Chem. Mater. **1997,** *9,* 1829−1836

Pillaring of a Saponite with Aluminum−Chromium Oligomers. Characterization of the Solids Obtained

R. Toranzo, M. A. Vicente,* and M. A. Bañares-Muñoz

Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad de Salamanca, Plaza de la Merced S/N, 37008-Salamanca, Spain

Received February 26, 1997. Revised Manuscript Received May 30, 1997[⊗]

Saponite, a magnesic trioctahedral smectite, from Yunclillos (Toledo, Spain) was intercalated and pillared with aluminum−chromium solutions. Seven intercalating solutions, containing different Al^{3+}/Cr^{3+} ratios and partially hydrolyzed with OH^- solutions, were used. Al^{3+} always polymerizes to form $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ polycation, while Cr^{3+} forms the trimer $[Cr_3(OH)_4(H_2O)_9]^{5+}$, the dimer $[Cr_2(OH)_2(H_2O)_8]^{4+}$, or does not polymerize, depending on the Al^{3+}/Cr^{3+} ratio in the solution considered. When chromium oligomers were used as the intercalating polycations, the pillared solid obtained had a basal spacing of 19 Å and was not thermally stable at temperatures higher than 200 °C. When aluminum Al_{13} oligomer was used, pillared compounds with a basal spacing of 18 Å and thermal stability up to 600 °C were obtained. The addition of aluminum to the chromium intercalating solutions improved the thermal stability of chromium pillared solids.

Introduction

Pillared clays are obtained by calcination of the intercalated compounds prepared by exchange of the interlayer cations of layered clays with bulk inorganic oligomers. These oligomers are obtained by partial hydrolysis of multivalent cations, such as Al^{3+}, Cr^{3+}, Ti^{4+}, Zr^{4+}, Ga^{3+}, Si^{4+}, Fe^{3+}, etc.[1−16] The pillaring process improves the surface area, the porosity, and the thermal stability of the clays, giving the solids obtained important catalytic applications, especially for the cracking of heavy oil fractions.[17−20] In recent years, these solids have been tested as catalysts in "fine chemistry" and as adsorbents.[21−42]

Montmorillonite is the smectite normally used in pillaring studies. Other layered clays, such as saponite, beidellite, hectorite, and even vermiculite, have also

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* To whom correspondence should be addressed. FAX: +34-23-29 45 14. E-mail: mavicente@gugu.usal.es.

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1997.

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S0897-4756(97)00117-8 CCC: $14.00

been used. $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, usually designated as Keggin Al_{13} polycation, is the metallic oligomer most widely used for these studies. In some papers, the use of other metallic polycations is also reported. In the case of chromium, the partial hydrolysis of Cr^{3+} solutions leads to the formation of polycations containing 2, 3, 4, 5, or 6 metallic atoms. Pillaring of montmorillonite with chromium polycations has been reported by different authors.[1−3,15,28,32,34,35,40−42] Chromium-pillared montmorillonites are thermally much less stable than the analogous aluminum-pillared solids. The pillaring of saponite with $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ oligomer has been recently studied, but to our knowledge the pillaring of this clay with chromium polycations has not been reported.

Saponite is a tetrahedrally charged trioctahedral smectite, originating as a product of the hydrothermal alteration and weathering of basalts and ultramafic rocks. Mg(II) is its octahedral cation, six Mg(II) occupying the octahedral sheet of the clay in its ideal unit-cell structure. Variable amounts of other cations, especially Al(III) and Fe(II,III), partially replace Mg(II) in natural samples.[43] The Yunclillos saponite deposit is situated in the Madrid Basin, provinces of Madrid and Toledo, in the center of Spain. This basin is very rich in Mg silicate deposits, sepiolite being the most important mineral. The presence of magnesic smectitic materials (saponite and stevensite) in this basin was first reported about 20 years ago, but the first detailed study of a bentonitic deposit was carried out some years later.[44] The Yunclillos saponitic deposit has been subsequently studied; this mineral and its acid activation have recently been described.[45]

The physicochemical properties of pillared saponites have been studied in recent years.[4−6,9−13,27,39] Synthetic saponites have been used for studying the pillaring mechanism, especially by IR and solid-state NMR techniques.[5,11−13] The catalytic ability of pillared saponites has been tested in cracking[23,27] and in other reactions.[22,39] Their capacity for the retaining of metals from solution has also been investigated.[11]

