the Al-pillaring agents

To obtain the different solid Al_{13} complexes with different ligands, we followed the Furrer *et al.* (1992) method: the hydrolysis of Al chloride solution with NaOH solution provided the basic aluminum chloride. Basic aluminum sulfate was then precipitated by adding a solution of Na sulfate. The basic aluminum nitrate was prepared by dissolution of the basic aluminum sulfate in Ba nitrate. Furrer studied the acid-base properties of the polynuclear Al_{13} complex in solution by alkalimetric titration, but he did not characterize the final product in the solid state.

1. Basic aluminum chloride. A solution (0.25 mol L^{-1}) of $AlCl_3.6H_2O$ was heated for 15 min in a water bath at 80ºC. A NaOH solution (0.25 mol L^{-1}) was then slowly added with stirring, maintaining the temperature at 80ºC (OH/Al = 2.4). The Al_{13} chloride solution formed was evaporated in an oven at 60ºC. NaCl in excess was not removed from the solid basic aluminum chloride by dialysis, as it would be removed by the washing after the pillaring process. The simplified overall reaction (2) scheme can be described by:

$$\begin{array}{l} AlCl_3.6H_2O + NaOH \rightarrow \\ \quad \text{basic aluminum chloride}_{aq} + NaCl + nH_2O \\ \qquad \downarrow \text{drying at 60ºC} \\ \quad \text{basic aluminum chloride}_{solid} + NaCl_{solid} \end{array} \qquad (2)$$

2. Basic aluminum sulfate. A Na_2SO_4 solution (0.1 mol L^{-1}) was added to the solution of basic aluminum chloride previously prepared. The precipitate, formed after 2 days, was filtered, washed with distilled water, and air dried for 2 days at room temperature, as shown by the reaction scheme 3.

$$\begin{array}{l} \text{basic aluminum chloride}_{aq} + Na_2SO_4 \xrightarrow{\text{Precipitation}} \\ \quad \text{basic aluminum sulfate}_{precip.} + NaCl + H_2O \\ \qquad \downarrow \text{washing, filtration and air drying} \\ \quad \text{basic aluminum sulfate}_{solid} \end{array} \qquad (3)$$

3. Basic aluminum nitrate. The Al_{13} nitrate solution was obtained by dissolving Al_{13} sulfate crystals (obtained as above), in a $Ba(NO_3)_2$ solution with an excess of Ba nitrate, with stirring for 5 h. After removing the $BaSO_4$ precipitate by filtration (0.1 μm, Millipore), solid Al_{13} nitrate was obtained by evaporating the clear filtrate in the oven at 60ºC as described below (4):

$$\begin{array}{l} \text{basic aluminum sulfate} + \underset{\text{(in excess)}}{Ba(NO_3)_2} \rightarrow \\ \quad \text{basic aluminum nitrate}_{aq} + Ba(NO_3)_2 + BaSO_{4\ precip.} \\ \qquad \downarrow \text{filtration and drying at 60ºC} \\ \quad \text{basic aluminum nitrate}_{solid} + Ba(NO_3)_{2\ solid} \end{array} \qquad (4)$$

As previously for NaCl, $Ba(NO_3)_2$ in excess was not removed from the solid basic aluminum nitrate by dialysis before evaporation as it would be removed by the washing after the pillaring process.

Preparation of Al-pillared Mt in concentrated media

The solid pillaring compound (0.3 g of oligomer) was ground with powdered montmorillonite (1 g) and dialyzed through a dialysis membrane using a limited volume of deionized water (5 mL of water/g of clay for each dialysis). The dialysis water was exchanged until its conductivity reached 13 μS. The resultant Al-intercalated clay was heated at 300ºC for 3 h. The detailed process was described by Aouad *et al.* (2005).

Characterization techniques

The reflection powder X-ray diffraction (XRD) patterns were obtained on a Philips diffractometer, using CuKα radiation. The oligomers were analyzed at steps of 0.04º at 4 s/step in the 2θ range 1.5−80º. To confirm precisely the presence of the 001 diffraction peak, the pillared clays were analyzed over the range 1.5−15º2θ at steps of 0.02º2θ at 10 s/step.

Transmission electron microscopy (TEM) (Philips CM20 operating at 200 kV) studies were performed on slices, ~50 nm thick, obtained with an ultramicrotome (Reicher ultracut) equipped with a diamond knife (Drukker). In order to minimize the superposition of information in the image, it was necessary to cut very thin sections of the unoriented sample. These sections were obtained from slurries of the pillared clay embedded in a Spurr resin. Optical adjustments were performed with the help of a low-dose camera.

Scanning electron microscopy (SEM) observations and qualitative chemical analysis by EDS of the oligomer crystals were performed using an HITACHI S4200 SEM with a field emission gun.

^{27}Al nuclear magnetic resonance (NMR) spectra were obtained at 94 MHz on a BRUKER spectrometer DSX 360. Spectra were externally referenced to $Al(NO_3)_3$ 1 M aqueous solution at 0 ppm. ^{27}Al spectra parameters were observed using 4 μs pulses, 1 s recycle delays and 4096 scans.

N_2 adsorption isotherms at 77 K were determined using a Micromeritics 2010 apparatus after outgassing the samples overnight at 140ºC. Specific surface areas were determined using the BET equation (Gregg and Sing, 1982); micropore volumes were obtained using the Horvath-Kawazoe (H-K) analysis (Gregg and Sing, 1982), and the total pore volumes were determined using the t-plot method (Gregg and Sing, 1982). The mesopore volumes were determined by subtracting the micropore volume from the total pore volume.

