SYNTHESIS OF Al-PILC ASSISTED BY ULTRASOUND: REDUCING THE INTERCALATION TIME AND THE AMOUNT OF SYNTHESIS WATER

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Abstract—Of all the known pillared layered clays (PILC), Al-PILC is the most studied. In spite of that, its use on a commercial scale is not yet possible due to the large amount of water required for its synthesis. The aim of the present work was to take advantage of the beneficial effects of ultrasound radiation for reducing intercalation time, and to optimize the synthesis parameters in order to find a viable industrial means of preparing Al-PILC.

A comprehensive study of the effect of ultrasonic radiation on the parameters which have a direct effect on the amount of water used in the synthesis was conducted, specifically on the effects of: (1) mmol of Al/g of clay ratio (R) by decreasing the volume of Al solution and keeping the amount of clay constant, (2) the concentration of clay in the initial suspension (or not suspending the clay at all), and (3) the concentration of the Al precursor solution. The use of ultrasonic radiation produced the expected reduction in exchange time which was attributed to a decrease of the clay-particle size. This decrease of particle size gave rise to an improvement in the diffusion of the Al precursor towards the core of the clay grain leading to solids with increased surface areas, basal spacing and X-ray diffraction peak definition. By optimizing the synthesis parameters directly involved in the consumption of water, it was possible to decrease the amount used by >60%.

Key Words—Al-PILC, Aluminum, Ultrasound Radiation.

INTRODUCTION

The synthesis of Al-PILC has been studied since 1977 and a broad spectrum of applications as catalysts and catalyst supports (Gil *et al.*, 2000; Kaloidas *et al.*, 1995; Moreno *et al.*, 1997; Fetter *et al.*, 1997; Storaro *et al.*, 1998; Katdare *et al.*, 1999, 2000; Yang and Li, 1995; Pérez Zurita *et al.*, 1999, 2003; Salermo *et al.*, 2001a, 2001b) and adsorbents (Pérez Zurita *et al.*, 1999; Moronta *et al.*, 2002) has been reported. Industrial application of Al-PILCs has been delayed, however, mainly because it is uneconomic. This is because conventional methods for PILC synthesis involve large amounts of water and long intercalation times. Some efforts were made in the past to try to produce Al-PILC at a 1 kg scale. Effective scaling-up methods for preparation of PILCs were reported by Kaloidas *et al.* (1995) and Moreno *et al.* (1997). Although good reproducible results were found in both studies, the problems of the large amount of water required and the long synthesis times were not overcome.

Vaughan (1988) stressed the importance of making additional efforts to approach industrial preparation conditions where scale-up processes could be carried out at competitive prices. He indicated some prerequisites for the making of real catalysts which eventually could be scaled up: (1) to use clay with minimal or no refining or pre-exchanging; and (2) pillaring in concentrated clay suspensions. Several researchers (Moreno *et al.*, 1997; Fetter *et al.*, 1997; Storaro *et al.*, 1998; Salermo *et al.*, 2001a, 2001b; Sanchez *et al.*, 1998; Schoonheydt and Leeman, 1992; Molina *et al.*, 1992; Storaro *et al.*, 1996; Sivakumar *et al.*, 1995) successfully obtained Al-pillared clays using highly concentrated clay suspensions. Such efforts decreased the amount of synthesis water used but, at best, the decrease was only ~20%. In addition to the suggestions of Vaughan (1988), other strategies such as increasing the concentration of the Al solution were adopted (Moreno *et al.*, 1997; Fetter *et al.*, 1997; Storaro *et al.*, 1998; Sanchez and Montes,1998; Schoonheydt and Leeman, 1992; Molina *et al.*, 1992; Storaro *et al.*, 1996; Katdare *et al.*, 2000). In some cases promising results were obtained.

Unconventional synthesis approaches such as microwave irradiation (Fetter *et al.*, 1997) and ultrasonic radiation (Katdare *et al.*, 1997, 1999, 2000; Sivakumar *et al.*, 1995; Chatakondu *et al.*, 1987; Lindley, 1999; Pérez Zurita *et al.*, 2001; De Bock *et al.*, 1999; Kooli *et al.*, 1997; Hu *et al.*, 1997; Ramaswamy *et al.*, 2002) have also been employed. Both methods proved to represent a faster and more effective method of clay pillaring with Al.