Chromia-pillared montmorillonites have been widely used as catalysts; the pillaring phase incorporated to the clay has itself remarkable catalytic activity. Thus, pillared montmorillonites have been shown to be active in reactions such as tiophene hydrodesulfuration,[28,34] 2-propanol decomposition,[28,35] isomerization and disproportionation of *o*-xylene,[32] dehydrogenation of cyclohexane,[40] and decane cracking.[40−42] The present aim of our work is the preparation of chromium-containing saponites able to be used as oxidation catalysts. Chromium-pillared clays are thermally much less stable than the analogous aluminum-pillared solids, the collapse of their structure provoking a decrease in the surface area and in the accessible porosity. For this reason, in the present paper we have used Cr−Al mixed pillaring solutions in an attempt to improve the thermal stability of the Cr-solids and to obtain solids with high surface area and high porosity. Yunclillos saponite has been pillared with Al−Cr polycations and the solids obtained have been characterized by chemical analyses, X-ray diffraction, thermal analyses, FT-IR spectroscopy, diffuse reflectance spectroscopy, and nitrogen adsorption−desorption isotherms.

Table 1. Amounts of $AlCl_3·6H_2O$ and $Cr(NO_3)_3·9H_2O$ Used for the Preparation of the Different Intercalating Solutions

solution stoichiometry	$AlCl_3·6H_2O$ (g)	$Cr(NO_3)_3·9H_2O$ (g)
$Al_{1.0}$	9.8656	
$Al_{0.9}Cr_{0.1}$	8.6922	1.6000
$Al_{0.8}Cr_{0.2}$	7.7248	3.2000
$Al_{0.5}Cr_{0.5}$	4.8290	8.0000
$Al_{0.2}Cr_{0.8}$	1.9300	12.8000
$Al_{0.1}Cr_{0.9}$	0.9658	14.4000
$Cr_{1.0}$		16.0000

Experimental Section

Preparation of Samples. The starting material used in this work is a natural saponite from the Yunclillos deposit (province of Toledo, Spain), supplied by TOLSA, S.A. The ≤2 μm fraction of the clay was obtained by careful aqueous decantation of the raw material. The chemical weight percent composition of this clay is SiO_2, 49.45; Al_2O_3, 4.72; Fe_2O_3, 1.29; MgO, 24.34; TiO_2, 0.20; MnO, 0.03; CaO, 0.78; Na_2O, 0.07; K_2O, 0.44; and loss by ignition, 18.31 wt %. X-ray diffraction shows that this fraction is impurified with small amounts of sepiolite and quartz. Considering these impurities, the structural formula of saponite, on the basis of 22 oxygen atoms, was found to be $(Si_{7.42}Al_{0.58})O_{20}$ $(Mg_{5.16}Fe_{0.14}Al_{0.26}Mn_{0.004}Ti_{0.02})(OH)_4$ $[Mg_{0.24}Ca_{0.124}Na_{0.020}K_{0.084}]$. Its cation-exchange capacity (CEC) was 1.15 mequiv/g.

Yunclillos saponite was intercalated with aluminum, chromium, and aluminum−chromium polycation solutions. Each solution has different Al^{3+}/Cr^{3+} ratios. Considering the relative amount of these cations, solutions of stoichiometries $Al_{1.0}$, $Al_{0.9}Cr_{0.1}$, $Al_{0.8}Cr_{0.2}$, $Al_{0.5}Cr_{0.5}$, $Al_{0.2}Cr_{0.8}$, $Al_{0.1}Cr_{0.9}$, and $Cr_{1.0}$ have been prepared.

In the $Al_{1.0}$ series, the aluminum polycation was prepared by addition of aqueous NaOH to a solution of $AlCl_3·6H_2O$, with a relation $OH^-/Al^{3+} = 2.2$. Pillaring solutions with stoichiometries $Al_{0.9}Cr_{0.1}$ and $Al_{0.8}Cr_{0.2}$ were prepared by hydrolysis of mixtures of $AlCl_3·6H_2O$ and $Cr(NO_3)_3·9H_2O$. The amounts of each salt added are given in Table 1. The volume of the pillaring solution was, in all cases, 600 mL. The solutions thus obtained were slowly added over suspensions of 8 g of saponite in 733 mL of water and maintained under stirring for 24 h. Previously, saponite had been in suspension for 16 h. The $(Al^{3+} + Cr^{3+})$ concentration in the final suspensions was always 0.03 M, and the $(Al^{3+} + Cr^{3+})$/clay ratio was 5.0 mmol/g. The suspensions were then centrifuged, introduced into dialysis bags, and washed by dialysis until chloride and nitrate anions were absent. At this moment, the samples (suspensions of about 50 mL) were centrifuged and the resulting solids dried at 50 °C, giving the intercalated compounds. Their calcination at 500 and 600 °C for 4 h, with a heating rate of 1 °C/min from room temperature up to the calcination temperatures, gave the corresponding pillared compounds.