The decomposition of the pillared clays was studied by thermogravimetric analysis (TG) (Setaram TG-DTA

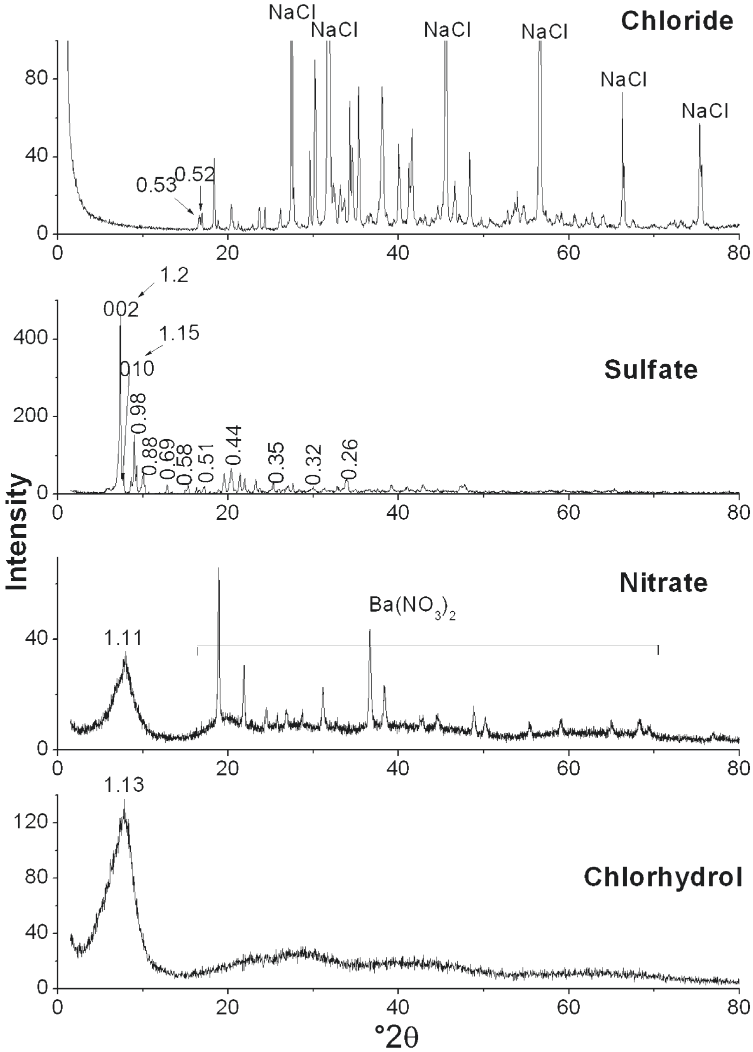

Figure 1. XRD patterns of Al complexes with different anions and commercial chlorhydrol, with *d* values in nm.

92-18). The samples were heated at 1.7°C min^{-1} in an argon atmosphere.

RESULTS

Characterization of the pillaring agents: chloride oligomer

XRD. The diffraction peaks of the compound (Figure 1) correspond to NaCl crystals (which, after drying, were not removed from the solid basic aluminum chloride), and to another unidentified crystalline phase. Because of the lack of reflections in the angular range equivalent to >0.5 nm, it seems highly unlikely that this phase corresponds to molecular crystals built with classical ε-Al_{13} units. Schönherr *et al.* (1981) prepared Al_{13} chloride from basic aluminum sulfate dissolved in Ba chloride, thus obtaining a practically X-ray amorphous material with a very diffuse diffraction peak at ~1.08 nm, but the XRD pattern was not published. Al_{13} chloride crystals were also obtained in a concentrated aqueous solution by Seichter *et al.* (1998). The XRD patterns led the authors to propose a novel type of Al_{13} monoclinic structure (space groupe $P2_1/c$) consisting only of interconnected AlO_6 octahedra. The cell parameters are a = 1.39 nm, b = 2.348 nm, c = 2.234 nm and β = 90.36°. This structure does not correspond to the experimental XRD pattern of the basic aluminum chloride obtained (Figure 1), the structure of which is still unknown.

SEM. The SEM image (Figure 2) of basic Al chloride shows two distinct phases. A crystallized phase (1) corresponds to NaCl crystals of very small size, identified by EDS. The large crystals (2), containing Cl, Al and O, as detected by EDS and shown on spectrum 2, probably correspond to the unidentified crystalline phase observed by XRD.

NMR. The spectrum of the basic aluminum chloride in solution (Figure 6a) shows only one peak at 79.8 ppm which splits in the spectrum of the solid compound into two peaks at 80.4 and 83 ppm. These three peaks close to