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528

The use of ultrasonic radiation for intercalating inorganic, organic or organometallic compounds into layered solids is not new. Chatakondu *et al.* (1987) found that using ultrasound significantly increased (as much as 200-fold) the rate of intercalation of organic and organometallic compounds into various layered inorganic oxide and sulfide host solids. They stated that sonification causes a significant decrease in the particle size of the host solids, regardless of the presence of a guest compound. Lindley (1992) claimed that his group in 1985 observed similar effects in the rate of intercalation of metallic ions into clays.

Sivakumar *et al.* (1995) reported on the preparation of alumina-pillared montmorillonite under sonification conditions, through intercalation of boehmite sol from a 10% suspension of the Na-exchanged montmorillonite. They found intercalation times as short as 20 min and stated that the "novel" technique had shown added advantages over the conventional method where long reaction times and small smectite concentrations were employed. They attributed their results to a better delamination of the alumino-silicate layers provoked by sonification, which may enhance the available space in between the layers thereby enhancing the extent of intercalation and reducing considerably the reaction time. After this work, several researchers reported on the use of ultrasonic radiation for the synthesis of PILCs (Katdare *et al.*, 1997, 1999, 2000; Pérez Zurita *et al.*, 2001; De Bock *et al.*, 1999) and pillared layered double hydroxides (Kooli *et al.*, 1997; Hu *et al.*, 1997). The most active group working in the area is, without doubt, that of Ramaswamy which has reported on the synthesis of Al-PILCs using ultrasonic radiation (Katdare *et al.*, 1997, 1999, 2000) and its use for immobilizing copper chlorophtalocyanine, also by ultrasound (Ramaswamy, 2002). Their latest papers (Katdare *et al.*, 1999, 2000) focused on the optimization of preparative conditions such as Al precursor type and concentration, effect of exchangeable cations on the clay, and the concentration of the clay in the suspension.

The influence of sonification, successive exchange and pH during and after the intercalation process in the synthesis of an Al-PILC was reported by De Bock *et al.* (1999). From their experiments they concluded that the ultrasonic treatment of the suspension during the synthesis is responsible for a significant increase in porosity.

As shown by the discussion above, the main concern of the work to date has been to understand the role of ultrasound in the properties of the final solid, with special emphasis on the dramatic decrease in synthesis time.

A survey of the patents introduced during the last 5 y related to PILC synthesis shows that all the claims are based on the conventional method of preparation. It is our belief that the important point in the search for optimal techniques, methods and synthesis parameters is

to find a way of synthesizing PILCs in an economically acceptable fashion, as suggested by Vaughan (1988). This must involve shorter synthesis times and, more importantly, acceptable amounts of synthesis water.

EXPERIMENTAL

Synthesis

A commercial bentonite known as KWK-200 from American Colloid Company (typical analysis — moisture free: 63.02% SiO_2, 21.08% Al_2O_3, 3.25% Fe_2O_3, 0.35% FeO, 2.67% MgO, 0.57% Na_2O, 0.65% CaO, 0.72% traces, 5.64% LOI, surface area 33 m^2/g and basal spacing 13 Å), was used during the study without further purification. The Al solution was prepared by drop-wise addition of a 0.2 M NaOH solution to a 0.2 M solution of $AlCl_3$ under vigorous stirring at room temperature. The amount of NaOH added was calculated in order to obtain an OH/Al molar ratio of 2.