In the $Cr_{1.0}$ series, the Cr polycation was prepared by hydrolysis of $Cr(NO_3)_3·9H_2O$ with a NaOH solution, with a relation $OH^-/Cr^{3+} = 2.0$, and by aging the solution for 10 days, the protocol used by Brindley and Yamanaka.[1] Pillaring solutions with stoichiometries $Al_{0.1}Cr_{0.9}$ and $Al_{0.2}Cr_{0.8}$ were prepared by hydrolysis of solutions containing the correspond-

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ing amounts of $AlCl_3{\cdot}6H_2O$ and $Cr(NO_3)_3{\cdot}9H_2O$. The amounts of each salt in each solution are indicated in Table 1. Intercalated and pillared samples were prepared by following the same protocol described in the Al series, with the difference that pillared samples were obtained after calcination at 200 and 300 °C.

Finally, the pillaring solution with stoichiometry $Al_{0.5}Cr_{0.5}$ was prepared by hydrolysis of a mixture of $AlCl_3{\cdot}6H_2O$ and $Cr(NO_3)_3{\cdot}9H_2O$ with NaOH, using a relation $OH^-/(Al^{3+} + Cr^{3+}) = 2.1$. Saponite was intercalated and pillared at 200, 300, 400, and 500 °C following the procedure described above.

Techniques. Elemental analyses of the solids were carried out by Activation Laboratories Ltd., Ancaster, Ontario, Canada, using inductively coupled plasma spectroscopy (ICPS) and atomic absorption spectroscopy (AAS).

Intercalating solutions were studied by visible spectroscopy using a Hewlett-Packard HP 8452A spectrophotometer. Diffuse reflectance spectra of intercalated and pillared solids were recorded on a Shimadzu UV-240 spectrophotometer, using 5 nm slits and MgO as reference.

X-ray diffraction patterns, from both oriented films and powder solids, were obtained by using a Siemens D-500 diffractometer, at 40 kV and 30 mA (1200 W) and employing Cu Kα filtered radiation. The equipment is connected to a DACO-MP microprocessor and uses Diffract-AT software.

Thermal analyses were performed on Perkin-Elmer analyzers, TGS-2 and 1700 for gravimetric and differential thermal analyses, respectively; both were connected to a 3600 data station. All measurements were carried out at a heating rate of 10 °C/min under a flow of air of 35 mL/min. Al_2O_3 was used as reference for the DTA measurements.

FT-IR spectra were recorded in the region 4000−350 cm^{-1} on a Perkin-Elmer 1730 Fourier transform infrared spectrometer, equipped with a 3700 data station, using the KBr pellet technique.

Specific surface area and textural analyses were determined from the corresponding nitrogen adsorption−desorption isotherms at 77 K, obtained from a Micromeritics ASAP 2010 analyzer, after outgassing the samples at 110 °C for 8 h. The BET method was used to calculate the surface area values.

Results and Discussion

(a) UV−Vis Spectroscopy. $Al_{1.0}$ oligomeric solution was prepared by hydrolysis of $AlCl_3{\cdot}6H_2O$ with NaOH, a process widely studied in the literature. Under the conditions used, with final pH of 4.1, most of the aluminum is present as $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, usually designated as Keggin Al_{13} polycation, although other aluminum species may also exist.[46,47]

$Cr_{1.0}$ oligomeric solution was prepared from $Cr(NO_3)_3{\cdot}9H_2O$ and NaOH with the conditions described above. The chemistry of chromium in solution is complicated. When adding OH^- to a solution of Cr^{3+}, the dimer $[Cr_2(OH)_2(H_2O)_8]^{4+}$, the trimer $[Cr_3(OH)_4(H_2O)_9]^{5+}$, the tetramers $[Cr_4(OH)_6(H_2O)_{11}]^{6+}$ and $[Cr_4(OH)_5O(H_2O)_{10}]^{5+}$ and even a pentameric and a hexameric polycation, not studied in detail, may exist.[48−52] The solution obtained when dissolving $Cr(NO_3)_3{\cdot}9H_2O$ in water is blue in color, with two peaks in the visible spectrum at 408 and 576 nm. The addition of NaOH to this solution makes it change to green and, at the same time, the peaks in the spectrum shift to 422 and 580 nm, respectively, the ratio between their extinction coefficients being 1.48 (Figure 1, Table 2). The pH of the solution after hydrolysis is 2.55. Stünzi and Marty, in a very thorough study of the solution chemistry of Cr^{3+}, found that the position of the two d−d band maxima (ca. 420 and 580 nm) and the ratio between the extinction coefficients of these maxima (ϵ_1/ϵ_2) provides information about the polymerization of chromium species. These authors obtained values of 408 and 575 nm ($\epsilon_1/\epsilon_2 = 1.17$) for the monomeric form, 417 and 582 nm ($\epsilon_1/\epsilon_2 = 1.18$) for the dimeric cation, 425 and 584 nm ($\epsilon_1/\epsilon_2 = 1.60$) for the trimer, 426 and 580 nm ($\epsilon_1/\epsilon_2 = 1.95$) for the tetrameric polycations, and 426 and 585 nm ($\epsilon_1/\epsilon_2 = 1.5−1.56$) for the hexameric oligomer.[50] Comparing these data, $Cr_{1.0}$ solution may be mainly formed by the trimer polycations.

