Al-PILLARING OF SAPONITE WITH THE Al POLYCATION $[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$ USING A NEW SYNTHETIC ROUTE

Miguel Angel Vicente[1],* and Jean-François Lambert[2]

[1] Departamento de Química Inorgánica, Universidad de Salamanca, Plaza de la Merced, s/n. 37008-Salamanca, Spain
[2] Laboratoire de Reactivité de Surface, Université Pierre et Marie Curie, 4 Place Jussieu, Tour 54, Casier 178, 75252 Paris Cedex 05, France

Abstract—The intercalation of a saponite with the Al polycation $[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$ is described. This polycation is obtained by reaction of alumina with Al chloride. The intercalation is achieved by reaction of very concentrated solutions of this polycation with the clay in powder form. Solids with a basal spacing of 18.9 Å were obtained in this way, stable up to 700ºC (17.0 Å). The Langmuir surface area of the intercalated solid was 366 m^2/g, and that value decreases to 119, 138 and 125 m^2/g for the solids pillared at 500, 600 and 700ºC, respectively.

Key Words—Al-pillaring, Nanocomposite, Pillared Clay, Saponite, Surface Area.

INTRODUCTION

Pillared clays are usually obtained in a two-step, soft-chemistry synthesis. The layered clay precursors are first intercalated with robust inorganic polycations by ion exchange; they are then calcined to induce the formation of covalent bonds between the pillars and the layers. The pillars obtained can be considered as an ultradisperse hydroxy-Al phase that represents an interesting model of the surface of Al_2O_3 oxides (Mitchell, 1990; Lambert and Poncelet, 1997). Thus, pillared clays can be regarded as nanocomposites in which sub-nm oxyhydroxide particles are incorporated in the interlayer space (Mitchell, 1990; Lambert and Poncelet, 1997; Gil *et al.*, 2000).

The intercalation of clays with the 'classical' polycation $[Al_{13}O_4(\mu_2\text{-}OH)_{24}(H_2O)_{12}]^{7+}$, with anti-Keggin structure ('[Al$_{13}$]-Keggin') has been studied widely. Following recent research on the solution chemistry of Al(III), we reported (Vicente and Lambert, 1999) the intercalation with a polycation of different structure, namely $[Al_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{12}(heidi)_6(H_2O)_6]^{3+}$ (or [Al$_{13}$]-heidi for short, the ligand "heidi" being the N-(2-hydroxyethyl)-iminodiacetate anion, $C_6H_8O_5N^{3-}$) Heath *et al.* (1995), Jordan *et al.* (1996)), in which part of the coordination positions of the Al(III) cations are occupied by organic ligands.

Pillared clays have not been prepared at the industrial scale due to the cost of their synthesis. In the case of Al-pillared clays, the anti-Keggin polycation is usually obtained by careful titration of AlCl$_3$.6H$_2$O solutions with NaOH up to pH = 4.0–4.3, followed by ageing at room temperature; the resulting solution is then added to an aqueous suspension of the clay. Very large volumes of water must to be used, both during initial intercalation and subsequent washings. Different authors have attempted to avoid these obstacles to facilitate the industrial synthesis of these solids. Thus, Schoonheydt and Leeman (1992) used concentrated "Al" solutions as intercalating agents, and Molina *et al.* (1992), Fetter *et al.* (1997) and Molina *et al.* (2000) used concentrated clay suspensions, in order to reduce the amount of water needed during synthesis. Kaloidas *et al.* (1995), Moreno *et al.* (1997) and Sánchez and Montes (1998) prepared Al-pillared clays at a 1 kg scale, approximately. The use of 'Chlorhydrol' (a commercial basic Al salt) as an intercalating agent is another way to circumvent the cumbersome preparation. Recently, Storaro *et al.* (1998) successfully used 'Chlorhydrol' to pillar concentrated clay suspensions.

In the present paper, we report on the use of a modified synthetic route of industrial interest for the intercalation/pillaring of saponite, probably involving an Al polycation with formula $[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$, and structurally related to [Al$_{13}$]-heidi. The synthesis of this polycation is carried out using a method described by Breuil (1965). This author observed that the reaction of 220 g of alumina with 1 kg of AlCl$_3$.6H$_2$O in 800 mL of water at 121ºC for 24 h yielded the formation of a salt the formula of which was then stated as $5AlCl_3.8Al(OH)_3.37.5H_2O$, but should be more correctly expressed as $[Al_{13}(OH)_{24}(H_2O)_{24}]Cl_{15}.13.5H_2O$. Recently, Seichter *et al.* (1998) solved its structure, finding that it is indeed based on $[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$ polycations similar to [Al$_{13}$]-heidi; further characterization of this polycation has been reported by Allouche *et al.* (2001). Its high positive charge makes it an interesting candidate for intercalation into clay layers.