For synthesis of the solids using ultrasonic radiation, a 50 kHz bath was used. For all preparations (unless otherwise stated) a suspension of 30% (w/w) clay in water was prepared and stirred at 35ºC for 20 min before the exchange process was conducted. To determine the optimal intercalation time, a previously aged solution of the Al precursor was slowly added to the water-clay suspension to give a 10 mmol Al/g clay ratio. After all the precursor solution was added, the mixture was divided into four portions and placed immediately into the ultrasonic bath which was kept at 44ºC. The portions were removed from the bath at various times (60, 75, 90 and 105 min), centrifuged at 3000 rpm for 6 min and washed five times with deionized water. The Al-PILCs obtained were dried at 120ºC for 24 h and calcined at 500ºC for 1 h. The temperature was increased at a rate of 1ºC/min. These samples were denoted as US_x, where x is the exchange time in min. Once the exchange time was optimized, the study of the effect of the parameters which could reduce the amount of water used in the synthesis was undertaken. Two strategies were followed: (1) reducing the ratio R (mmol of Al/g of clay) by reduction of the solution volume keeping the amount of clay constant, and (2) using a concentrated solution of the intercalating agent. Samples obtained when changing the ratio R between 3 and 12 mmol of Al/g of clay were denoted as $_yUS_x$ (where x is the optimal exchange time (min) and y is the ratio R). Samples obtained when the concentration was increased were denoted as $_yUSC_x$ (C referring to concentrate).

In order to decrease the amount of water used in the synthesis further, the concentration of the initial clay-water suspension was studied. These samples were denoted $A-_yUSC_x$ (where A indicates the percentage of clay in the suspension). For example, $30-_{10}USC_{75}$ denotes an Al-PILC prepared with a 30% clay-water suspension, 10 mmol of Al/g of clay, a concentrated solution of the pillaring agent and 75 min of exchange time.

A sample synthesized by the conventional method was prepared as a reference. This sample was denoted CONV. For this preparation, a suspension of 1% (w/w) clay in water was prepared and stirred at 35ºC for 20 min. A previously aged solution of the Al precursor was added slowly to give a 10 mmol Al/g clay ratio. The suspension and exchange solution were stirred for 18 h at 60ºC. Finally, the suspension was centrifuged at 3000 rpm for 6 min and the sedimented solids washed five times with deionized water. The Al-PILC obtained was dried at 120ºC for 24 h and calcined at 500ºC for 1 h. The temperature was increased at a rate of 1ºC/min.

Characterization

The characteristics of the samples studied were determined by X-ray diffraction (XRD), scanning electron microscopy (SEM), chemical analysis, differential thermal analysis (DTA) − thermogravimetric (TG) analysis and BET surface area measurements. Basal spacing and the specific surface area were used as the main product-quality characteristic.

X-ray diffraction patterns were recorded on a Bruker AXS model D8 Advance instrument using CuKα radiation. Rock powders were scanned from 2 to 8º2θ and basal spacing was determined from the position of the d_{001} peak.

The SEM studies were conducted on a HITACHI S-500 device using an accelerating voltage of 20 kV. The samples were suspended in a 40% ethanol solution and introduced into an ultrasonic bath for 3 min. The suspension was then placed on a brass stub and coated with gold using an Eiko Eng. Ion coater model 1B-2. Chemical analyses of the samples were performed by atomic absorption on a GBC Avanta and on a mass spectrometer with ICP, Perkin-Elmer Elan 6000. Differential thermal analysis-thermogravimetric analysis was conducted using a TG-DTA V1.1B TA Instruments 2100 by heating 15 mg of the specimen in air (100 mL/min) over the range 25−1000ºC at a heating rate of 10ºC/min. α-Al$_2$O$_3$ was used as a ref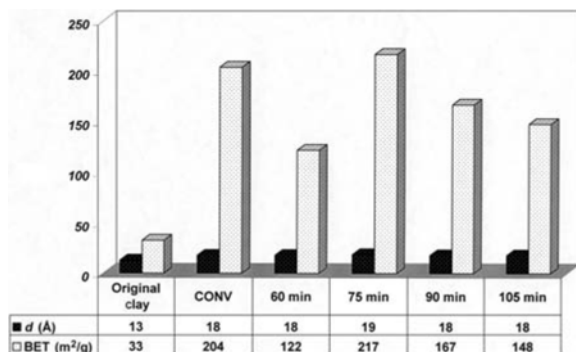erence material. Surface area measurements were conducted on a Flow Sorb II 2300 Micromeritics device. All samples were outgassed at 200ºC for 90 min.

RESULTS AND DISCUSSION

The effect of ultrasonic radiation on exchange time, mmol of Al/g of clay ratio (R), concentration of clay on initial suspension, and concentration of the Al precursor solution was studied.