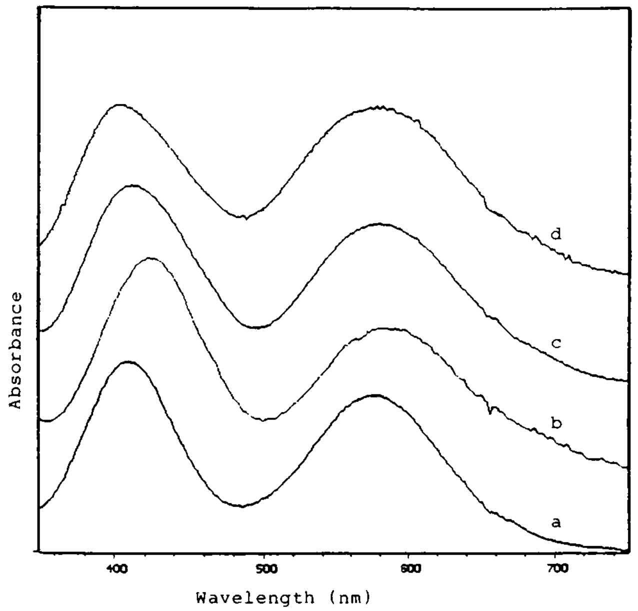

Figure 1. Visible spectra of $Cr(NO_3)_3{\cdot}9H_2O$ (a) and Cr-intercalating solutions: $Cr_{1.0}$ (b), $Cr_{0.5}Al_{0.5}$ (c), and $Al_{0.9}Cr_{0.1}$ (d).

Table 2. Wavelength of Maximum Absorption in the Visible Spectra and Ratio between the Two Peaks Extinction Coefficients of Chromium Nitrate and the Different Cr-Intercalating Solutions

solution	λ_1 (nm)	λ_2 (nm)	ϵ_1/ϵ_2[a]
$Cr(NO_3)_3{\cdot}9H_2O$	408	576	1.17
$Al_{0.9}Cr_{0.1}$	406	572	1.16
$Al_{0.8}Cr_{0.2}$	406	578	1.17
$Al_{0.5}Cr_{0.5}$	416	580	1.27
$Al_{0.2}Cr_{0.8}$	424	586	1.46
$Al_{0.1}Cr_{0.9}$	422	582	1.46
$Cr_{1.0}$	422	580	1.48

[a] See notation in the text.

In similar experiments, Brindley and Yamanaka obtained absorption bands at 425 and 587 nm in their intercalating solution, suggesting that it can be composed of the dimer $[Cr_2(OH)_2(H_2O)_8]^{4+}$, but without giving conclusive data.[1] Volzone has described the change in color from blue to green, obtaining peaks at 424 and 585 nm in the visible spectra, but she has not discussed in detail the composition of this solution.[15]

Aluminum and chromium species coexist in the solutions of stoichiometries $Al_{0.9}Cr_{0.1}$, $Al_{0.8}Cr_{0.2}$, $Al_{0.5}Cr_{0.5}$, $Al_{0.2}Cr_{0.8}$, and $Al_{0.1}Cr_{0.9}$. Their visible spectra are given in Figure 1, and the positions of the bands in these spectra are summarized in Table 2. The positions of

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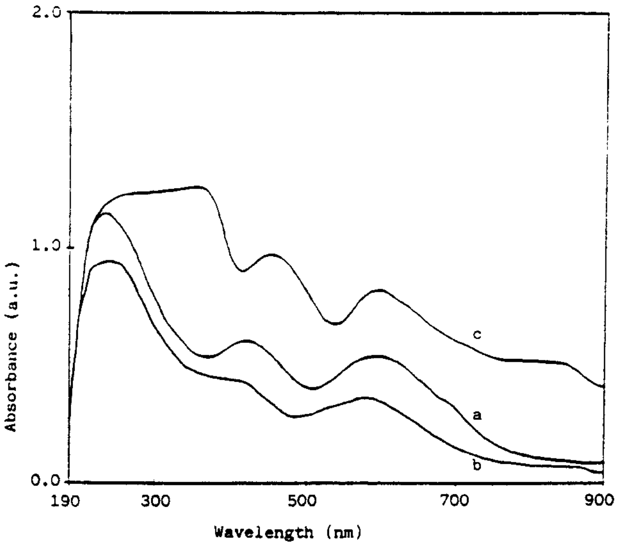