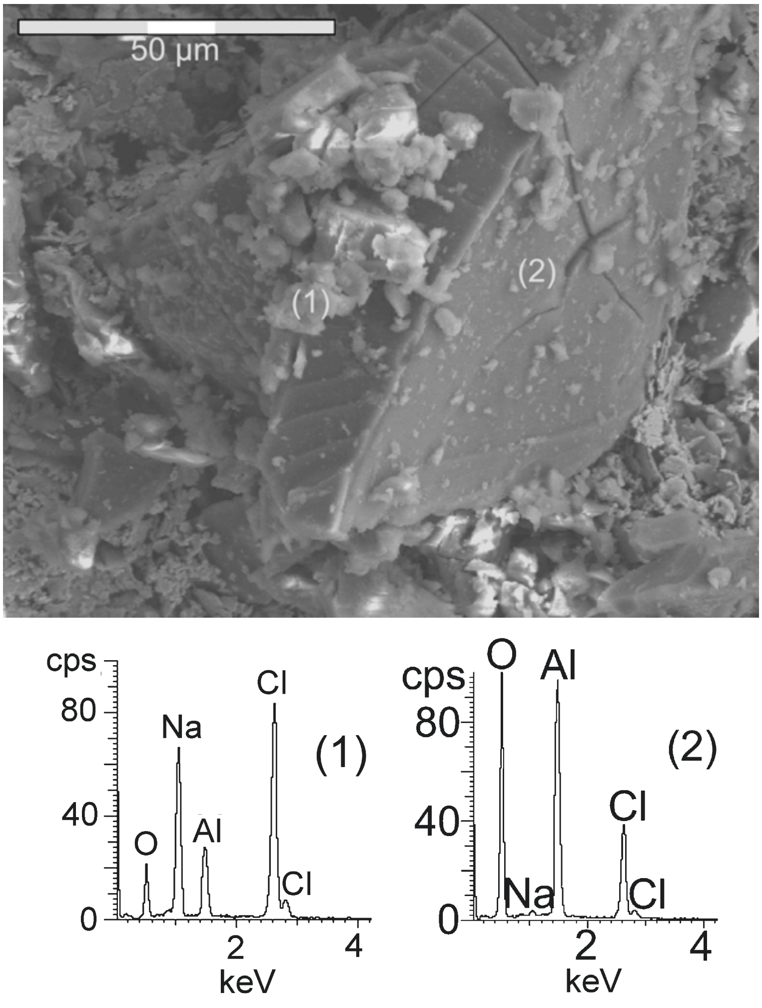

Figure 2. SEM image and EDS analysis of basic Al chloride.

80 ppm could correspond to tetrahedral coordination of Al in another unknown Keggin polycation species. Allouche and Taulelle (2003) attributed a low-intensity signal at 81 ppm found in the NMR spectrum of heated basic Al nitrate solution to β-Al_{13}, but the attributions of the two peaks at ~80 ppm in our results remain uncertain. Moreover, the spectrum of the solid basic Al chloride shows a broad peak at 9.1 ppm. This observed peak could correspond to the octahedral Al of the unknown Keggin polycation, although Allouche *et al.* (2001) attributed a peak at 9.1 ppm to (AlO_6) to an intermediate configuration between the ε- and δ-Keggin trimers.

The identification of the Al_{13} Keggin species is usually based on the observation of the signal at 63 ppm due to the central Al, which is in a highly symmetrical tetrahedral environment (small quadrupole coupling constant Q_c). The 12 non-symmetrical octahedral Al are scarcely discernible owing to the large quadrupole coupling constant Q_c. In our case, the characteristic peak due to the tetrahedral Al of the classical Keggin ε ion is not present.

Characterization of the pillaring agents: sulfate oligomer

XRD. The XRD pattern of the powdered Al_{13} sulfate shows that this complex is well crystallized (Figure 1), with d_{hkl} values similar to those reported by Kloprogge *et al.* (1992) for the same sulfate compound precipitated from hydrolyzed Al nitrate. In agreement with these authors, all the peaks are indexed and the XRD pattern effectively corresponds to Al_{13} sulfate with the formula:

$$Na_{0.1}[Al_{13}O_4(OH)_{24}(H_2O)_{12}](SO_4)_{3.55}.nH_2O$$

crystallizing in the monoclinic system, with cell parameters: $a = 2.02$ nm; $b = 1.15$ nm; $c = 2.5$ nm; $\beta = 103°$ and space group *Pa* or *P*2/*a*. This monoclinic structure, described by Johansson (1963), leads to the determination of the size of the Keggin ion associated with sulfate anion by the 010 reflection as ~1.15 nm (1.146 nm obtained on the experimental XRD pattern, Figure 1).

SEM. The Al_{13} sulfate shows different morphologies in agreement with Wang and Muhammed (1999) who showed several shapes for the sulfate oligomer. The well crystallized Al_{13} sulfate is monoclinic, forming rectangular, plate-like crystals (Figure 3a) with large size distribution (2000−10,000 nm). The rectangular crystals were also observed by Tsuchida *et al.* (1995). However, the morphology of the crystals depends on the duration of the precipitation: a tetrahedral morphology is also obtained when the crystals are left in the reaction liquid for four days (Figure 3b). Furrer *et al.* (1992) reported only the tetrahedral forms with a typical diameter of 0.1 nm. The images in the paper by Duong *et al.* (2005) show only the tetrahedral form, which was described by Johansson (1960a) and corresponds