Effect on exchange time

Figures 1 and 2 show the results obtained for the synthesized solids when the exchange time was varied from 60 to 105 min using the ultrasonic bath. In Figure 1, the results obtained are compared with those of the original clay and the conventional solid. An increase in surface areas and basal spacing to a maximum of 217 m^2/g and 19 Å, respectively, for the ultrasound preparation, was attained when the exchange time was 75 min. Microporous volumes also increased dramatically from 0.0039 to 0.0972 cm^3/g.

As reported by other groups, the intercalation time is drastically reduced when using ultrasonic radiation (Katdare *et al.*, 1997, 1999, 2000; Sivakumar, 1995; Pérez Zurita, 2001). In the present work a reduction from 18 h for the conventional preparation to 75 min, without loss of properties, was attained. The XRD patterns of the

Figure 1. Effect of exchange time, under ultrasound radiation, on surface area and basal spacing.

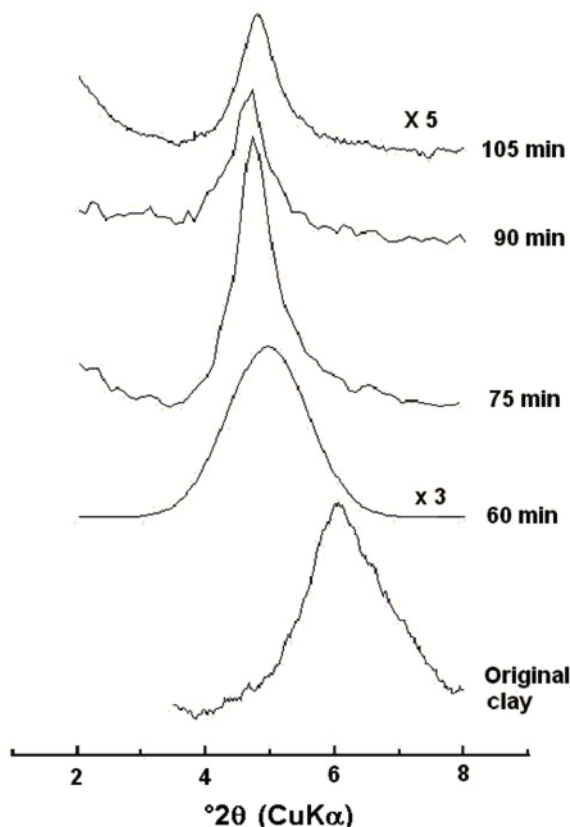|	Original clay	CONV	60 min	75 min	90 min	105 min
■ *d* (Å)	13	18	18	19	18	18
□ BET (m²/g)	33	204	122	217	167	148

Figure 2. Effect of exchange time, under ultrasound radiation, on the XRD patterns in the region of the 001 reflection.

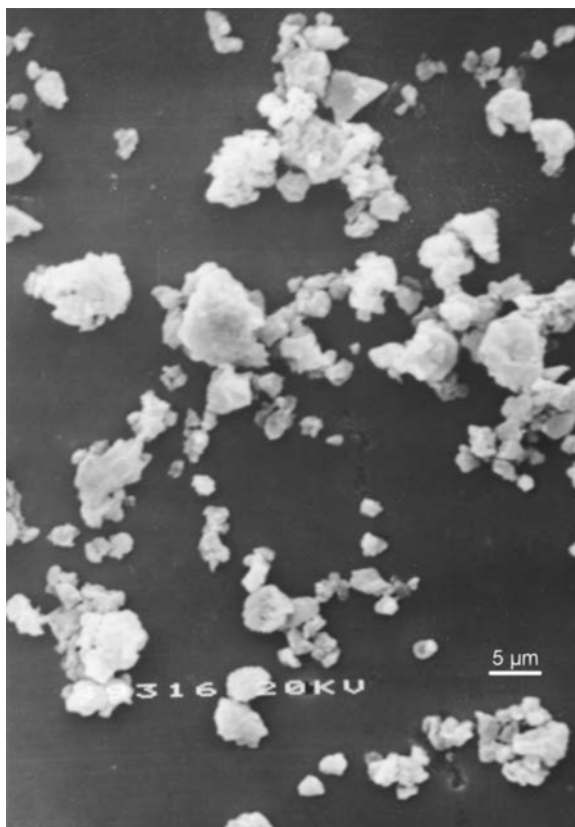Figure 3. SEM image of the solid Al-PILC 30_7US_{75}.

in the diffusion of the Al precursor into the gallery region of the clay. Sivakumar *et al*. (1995) attributed their results to a better delamination of the alumino-silicate layers provoked by sonification, which may increase the space available between the layers, thus enhancing the extent of intercalation and reducing considerably the reaction time.