Figure 2. DRS spectra of the intercalated solids of $Cr_{1.0}$ (a) and $Al_{0.5}Cr_{0.5}$ (b) series and of the solid of $Cr_{1.0}$ series calcined at 500 °C (c).

the bands varies depending on the stoichiometry of the solution. The comparison of the data from these spectra with those reported by Stünzi and Marty indicates that chromium mainly forms the trimer $[Cr_3(OH)_4(H_2O)_9]^{5+}$ in the solutions $Al_{0.2}Cr_{0.8}$ and $Al_{0.1}Cr_{0.9}$, the trimer and the dimer $[Cr_2(OH)_2(H_2O)_8]^{4+}$ in the solution $Al_{0.5}Cr_{0.5}$ and does not polymerize in the solutions of stoichiometries $Al_{0.9}Cr_{0.1}$ and $Al_{0.8}Cr_{0.2}$. Considering the pH of these solutions, about 4.0, a mixture of $[Cr(H_2O)_6]^{3+}$ and $[Cr(OH)(H_2O)_5]^{2+}$ may coexist in these solutions.

Diffuse reflectance spectra (DRS) of the intercalated solids agree with the data presented above (Figure 2). Bands at about 408 and 575 nm are obtained for the $Al_{0.9}Cr_{0.1}$ and $Al_{0.8}Cr_{0.2}$ series, indicating that Cr(III) cations do not polymerize. These bands, designated as ν_1 and ν_2, are ascribed to the ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ spin-allowed transitions of Cr^{3+} cations, respectively. These bands appear at lower energy, about 420 and 585 nm for $Al_{0.5}Cr_{0.5}$, $Al_{0.2}Cr_{0.8}$, $Al_{0.1}Cr_{0.9}$, and $Cr_{1.0}$ intercalated solids, thus indicating the different polymerization of chromium species,[42] as observed in the intercalating solutions. Moreover, bands at about 240 nm (ν_3, ascribed to the spin-allowed ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transition) and at 690 nm (ν_4, ascribed to the spin-forbidden ${}^4A_{2g}(F) \rightarrow {}^2E_g$ transition usually called "ruby line") are observed in the spectra of all the intercalated solids. In the pillared solids, ν_1 and ν_2 bands shift to higher wavelengths, to the positions characteristic of chromium oxide, while the ν_3 band is masked by a very strong charge transference band at 230–240 nm and the ruby line does not change.

The different polymerization degree of chromium depending on the Al^{3+}/Cr^{3+} ratio may be explained by the acid properties of both cations. The cationic radius of Al^{3+} (0.535 Å) is smaller than that of Cr^{3+} (0.615 Å), hence Al^{3+} is more acidic than Cr^{3+}, having a higher tendency to form hydroxobridged polynuclear species and easier forming polymeric cations.[53] Moreover, the formation of Al_{13} polycation involves a large amount of OH^- groups (2.46 OH^- groups/aluminum atom), while the formation of chromium polymeric cations involves lower amounts of hydroxyl groups (1.0 and 1.33 OH^- per chromium atom for the dimer and the trimer, respectively). When adding OH^- to a solution containing both Al^{3+} and Cr^{3+} cations, Al^{3+} first polymerizes, and only when the polymerization of this cation is completed does the polymerization of Cr^{3+} begin. In solutions of stoichiometries $Al_{0.9}Cr_{0.1}$ and $Al_{0.8}Cr_{0.2}$, the large amount of Al^{3+} in the solutions makes it consume all the hydroxyl groups, and Cr^{3+} cannot polymerize. In the $Al_{0.5}Cr_{0.5}$ solution, the relative amount of Al^{3+} is lower; when the polymerization of this cation finishes, the amount of OH^- groups is sufficient to permit the dimerization of chromium but not the formation of higher polycations. In the $Al_{0.2}Cr_{0.8}$ and $Al_{0.1}Cr_{0.9}$ series, the amount of Al^{3+} is very low, and it consumes a low amount of hydroxyl groups, so that Cr^{3+} cations have sufficient OH^- for their polymerization, mainly forming the trimer polycation, just as occurs in the $Cr_{1.0}$ solution, in which there are no Al^{3+} cations.