EXPERIMENTAL

To synthesize the polycation we used a similar method to that of Breuil (1965): 2.0 g of γ_c-alumina (Institut Français du Pétrole, ref. E8648, 150–400 µm in

* E-mail address of corresponding author:
mavicente@usal.es

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size), 9.09 g of AlCl$_3$.6H$_2$O (Prolabo) and 7.27 g of water were heated under reflux for 24 h. After this time, the unreacted alumina was filtered off. Actually, part of this alumina could not be separated from the solution since it formed a colloidal suspension of very small particle size (attempts were made using 0.8 µm Whatman filters and centrifugation at 10000 rpm). This suspension was in direct contact with Ballarat saponite, 2.0 mL of the suspension and 1.0 g of powder Ballarat saponite being introduced into a dialysis bag, and immediately submitted to washing by dialysis. After five washings, no further Cl$^-$ anions could be detected (Ag$^+$ test). During successive washings, the volume of the dialysis bag increased significantly, indicating considerable osmotic pressure. The solid phase was separated by centrifugation, dried in air at 40ºC and characterized by X-ray diffraction (XRD) and N$_2$ physisorption; parts were calcined at 500, 600 and 700ºC for 4 h, with a heating rate of 0.6ºC/min from room temperature to the final calcination temperature. This synthetic route is schematized in Figure 1. Compared to the usual procedure of [Al$_{13}$]-Keggin intercalation, the method used here has two main advantages: (1) an easier preparation of the polycation; and (2) the use of very concentrated polycation solutions

and of the clay in powder form meant that the intercalation reaction occurred within the dialysis bag. Thus, it was not necessary to use large water volumes as in the classical procedure.

RESULTS AND DISCUSSION

The dried sample collected after dialysis has a Langmuir surface area (Rouquerol *et al.,* 1999) of 366 m^2/g, similar to that usually reported for [Al$_{13}$]-Keggin-intercalated solids. This in itself does not prove intercalation, since, as we have mentioned, an unknown amount of finely dispersed colloidal alumina must be present in the sample (the starting γ$_c$-alumina had a surface area of only 190 m^2/g, but it could have increased upon partial dissolution). However, additional information from XRD strongly suggests polycation intercalation: the dried solid shows a basal spacing of 18.9 Å *vs.* 14.0 Å for the natural saponite (Figure 2). This corresponds to an interlayer spacing of 9.0 Å, comparable with the value observed after intercalation of [Al$_{13}$]-Keggin polycations. This solid has a high crystallinity (fwhm index = 0.677º, *vs.* 1.010º for the natural saponite). The d_{002} reflection peak is clearly visible in the dried sample at 9.6 Å.
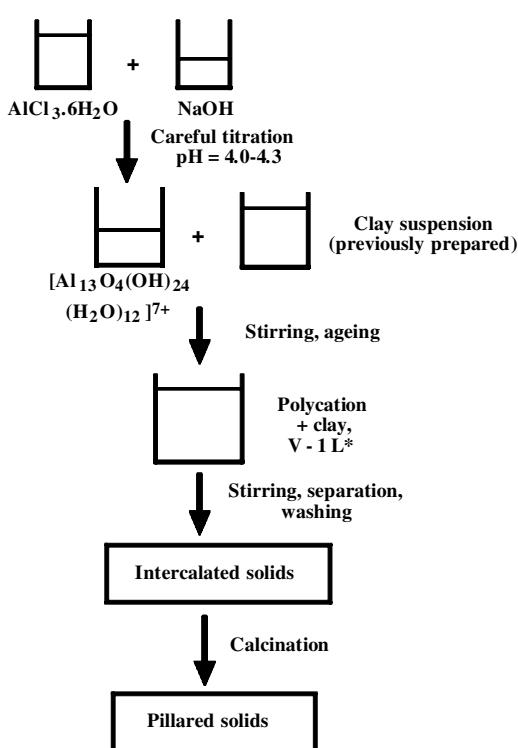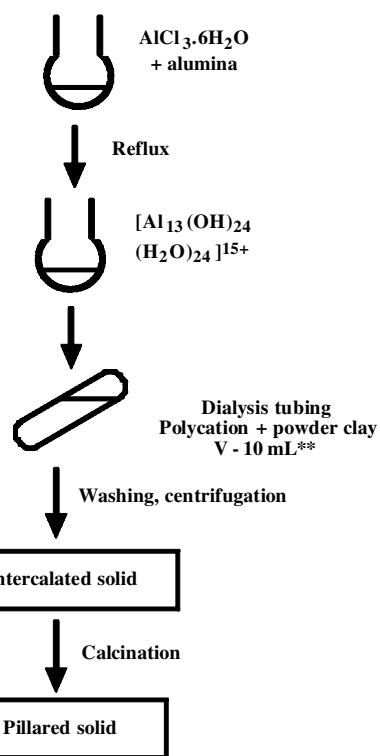