A different approach was made by Suslick and Price (1999). They reported that ultrasonic radiation enhanced liquid-solid reaction rates by inducing an increase in the available surface area of the solid by fragmentation.

Scanning electron microscopy measurements were carried out in an attempt to explain our results. Figure 3 shows an SEM image of Al-PILC $30_{-10}US_{75}$ solid. A broad particle-size distribution between 0.5 and 3.6 μm was obtained. This result was expected because, following Vaughan's (1988) suggestion, an unpurified commercial bentonite was used. Even though this does not allow us to draw any definitive conclusions, analysis of the particle-size distribution shows some trends.

The particle size of the untreated clays is <2 μm. After intercalation, the clay particles can reach a maximum size of 3 μm. For this reason the particle-size distribution of the particles in the range 2−3 μm was studied on the pillared samples Al-PILC$_{CONV}$ and Al-PILC $30_{-10}US_{75}$. Figures 4 and 5 show the particle-size distributions obtained for these two samples.

Even though the mean particle size was almost the same in both solids (2.45 μm for Al-PILC$_{CONV}$ *vs*. 2.32 μm for Al-PILC $30_{-10}US_{75}$) a broader particle-size distribution was obtained for Al-PILC $30_{-10}US_{75}$ indicating the presence of additional particle sizes. Furthermore, the presence in the Al-PILC $30_{-10}US_{75}$ solid of a significant number of particles with a size of 2.4 μm (not present in the conventional sample) could indicate solid fragmentation.

Our observations support the pioneering work of Chatakondu (1987), who determined from transmission

synthesized series are shown in Figure 2. The solid $30_{-10}US_{75}$ shows a better-defined XRD peak, indicating regular pillar spacing, in addition to increased surface areas and basal spacing.

The role of ultrasonic radiation is the subject of debate. Katdare *et al*. (1999, 2000) attributed the dramatic decrease in exchange time to an improvement
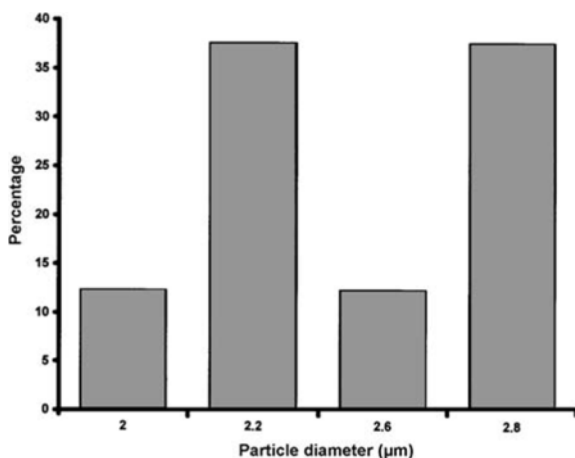

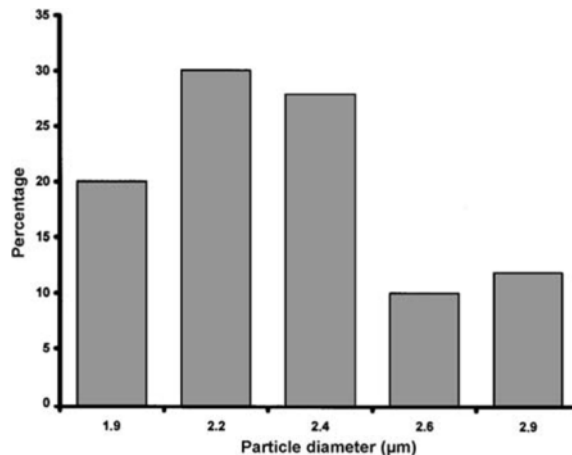Figure 4. Particle-size distribution of the Al-PILC CONV sample.