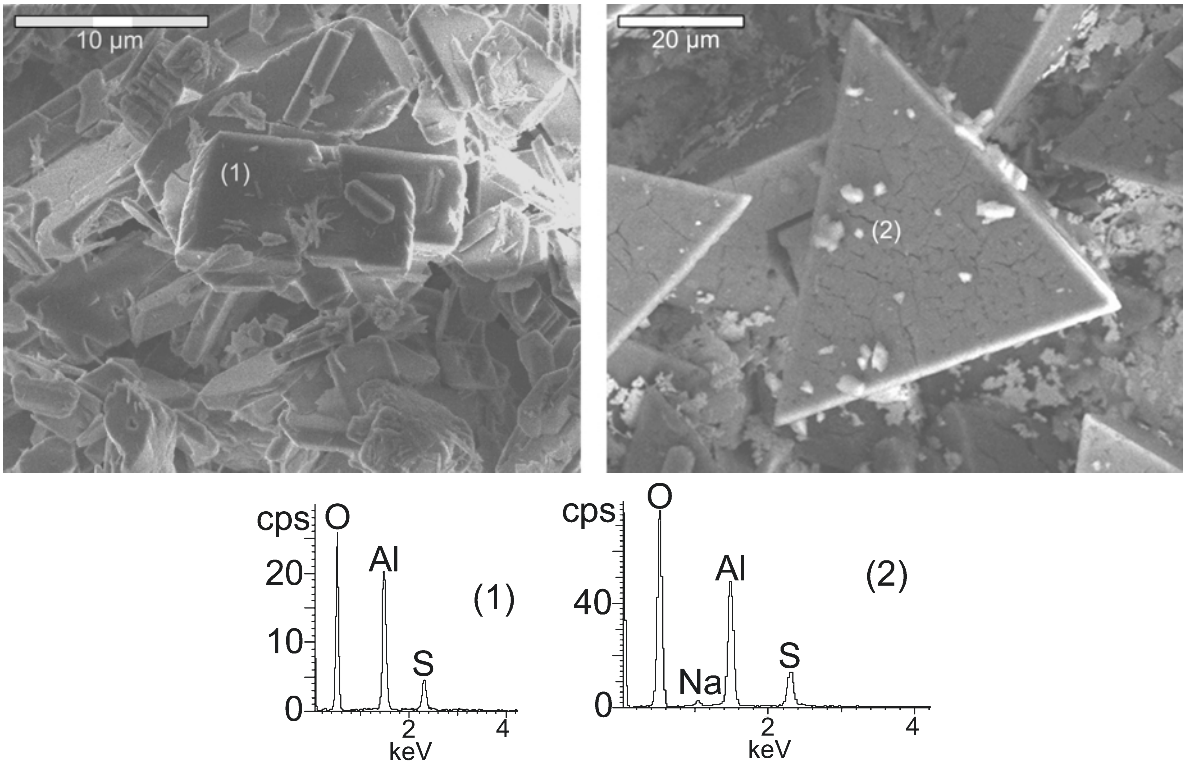

Figure 3. SEM image and EDS analysis of basic Al sulfate.

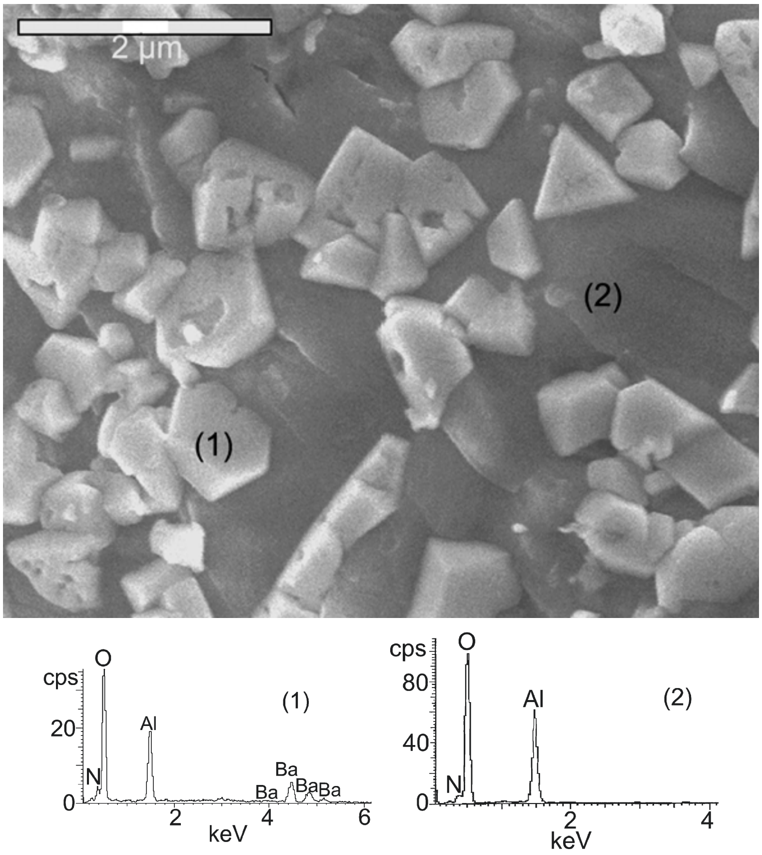

Figure 4. SEM image and EDS analysis of basic Al nitrate.

to the cubic system. The EDS analysis of both the tetrahedral and rectangular crystals shows the peaks characteristic of Al, O and S (Figure 3).

NMR. In the case of basic Al sulfate, the experimental spectrum (Figure 6b) shows, as expected, two peaks at 61 ppm and 9.8 ppm characteristics of ε-Al_{13} polycations.

Characterization of the pillaring agents: nitrate oligomer

XRD. The Al_{13} complex obtained with the nitrate anions is poorly crystallized. The XRD pattern (Figure 1), which shows a broad peak at ~1.11 nm, is similar to that observed by Teagarden *et al*. (1981) for chlorhydrol at 1.18 nm. It was attributed to the Al_{13} complex. A series of well defined peaks is also observed which corresponds to the excess barium nitrate not removed at this step from the initial nitrate solution.

SEM. Figure 4 shows two phases: (i) a crystallized phase of very small size (indicated by 1) corresponding to $Ba(NO_3)_2$ crystals, already confirmed by XRD and identified by EDS (spectrum 1); and (ii) large, dark blocks corresponding to the Al_{13} nitrate phase (indicated by 2 in Figure 4) and clearly identified by the Al and O lines (spectrum 2). These lines are also present in spectrum 1 owing to the Al_{13} nitrate phase also present under the $Ba(NO_3)_2$ crystals.

NMR. The peaks at 63.1 ppm and 62.5 ppm observed in the spectra of the dissolved and solid tetrahedral Al_{13} nitrate, respectively, (Figure 6c) correspond to the values generally given as reference for the symmetrical AlO_4 of the ε-Keggin ion (Akitt and Farthing, 1978). The peak at 0.1 ppm observed for the solution corresponds to monomeric Al. The octahedral environment of Al in ε-Keggin ion, which is not observed with the solution because of the large quadrupole constant, is represented, as expected, by a wide, weak line in the solid compound at ~8.5 ppm.

Characterization of the pillaring agents: chlorhydrol

XRD. The broad peak observed in the XRD pattern of the commercial solid chlorhydrol at 1.13 nm (Figure 1) is attributed to ε-Al_{13} polycations. It is similar to that at 1.18 nm observed by Teagarden *et al*. (1981) with the solid obtained by air drying the solution of commercial chlorhydrol.