Table 3. Basal Spacing and fwhm Index for the Intercalated and Pillared Solids

sample		d_{001} (Å)	fwhm (deg 2θ)
$Al_{1.0}$	intercalated	18.8	1.141
	pil 500 °C	18.4	1.183
	pil 600 °C	18.2	1.371
$Al_{0.9}Cr_{0.1}$	intercalated	18.7	1.266
	pil 500 °C	17.1	1.509
	pil 600 °C	16.3	1.554
$Al_{0.8}Cr_{0.2}$	intercalated	19.0	1.242
	pil 500 °C	15.3	1.536
	pil 600 °C	14.9	1.519
$Al_{0.5}Cr_{0.5}$	intercalated	19.5	1.419
	pil 200 °C	18.1	1.338
	pil 300 °C	17.2	1.358
	pil 400 °C	16.6	1.320
$Al_{0.2}Cr_{0.8}$	intercalated	19.9	1.242
	pil 200 °C	16.7	1.536
	pil 300 °C	16.6	1.519
$Al_{0.1}Cr_{0.9}$	intercalated	18.0	1.266
	pil 200 °C	16.9	1.509
	pil 300 °C	12.0	
$Cr_{1.0}$	intercalated	18.9	1.141
	pil 200 °C	16.5	1.183
	pil 300 °C	12.1	
	pil 500 °C	11.9	

(b) X-ray Diffraction. The intercalation of saponite begins during the addition of the intercalating solution to the clay suspension, and it is completed during the dialysis washing. This behavior is very similar when aluminum, chromium, and aluminum–chromium solutions are considered. Before dialysis, only some of the clay sheets are intercalated and a wide band is observed for the d_{001} reflection. This band is narrower and more intense after dialysis; almost all the sheets are now intercalated, and they are better ordered. This effect has been observed by different authors during intercalation of montmorillonite and saponite with Al_{13} polycations, and we have now observed that it also happens during the intercalation of chromium polycations.

The basal spacings of intercalated solids are given in Table 3. The fwhm index of the different intercalated samples, also given in Table 3, shows that all of them are very crystalline solids, with basal spacings between 18.0 and 19.9 Å. Considering the minimum spacing of saponite (9.8 Å), the length of the polycations in the interlayer space varies from 8.2 to 10.1 Å. The solid of series $Al_{1.0}$ has a basal spacing of 18.8 Å, which gives a depth of 9.0 Å for the polycation Al_{13}, similar to that usually reported for clays intercalated with this cation. The crystalline size of unhydrated Al_{13} cation is 5.4 Å,[54]

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(53) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984.

while its radius in water solution is 9.8 Å;[46] these are intermediate values obtained when the cation is intercalated in the interlayer space of smectites.

The basal spacing of the $Cr_{1.0}$ intercalated solid is 18.9 Å, with a depth of 9.1 Å for the interlayer cations. Volzone indicates that the dimeric chromium polycation has a depth of 4.0 Å, the trimeric one of 5.0 Å and the tetramer of 6.5 Å,[15] postulating that the intercalation with these species consists in the superposition of two oligomers. In our case, the intercalation with dimeric or trimeric polycations agrees with these bibliographic data; visible spectroscopy indicates that the intercalating solution is mainly composed of $[Cr_3(OH)_4(H_2O)_9]^{5+}$ oligomer. The basal spacings in our samples are similar to those reported by Brindley and Yamanaka,[1] Bornholdt et al.,[2] and Volzone et al.[15] with similar experiments in montmorillonite; other authors, using different experimental conditions have found larger basal spacings, up to 27 Å.[28,34,40,41]

In the series in which the intercalating solutions contain both aluminum and chromium, saponite is intercalated by different species. In the series $Al_{0.9}Cr_{0.1}$ and $Al_{0.8}Cr_{0.2}$, only Al_{13} acts as intercalating polycation; Cr^{3+} cations do not polymerize. The basal spacing of these intercalated solids, 18.7 and 19.0 Å, respectively, is consistent with the intercalation of this oligomer. In the $Al_{0.1}Cr_{0.9}$ and $Al_{0.2}Cr_{0.8}$ series, the basal spacing of intercalated solids is consistent with the intercalation of Al_{13} and $[Cr_3(OH)_4(H_2O)_9]^{5+}$ polycations, species observed by visible spectroscopy. In the $Al_{0.5}Cr_{0.5}$ series, the basal spacing, 19.5 Å, is also consistent with the intercalation of Al_{13} and $[Cr_3(OH)_4(H_2O)_9]^{5+}$, while visible spectroscopy shows that this intercalating solution is mainly composed of the dimer $[Cr_2(OH)_2(H_2O)_8]^{4+}$. Intercalation with the dimer oligomer will give a basal spacing of $9.8 + (2 \times 4.0) = 17.8$ Å, much lower than the experimental value. The dimer may be transformed into the trimer during the intercalation process, a transformation favored by the alkaline pH of the saponite suspension, 8.0, which may give the OH^- groups that are necessary for this transformation.