Figure 5. Particle-size distribution of the Al-PILC 30_7US_{75} sample.

electron microscopy results that sonification causes a significant decrease in the particle size of the host solids.

Although further work must be done to make definitive conclusions, our results and those from the literature seem to suggest that the main effect of ultrasonic radiation is to reduce the size of the clay grain and, as a consequence, improve the diffusion of the Al precursor towards the core of the particle.

A short exposure time to ultrasonic radiation leads to solids with poor surface area indicating a poor degree of exchange, possibly due to a small driving force for the mass transfer. On the other hand, long exposure times also produce a solid with a smaller surface area and basal spacing. This could be attributed to either a delamination of the clay layered structure forming the so-called "house of cards" (Figueras, 1988) or to the breaking up of the Al polyhydroxycation.

Effect on the mmol of Al/g of clay ratio (R)

Once the optimal exchange time was obtained, the study of the mmol Al/g clay ratio was conducted by reducing the volume of the pillaring solution while keeping the weight of the clay constant. Table 1 shows the results obtained. The surface area and basal spacing are greatest when R decreases from 12 to 7. A further decrease of R leads to smaller surface area and basal spacing. This would appear to indicate that a large volume of the Al solution favors delamination while a minimal volume of liquid is required for an effective swelling of the clay. Our results show that when using ultrasonic radiation, the mmol of Al/g of clay ratio can be reduced and it was possible to obtain an Al-PILC with a similar surface area and basal spacing while using 20% less water as compared with the conventional preparation.

Effect on the concentration of clay in the initial suspension

Another parameter which greatly affects the amount of water used in the synthesis of PILCs is the concentration of clay in the initial suspension water-clay.

Highly concentrated suspensions have been used by other authors. The highest concentration was reported by Fetter *et al.* (1997) who used concentrated suspensions up to 50% (w/w) and Montes (1998) who added the Al precursor solution over the dried clay. For this study we added the dry clay to the precursor solution and again studied the mmol of Al/g of clay ratio in order to optimize synthesis conditions further. Table 1 shows the results obtained. In this case, the properties of the resulting solids seem to be slightly modified and a marginal decrease in surface area and the intensity of the d_{001} peak in the XRD pattern were observed. These results can be attributed to a partial delamination of the clay. Figure 6 shows the XRD patterns of the original clay and the best solid of this series (100_7US_{75}) in the region of the 001 reflection. This small loss of surface area is very much compensated by the reduction in the amount of water required; >60% less is needed than in the conventional method.

Effect on the concentration of the Al precursor solution

Finally, the effect of the concentration of the precursor Al solution under ultrasonic radiation was studied and the results are shown in Table 1. A
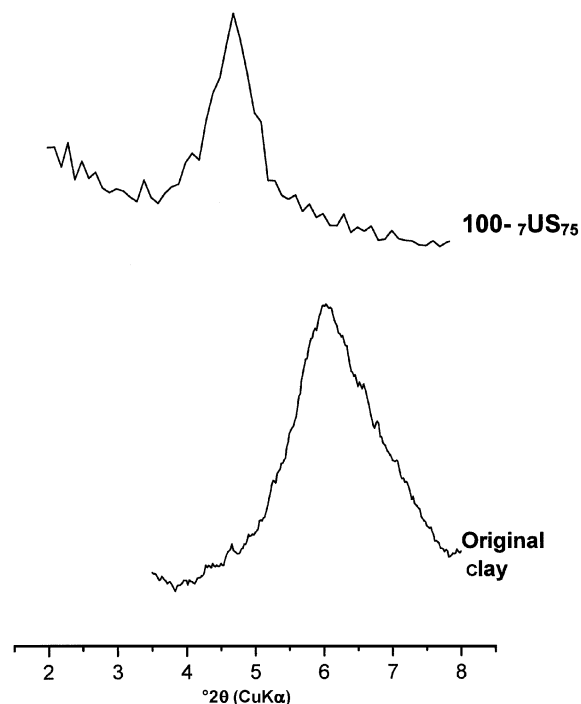
Table 1. Effect of ultrasonic radiation on the mmol of Al/g of clay ratio (R), concentration of clay in the initial suspension and concentration of the aluminum precursor solution.