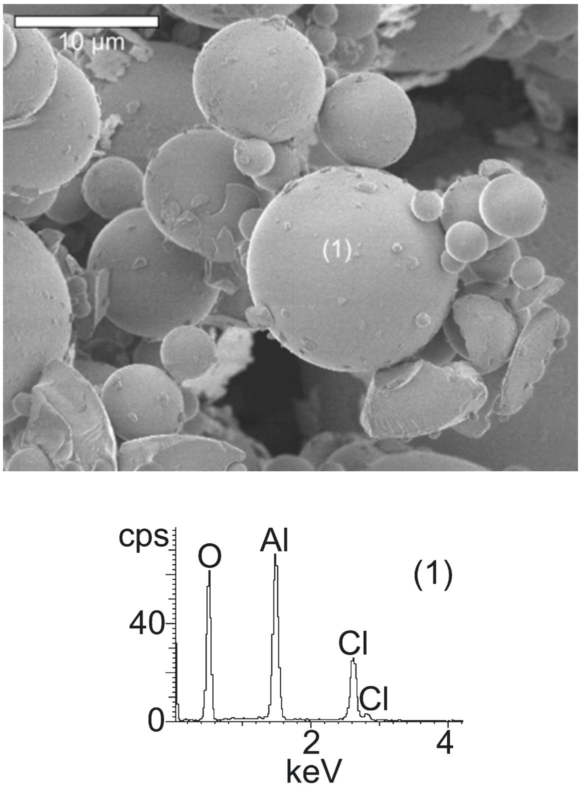

Figure 5. SEM image and EDS analysis of solid, commercial chlorhydrol.

SEM. The chlorhydrol (Figure 5) shows spherical form with different sizes (2500−15,000 nm in diameter). This smooth spherical shape is probably due to the manner of drying of the commercial samples (perhaps spray-drying). The EDS analysis confirms the presence of Al, O and Cl shown in the compound, the chemical formula of which is given above.

NMR. The spectra of solid chlorhydrol (Figure 6d) presents two peaks at 6.4 ppm and 66.8 ppm. The first intense peak probably corresponds to monomeric octahedral Al species. The second peak could result from the overlap of two different resonances: one at 62.5 ppm (AlO_4 in ε-Al_{13}) and the other at ~70 ppm, already observed but not attributed to a specific tetrahedral species (Akitt and Mann, 1981). A peak at 70 ppm was more recently observed by Shafran *et al.* (2004) who attributed this peak to (AlO_4) in an Al_{30} species.

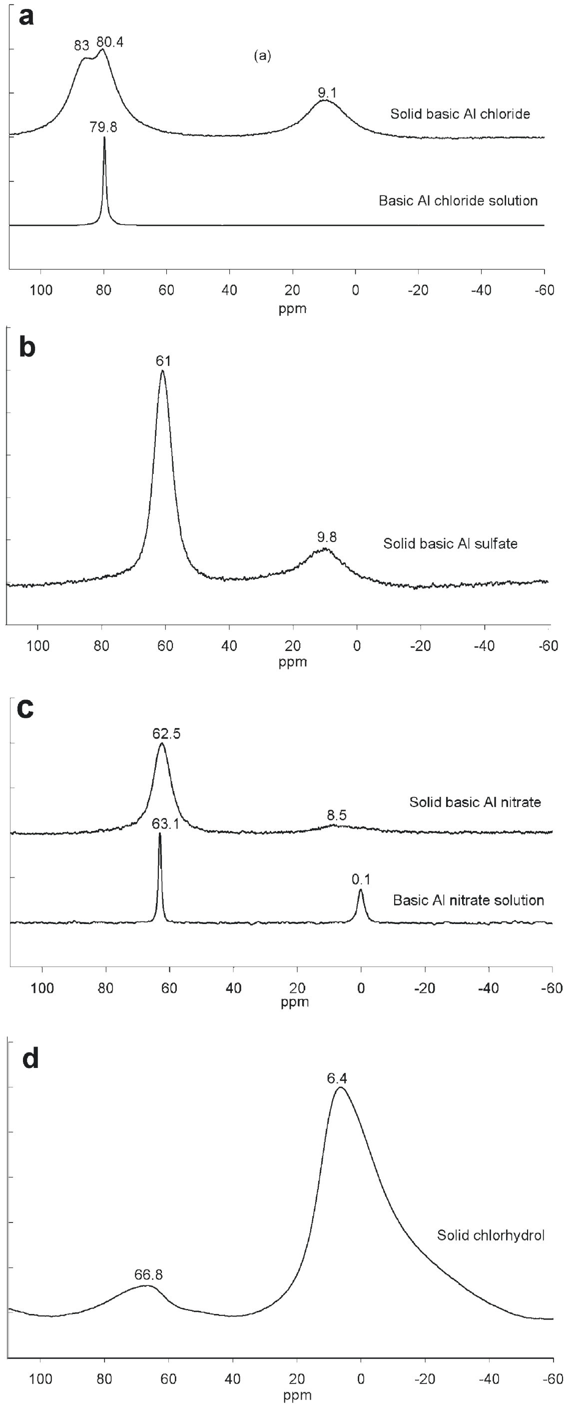

Figure 6. ^{27}Al NMR of solid (and in solution) basic Al complexes with different anions and commercial chlorhydrol.

Characterization of the pillared Mt

The different complexes were used to prepare intercalated and then pillared Mt samples. The number of dialyses (or the amount of water) depends on the nature of the anion: 16 dialyses for the nitrate (266 mL/g of oligomer), 23 dialyses for the sulfate (383 mL/g of oligomer) and 50 dialyses for the chloride and chlorhydrol (833 mL/g of oligomer). Intercalation is controlled by following the increasing intensity of the 001 XRD peak after the successive dialyses (for each dialysis, 5 mL of water/g of clay or per 0.3 g of each oligomer) followed by conductivity measurements of the dialysis water.