Intercalated samples from the $Al_{1.0}$, $Al_{0.9}Cr_{0.1}$, and $Al_{0.8}Cr_{0.2}$ series were calcined at 500 and 600 °C, to form pillared solids. It is well-known that Al-pillared montmorillonites and saponites have this thermal stability. Chevalier et al. have even reported an Al-pillared saponite whose thermal stability reaches 750 °C.[10] In the $Al_{1.0}$ series, the intercalated compound has a basal spacing of 18.8 Å, which decreases to 18.4 Å when pillaring by calcination at 500 °C. The layered pillared structure is maintained after calcining at 600 °C, the basal spacing of this solid being 18.2 Å. Cr-pillared clays have low thermal stability, so the addition of Cr^{3+} can be expected to make the thermal stability of Al-pillared saponite decrease. The addition of small amounts of Cr^{3+} to the Al oligomeric solutions results in a decrease in the basal spacings of the intercalated and pillared solids. In the series $Al_{0.9}Cr_{0.1}$, basal spacings of 18.7, 17.1, and 16.3 Å are observed for solids intercalated and pillared at 500 and 600 °C, respectively. In the $Al_{0.8}Cr_{0.2}$ series, basal spacings of 19.0, 15.3, and 14.9 Å are observed for these solids. The fwhm index increases both when increasing the calcination temperature and when increasing the amount of chromium in the intercalating solutions, showing loss of crystallinity in both cases. So, the addition of small amounts of Cr^{3+} (20% in number of moles) to the intercalating solutions containing Al^{3+} provokes a decrease in the basal spacing of the pillared solids, but the thermal stability of the solids obtained is not greatly affected; they maintain the layered structure up to 600 °C (Figure 3).

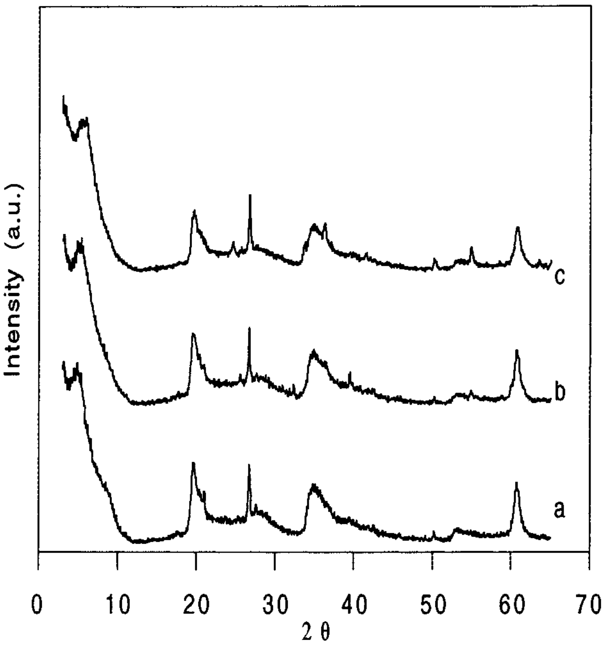

Figure 3. X-ray diffraction patterns of solids of $Al_{1.0}$ (a), $Al_{0.9}Cr_{0.1}$ (b), and $Al_{0.8}Cr_{0.2}$ (c) series calcined at 600 °C.

When saponite is treated with $Cr_{1.0}$ solution, the intercalated solid has a basal spacing of 18.9 Å, which decreases to 16.5 Å when calcined at 200 °C, this peak disappearing at higher temperature. Peaks at 12.1 and 11.9 Å, corresponding to nonpillared dehydrated saponite, are obtained after calcination at 300 and 500 °C, respectively. Solids in $Al_{0.1}Cr_{0.9}$ series have a very similar behavior. The intercalated solid has a basal spacing of 18.0 Å, which decreases to 16.9 Å when calcined to 200 °C and to 12.0 Å, nonpillared saponite, when calcined at 300 °C. These results indicate that Cr-pillared saponite has a thermal stability very similar to that reported for Cr-pillared montmorillonite, about 200 °C.