Solid	$d \pm 1$ (Å)	BET surface area ± 2 (m^2/g)
$CONV_{1080}$	18	204
$30_{12}US_{75}$	17	142
$30_{10}US_{75}$	19	217
30_8US_{75}	18	199
30_7US_{75}	19	222
30_5US_{75}	17	166
30_3US_{75}	18	161
$100_{10}US_{75}$	19	211
100_8US_{75}	18	208
100_7US_{75}	18	192
$30_{20}USC_{75}$	18	114
$30_{13}USC_{75}$	17	113
$30_{10}USC_{75}$	16	101
30_7USC_{75}	16	107
100_7USC_{75}	18	157

Figure 6. XRD patterns of the original clay and the Al-PILC 100_7US_{75} sample in the region of the 001 reflection.

detrimental effect of the concentrated solution was observed as the surface area and basal spacing were smaller than that obtained with a less concentrated solution. Moreover, the XRD peaks obtained for the solids produced from concentrated solutions were wider and less intense compared with the sharp peak obtained with samples in less a concentrated media. This could be attributed to the fact that high concentrations favor a faster exchange at the surface and outer part of the clay thereby blocking the pores. The Al cations deposited at the outer surface of the clay could make the exchange at the core of the clay particles more difficult, producing a less homogeneous intercalation.

Different explanations are given in the literature. Gil *et al.* (2000) studied the same effect and related their results to the ion exchange capacity of the clay. They stated that high concentrations could produce deposition of the excess cations of the solution and low concentrations could give rise to a small rate of diffusion and, as a consequence, to a small exchange rate. Two different explanations were given by Katdare *et al.* (1997, 1999) who stated that in the diluted solution, extensive depolymerization occurs due to rehydrolysis of the polycation and that a concentrated solution is also ineffective because of the very slow hydrolysis. Katdare *et al.* (1999) reported that in the highly concentrated solution, Al_{13} further polymerizes and that diffusion of such species is limited. Sanchez and Montes (1998) attributed this result to the intercalation of Al species other than the Keggin ion.

Thermal stability

In order to assess the thermal stability of the Al-PILC synthesized, the best samples were calcined at 500°C. Table 2 shows the surface area and basal spacing before and after thermal treatment.

Table 2. Thermal stability of the best solids.

Solid	Surface area (m^2/g) Fresh $\pm$ 2	Surface area (m^2/g) Calcined 500°C $\pm$ 2	% surface area lost
Conv. $_{1080}$	204	186	9
$30-_{10}US_{75}$	217	199	8
$30-_8US_{75}$	199	115	42
$30-_7US_{75}$	222	227	0
$100-_8US_{75}$	208	204	2
$100-_7US_{75}$	192	175	9

All solids, with the exception of Al-PILC $30-_8US_{75}$ maintain their surface area almost unchanged after the thermal treatment. The reduction in surface area can be related to the dehydroxylation of the pillaring species resulting in the degradation of the pillar. Ge *et al.* (1994) proposed that the cause of thermal instability could be related to a destabilization of the clay by partial hydrolysis of Si−O−Al bonds. Further evidence of thermal stability was obtained by TG analysis. Figure 7 shows the pattern obtained for the $30-_7US_{75}$ sample and three weight-loss stages are evident. A first weight loss of 8% (w/w), associated with an endothermic change between 30 and 120°C, could be attributed to adsorbed water. The fundamental characteristics of the crystalline structure of montmorillonite justify the retention of water. A second loss of 2% between 210 and 370°C could be associated with the dehydration of the polyhydroxycation of aluminium. A third weight loss of 5% (w/w), associated with an endothermic change between 370 and 750°C, could be attributed to the dehydroxylation of the clay. A total weight loss of only 15% demonstrates the thermal stability of the solid.
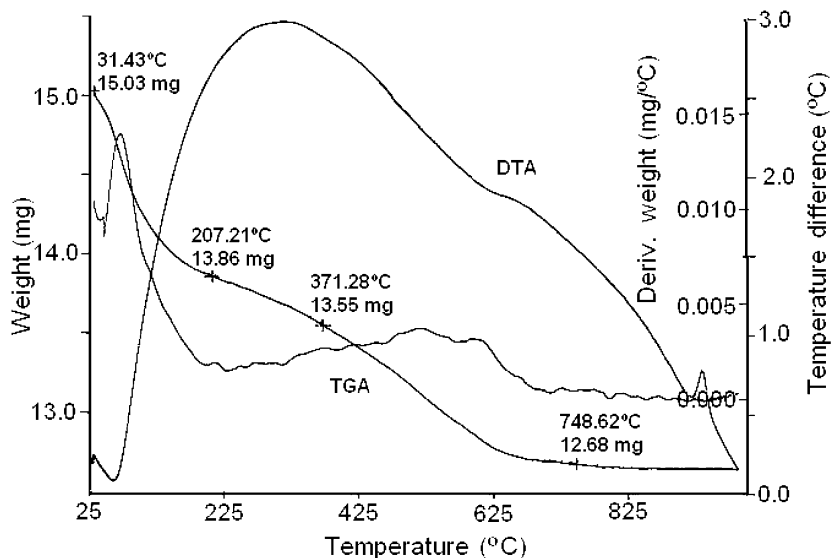