Figure 1. Schematic view of the suggested synthetic route, compared with the classical procedure.
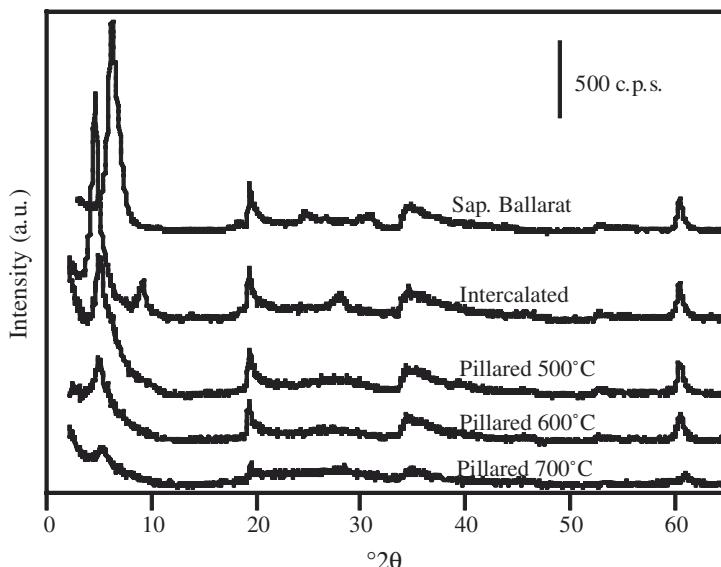
Figure 2. XRD patterns of Ballarat saponite and intercalated and pillared samples.

The amount of Al fixed during the intercalation process is 11.42% (expressed as amount of Al in the dried solids and compared with the Mg content in the natural Ballarat saponite, 16.13%). As seen in Table 1, this is significantly more than in the saponite intercalated with Al_{13}-Keggin polycations, where a mere additional 4.89% of Al was fixed. If Al fixation was only due to the intercalation of $[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$ polycations compensating the clay layer charge, a smaller amount of fixed Al would be expected since the charge per Al atom is actually about twice as much as per Al_{13}-Keggin (15/13 instead of 7/13). The observed difference is probably attributable to colloidal alumina particles present in the sample alongside intercalated clay tactoids. It is then easy to calculate that colloidal alumina particles represent at most 15% of the total sample weight (insufficient to explain the large surface area).

Upon calcination at 500°C, the surface area decreases to 119 m^2/g. This is less than the values usually reported for saponites pillared with the classical Al_{13}-Keggin polycation and calcined at the same temperature. The presence of colloidal alumina particles may partly block the porosity of the solids; in addition, thermal transformations of the alumina itself (*e.g.* AlOOH to Al_2O_3) may somehow contribute to this decrease. At any rate, the

calcined sample definitely maintains a layered structure, with a basal spacing of 17.7 Å and a fwhm index of 0.873°. We can therefore claim with reasonable confidence that pillaring has been achieved using this procedure.

Calcination at higher temperatures (600 and 700°C) gave surface areas of 138 and 125 m^2/g, respectively. These values do not show any significant trend towards further surface decrease, while in Al_{13}-Keggin-pillared clays the surface area decreases when increasing the calcination temperature in this range. In addition, the layered structure is still maintained after calcination at 600°C (*d* = 17.7 Å, fwhm = 0.935°) and even at 700°C (*d* = 17.0 Å, fwhm = 1.139°). The particularly good thermal stability suggests that the pillaring species are significantly different from those obtained after Al_{13}-Keggin intercalation.

Our results demonstrate the potential for the production of Al-intercalated and pillared clays using concentrated solutions obtained through dissolution of a commercial alumina support. The classical method of pillaring is shortened considerably and solids with a pillared structure stable up to 700°C and good textural properties have been obtained. The procedure must still be optimized to avoid contamination by residual colloidal alumina; this could probably be achieved by changing the initial solid phase constituting the source of Al ions.

The exact nature of the Al intercalating species remains to be investigated. They seem to be different from Al_{13}-Keggin polycations; the known chemistry of the intercalating solution suggests them to consist of highly-charged $[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$ polycations of the 'Breuil-Seichter' structural type. However, the effective presence of these ions in the intercalating solutions, and later in the intercalated solids, must be

Table 1. Chemical composition (wt.%) of Ballarat saponite and of the intercalated clay. The analyses of a sample intercalated with the anti-Keggin Al-polycation are given for comparison (Vicente and Lambert, 1999).

Sample	Si	Al
Ballarat saponite	22.32	2.36
$[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$ interc.	20.76	13.78
Al_{13}-Keggin intercalated clay	22.73	7.25

checked by spectroscopic techniques. ^{27}Al MQ-MAS NMR, which has shown its potential in the related Al_{13}-heidi/saponite system (d'Espinose de la Caillerie *et al.*, 2002), might be a suitable technique to accomplish this.

CONCLUSIONS

The Al-polyoxocations prepared by the dissolution of alumina when reacting with an Al chloride solution have been shown to be useful agents for the pillaring of a saponite. The pillared solids have a well-ordered layered structure with a high thermal stability, and high surface area values. However, some of the results obtained, such as the very large amount of Al incorporated in the solid during the intercalation process, suggest that new studies are necessary in order to elucidate the exact nature of the intercalating species and their interaction with the clay.

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