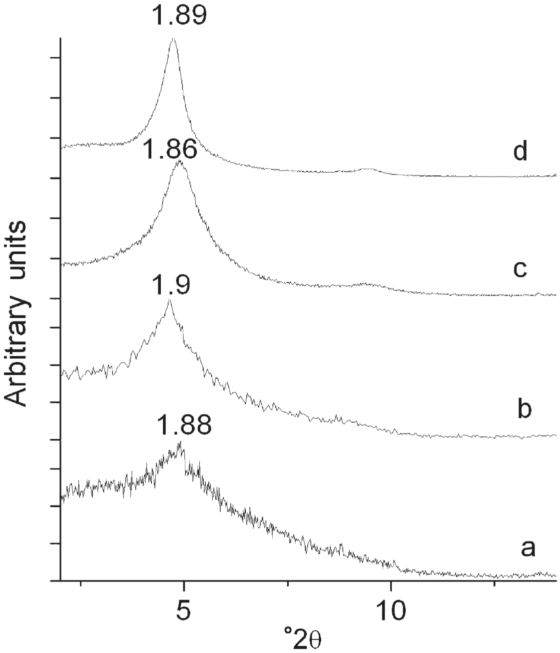

Figure 7. XRD patterns of pillared Mt in concentrated media using different complexes: (a) chloride; (b) sulfate; (c) nitrate; and (d) chlorhydrol. Spacings in nm.

XRD. Figure 7 shows the XRD pattern and the d_{001} peak of clay pillared with Al_{13} chloride, sulfate or nitrate anions and the commercial chlorhydrol. The four peaks are at ~1.9 nm. This distance corresponds to pillaring by an Al_{13} oligomer. In the cases of chloride and sulfate, the XRD patterns indicate very heterogeneous samples in which few layers are intercalated with the Keggin ion. The clays pillared with Al_{13} nitrate and chlorhydrol are well organized, but pillaring with commercial chlorhydrol gives larger intercalated clay layer stackings (~12 layers/particle) than that obtained with Al_{13} nitrate (about 8 layers/particle). The thickness of the clay layers was determined from the Scherrer formula: $L = 0.89\lambda/\cos\theta\ \delta\theta$, where λ is Cu wavelength. Although the two pillared clays produced with chloride (*i.e.* using the chlorhydrol and chloride oligomers) share the same counteranion, they differ significantly in the nature of the Al species generated when the compounds dissolve.

TEM. Observation by TEM was performed only on well organized samples, *i.e.* the Mt pillared with Al_{13} nitrate and chlorhydrol (Figures 8 and 9). The samples are homogeneous (absence of precipitated phases), with layer spacings of 1.8 nm, as confirmed by XRD. In the case of nitrate, isolated layers separated by slit-shaped mesoporosity appear, as shown in Figure 8. A lenticular porosity (LP) is also observed due to the deformation of adjacent layers between two particles. In the case of chlorhydrol (Figure 9), image observation confirms the presence of a large number of stacking layers as deduced from XRD.

Adsorption isotherms. Figure 10 shows the N_2 adsorption-desorption isotherms corresponding to the parent material and Al-pillared samples with the Keggin ion associated with different anions. All the isotherms are of Type II (BDDT classification) with an H_3 hysteresis loop (IUPAC classification – Sing *et al.* 1985), confirming the presence of a slit-shaped porosity between plate-like particles, as observed by TEM. The values of the surface areas and pore volumes are reported in Table 1.

The identical shape of the hysteresis loops indicates that the mesoporosity of the samples does not change after pillaring, whereas the volume adsorbed at low relative pressure, which is indicative of the microporosity, increases more for Mt pillared with chlorhydrol and Al_{13} nitrate than for Mt pillared with sulfate or chloride.

Measurement of the textural properties confirms the results of XRD. The surface increases after pillaring by

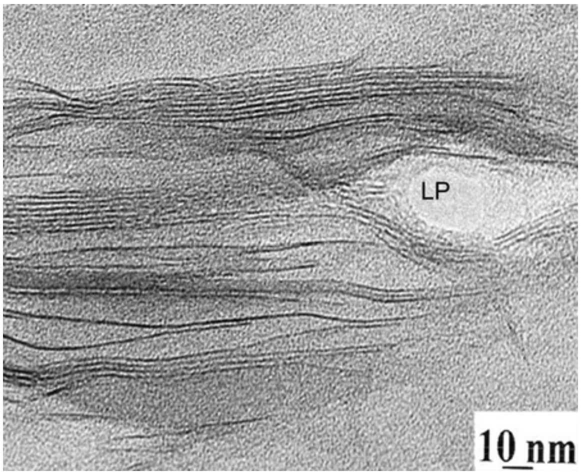

Figure 8. TEM image of Al-pillared Mt in concentrated media using a nitrate anion.

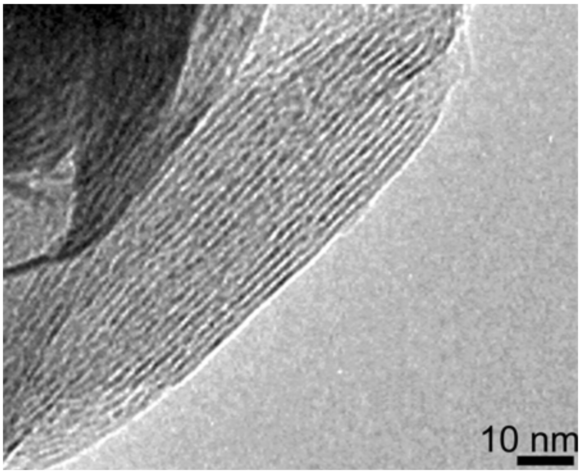

Figure 9. TEM image of Al-pillared Mt in concentrated media using commercial chlorhydrol.