Figure 7. DTA-TGA thermogram of the solid 30_7US_{75}.

Chemical analyses

Table 3 shows the results of the chemical analyses. As expected, there was a significant decrease in the Si/Al ratio compared with that obtained for the original clay. One interesting point is that the solids with better thermal stability showed smaller Si/Al ratio values. Moreover, optimal synthesis conditions using ultrasonic radiation (*e.g.* 30-$_7$US$_{75}$) led to solids with smaller Si/Al ratios and greater thermal stability than the conventional solid. This allows us to conclude that thermal stability can be related to the number of pillars in the structure. Similar results on Fe-PILC samples were reported by Pérez Zurita *et al.* (1996). For sample 30-$_7$USC$_{75}$, synthesized using a concentrated solution of the precursor Al solution, the Si/Al ratio was within the range shown by the other samples indicating that the Al present was exchanged. However, for sample 100-$_7$USC$_{75}$, the smaller Si/Al value seems to indicate that it is possible that Al cations are deposited at the outer surface of the clay. Further washing could lead to greater surface areas and porosities.

CONCLUSIONS

From our results it is possible to conclude that the use of ultrasonic radiation allows the synthesis of solids with characteristics comparable with conventional preparations but using shorter intercalation times. By optimizing the synthesis parameters directly involved in the consumption of water, it was possible to decrease the amount of water needed by ~60% compared with conventional preparations.

The main effect of ultrasonic radiation is to reduce the size of the clay grain and, as a consequence, the diffusion of the Al precursor towards the core of the particle improves. This did not change the properties of the samples; on the contrary, improved surface areas, basal spacing and XRD peak definition were found. The

Table 3. Chemical analyses.

Solid	Wt.% SiO$_2$ ± 0.2	Wt.% Al$_2$O$_3$ ± 0.2	Si/Al ± 0.2
Original clay	44.1	9.8	2.1
CONV	44.7	17.4	1.2
30$_{10}$US$_{60}$	41.7	12.2	1.6
30$_{10}$US$_{75}$	45.1	17.6	1.2
30$_{10}$US$_{90}$	39.6	15.4	1.2
30$_{12}$US$_{75}$	41.5	16.2	1.2
30$_8$US$_{75}$	39.6	15.4	1.2
30$_7$US$_{75}$	38.9	16.5	1.1
30$_5$US$_{75}$	38.3	13.8	1.3
100$_{12}$US$_{75}$	39.6	16.8	1.1
100$_8$US$_{75}$	41.7	17.7	1.1
100$_7$US$_{75}$	43.2	18.4	1.1
30$_7$USC$_{75}$	39.6	15.4	1.2
100$_7$USC$_{75}$	31.2	18.2	0.8

use of concentrated clay-water suspensions and reduced volumes of the intercalation solution gave rise to solids with greater surface areas and d_{001} spacing. A promising route for synthesizing Al-PILC on a larger scale would appear to have been found.

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