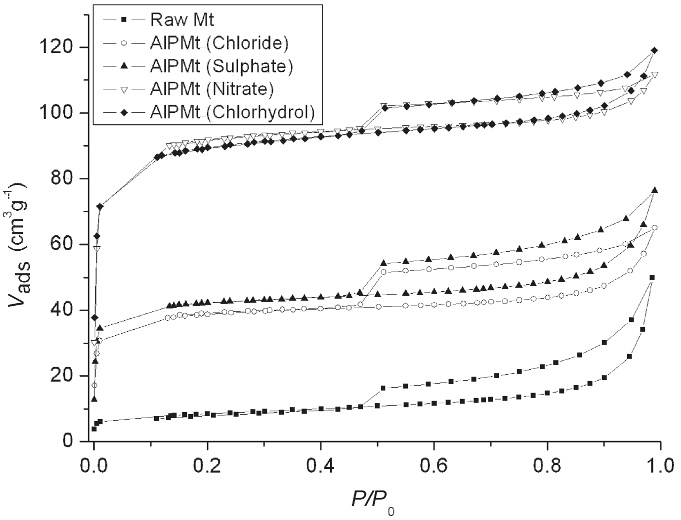

Figure 10. N_2-adsorption isotherms of initial montmorillonite and Al-pillared Mt using chloride, sulfate, nitrate and chlorhydrol.

different oligomers (Table 1): a tenfold increase of the BET surface when the anion of the Al_{13} pillars is nitrate and when chlorhydrol is used, but only about fivefold when the anions are sulfate or chloride.

The measurements of porosity (Table 1) give similar results and indicate that the increased surface is essentially due to the creation of microporosity, which depends on the nature of the anion. The microporosity increases 30-fold in the case of Mt pillared with Al_{13} nitrate and chlorhydrol in comparison with the raw clay, and only 13- or 12-fold, respectively, with Al_{13} sulfate or Al_{13} chloride. However, the mesoporosity decreases slightly for Al_{13} nitrate, chloride or sulfate and remains constant for chlorhydrol.

The spectacular increase of microporosity in the case of Al_{13} nitrate and chlorhydrol indicates that a large proportion of interlamellar spaces could be occupied by the Keggin ions. This is in agreement with the XRD results. The intercalation is much more difficult with sulfate or chloride.

Table 1. Effect of anions associated with the Al_{13} oligomer on the surface properties of pillared clays: surface area (S_{BET}), total porous volume (Vp), microporous volume (Vip) and mesoporous volume (Vmp)

Samples	S_{BET} (m^2/g)	Vp (cm^3/g)	Vip (cm^3/g)	Vmp (cm^3/g)
Raw Mt	29	0.077	0.004	0.073
AlPMt (chlorhydrol)	289	0.180	0.110	0.070
AlPMt (nitrate)	283	0.173	0.120	0.053
AlPMt (sulfate)	153	0.118	0.053	0.065
AlPMt (chloride)	140	0.101	0.047	0.054

TGA. The TGA curves for the raw clay and its derivatives pillared with different complexes (nitrate, sulfate, chloride or chlorydrol) are shown in Figure 11.

The curves obtained with the Al-pillared Mt obtained from the three laboratory-synthesized oligomers are similar and show continuous weight loss from room temperature to 720ºC. For chlorhydrol, the shape is also similar as shown in the insert at a smaller magnification, but the total weight loss is smaller. For chloride, sulfate or nitrate, the total weight loss is three times greater than that of the raw clay. The first weight loss, corresponding to >40% of total weight loss, occurs at a temperature of <190ºC. It corresponds to the dehydration of water adsorbed on the surface of pillared samples. The second loss (17%) between 190 and 520ºC corresponds to the water adsorbed in the interlayer space of the pillared clay and the dehydroxylation of the pillars. This weight loss is independent of the nature of the anion. The dehydroxylation of the montmorillonite layers occurs in the temperature range 500–700ºC with ~4% weight loss. Between 800 and 1000ºC, an additional very weak loss is observed in the case of Mt pillared by Al_{13} sulfate (Figure 12b), which is not observed in raw Mt (Figure 12c). It corresponds to the decomposition of sulfate ions as observed in the DTG curve of pure Al_{13} sulfate (Figure 12a). It indicates that a part of the Al_{13} complex sulfate is not dissociated and probably precipitated on the clay.

As mentioned previously, the thermal analysis of Mt pillared by chlorhydrol indicates a continuous weight loss from room temperature to 720ºC very weak compared the other AlPILMt, and even in comparison with raw Mt. It can be explained by lower hydration of

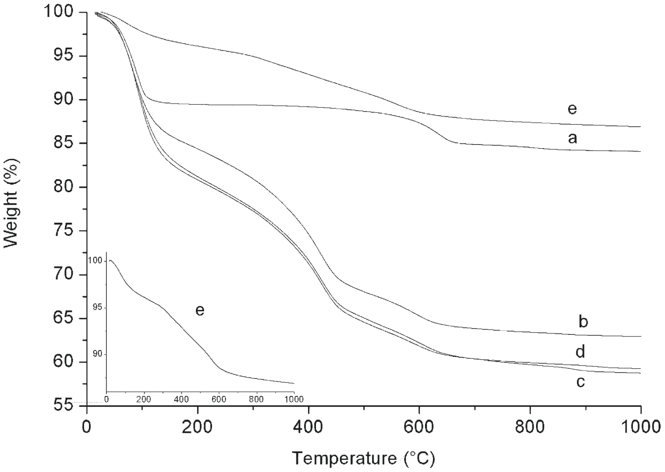

Figure 11. TG of raw Mt (a) and AlPMt by Al_{13} oligomers associated with different anions: (b) chloride; (c) sulfate; (d) nitrate; and (e) commercial chlorhydrol.

the more compact and large particles, as shown in the TEM image (Figure 9). This hypothesis is supported by the comparison of the TEM images of AlPIL obtained with nitrate and chlorhydrol (Figures 8) and the TG results of these two samples showing the largest and smallest weight loss among the samples studied, respectively. This suggests that the amount of water adsorbed in the interlayer spaces is not anion dependant but rather depends on the dispersion or stacking of the layers in the pillared clays.

DISCUSSION AND CONCLUSIONS

Montmorillonite treated with Al complexes with different anions in concentrated media leads in all cases to pillared materials. The formation of better ordered and well organized microporous pillaring depends significantly on the nature of the anion associated with the Al species in the starting compounds.

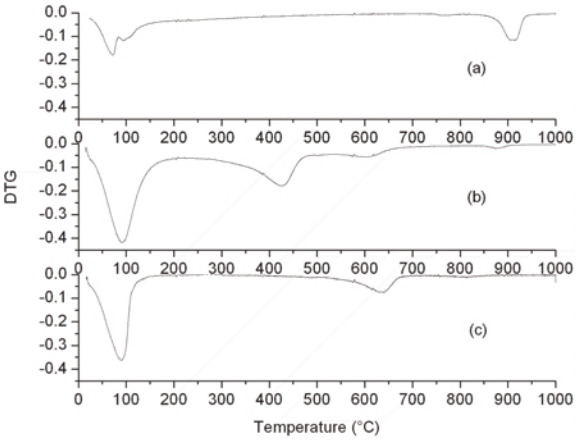

Figure 12. DTG of Al_{13} sulfate (a); AlPMt with Al_{13} sulfate (b); and raw Mt (c).

All of the XRD, TG, TEM and BET results show that the changes observed in the pillared samples are not due to the nature of the anions used in the oligomers alone. For example, pillared samples obtained with the same chloride anions show different structural and physicochemical properties depending on operating conditions, which are probably largely responsible for the degree of hydrolysis and for the nature of the Al oligomers obtained and affect the structure of the resulting species.

It is curious that although the hydrolysis of Al salts has been studied extensively, confusing NMR results are still not fully understood in the literature as regards the nature of the oligomeric species obtained both in solution and in the solid state. ^{27}Al NMR spectroscopy is used as one of the best analytical tools for Al speciation. However, there are several difficulties associated with the method, such as quadrupolar broadening of certain signals and insufficient sensitivity to the relatively low concentrations of Al species (Shafran and Perry, 2005). Further NMR investigations need to be carried out on the solid Al complexes carefully prepared in solutions.

For the AlPMt obtained with basic chloride, the presence of the weak broad peak at 1.9 nm in XRD indicates the presence of Al_{13} in a very small proportion. This could explain the lack of detection of these species in the pure chloride oligomer by NMR and XRD. Similarly, the basic Al sulfate which contains exclusively Al_{13} species, as confirmed by XRD and NMR, shows in the XRD pattern that only a small amount of Al_{13} species can be intercalated between the layers of the clay, probably because of the tendency to sulfate precipitation which is confirmed by the presence of sulfate as shown by TG analysis.

In the case of the chlorhydrol, ^{27}Al NMR analysis has shown that most of the species present are monomeric Al. These species can probably exchange the exchangeable Na^+ cations more rapidly than the Al_{13} present in small amounts in chlorhydrol. The expected effect of this exchange is the formation of thicker particles. The subsequent slower exchange of Al^{3+} by Al_{13} does not affect the long-range organization of these particles and leads to a pillared sample with a very intense sharp XRD peak. In the case of nitrate, the exchange of Na^+ by Al_{13} leads to smaller pillared layer stacking, which could explain the lower intensity and broadness of the XRD peak. Pillaring of previous Al^{3+}-exchanged clay should probably give better results, as obtained with commercial chlorhydrol.

The microporosity increases 30-fold in comparison with the raw clay for Mt pillared with Al_{13} nitrate and chlorhydrol and only 13- or 12-fold, respectively, in comparison with Al_{13} sulfate or chloride. However, the mesoporosity remains roughly constant.

When performing pillaring in very concentrated media, the addition of a given amount of water (or a number of dialyses) is necessary in order to have an adequate amount of solvent for the dissolution of the Al species. The transformation from solid Al_{13} complex to Al_{13} ions involves two successive processes: the first corresponds to the dissolution of crystals (5) and the second to molecular dissociation (6) which allows the mobility and the intercalation of Al_{13}^{7+} ion:

$$\underset{\text{solid}}{Al_{13}\text{ complex}} \xrightarrow{H_2O} \underset{\text{in aqueous solution}}{Al_{13}\text{ complex}} \qquad (5)$$

$$\underset{\text{in aqueous solution}}{Al_{13}\text{ complex}} \xrightarrow{H_2O} Al_{13}^{7+} + \text{anion} \qquad (6)$$

The dissolution (5) of the different complexes studied depends on their solubility, which itself depends on the nature of the anions, *e.g.* 16 dialyses for nitrate (266 mL/g of oligomer) 23 dialyses for sulfate (383 mL/g of oligomer) and 50 dialyses for chloride and chlorhydrol (833 mL/g of oligomer). The nitrate is the most rapidly soluble, but the chlorhydrol, which leads to the best results in terms of pillaring, has the lowest kinetic solubility.

The success of pillaring depends essentially on the second process, namely molecular dissociation (6), which entails the ability of the anion to dissociate from the Al_{13} cation. In the case of nitrate or chlorhydrol, this process seems easier than for chloride or sulfate.

In conclusion, the structure of the pillared clay obtained in concentrated media depends not only on the anion associated with the oligomer but also on the Al species present in this oligomer. The presence of monomeric Al besides the Al_{13} Keggin ions could improve the pillaring, giving well organized and larger layer stackings. Further investigations of the chemistry of these complexes are needed to elucidate the different species likely to be formed in solution, their evolution during the transformation to the solid state and their structure after pillaring.

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