The thermal stability of pillared solids increases in the $Al_{0.2}Cr_{0.8}$ and $Al_{0.5}Cr_{0.5}$ series. In the first of them, the basal spacing of the intercalated solid is 19.9 Å, which decreases to 16.7 Å when calcined at 200 °C and to 16.6 Å when calcined at 300 °C, the XRD pattern of this latter solid clearly indicating that it maintains the layered pillared structure. The behavior in the $Al_{0.5}Cr_{0.5}$ series is very similar: the basal spacing of the intercalated solid, 19.5 Å, decreases to 18.1, 17.2, and 16.6 Å when calcined at 200, 300, and 400 °C, respectively, and collapses when calcined at 500 °C. The thermal stability of the pillared solids runs parallel to the content of aluminum in the intercalating solution, the higher the content in aluminum, the higher the thermal stability of the solid (Figure 4). The addition of 20% of Al^{3+} (in number of moles) to a solution of Cr^{3+} increases the thermal stability of the final pillared solid up to 300 °C, and if the content of Al^{3+} in the intercalating solution is 50%, the thermal stability of the final solid is 400 °C. The increase in the number of Al_{13} units in these solids when the amount of Al^{3+} in the interca-

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(54) Johanson, G. *Acta Chem. Scand.* **1960**, *14*, 769.

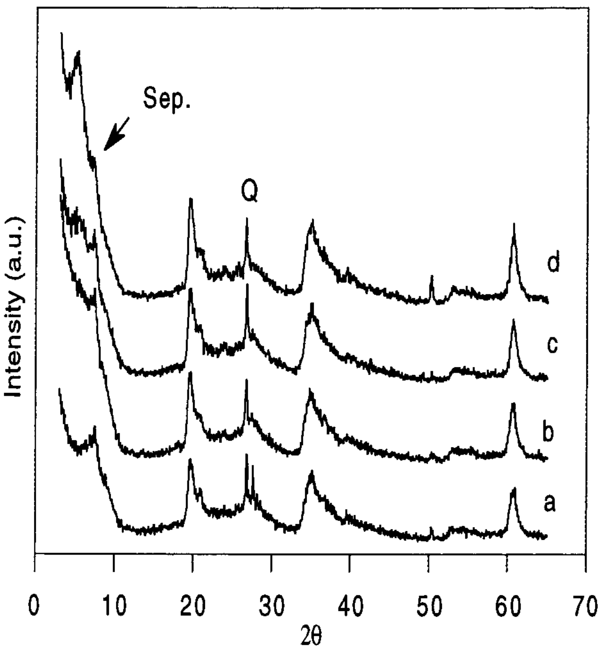

Figure 4. X-ray diffraction patterns of solids of $Cr_{1.0}$ (a), $Al_{0.1}Cr_{0.9}$ (b), $Al_{0.2}Cr_{0.8}$ (c), and $Al_{0.5}Cr_{0.5}$ (d) series calcined at 300 °C. Positions of sepiolite (sep) and quartz (Q) reflection peaks are indicated.

lating solution is increased is probably responsible for this stability.

On the other hand, if the solids of the $Al_{0.5}Cr_{0.5}$ series are compared with those of series $Al_{1.0}$, $Al_{0.9}Cr_{0.1}$, and $Al_{0.8}Cr_{0.2}$, it can be seen that the addition of chromium impairs the thermal behavior of Al-pillared solids. At the same time, the basal spacing of the pillared solids decreases when the amount of chromium in the intercalating solution is increased. Chromium polycation structure collapses at this temperature, and as the number of Al_{13} units decreases, it is more difficult for these units to keep the clay sheets separated and pillared.

The calcination at high temperatures of chromium-pillared smectites produces chromium oxides. For years, it was considered that Cr_2O_3 is the only oxide formed. In a recent study using EXAFS technique, Bornholdt et al.[2] have observed the presence of both Cr(III) and Cr(VI) species, giving the mixed oxide Cr_5O_{12}. These authors indicate that Cr(VI) may be formed by the oxidation of Cr(III) initial species. However, Drljaca et al. did not observe the presence of Cr(VI) species.[3] After careful calcination of chromium-intercalated montmorillonite in air and nitrogen atmospheres, these authors observed Cr_2O_3 as the only chromium oxide, discarding the presence of Cr_5O_{12} and also of CrO_3. Carrado et al.,[42] using the EPR technique, found the presence of Cr(V) and Cr(VI) species, while Sychev et al., using the XPS technique, reported the presence of Cr_2O_3, not finding evidence for the presence of Cr(VI) or metallic chromium.[34]

In the present study, we calcined the intercalated solid of the $Cr_{1.0}$ series at 500 °C and studied the obtained solid by X-ray diffraction. The comparison of its XRD pattern with JCPDS files shows that chromium crystallizes as Cr_2O_3 eskolaite, JCPDS File 38-1479.[55] Neither CrO_3 nor Cr_5O_{12} could be detected.

(c) Chemical Analyses. Important amounts of aluminum and chromium were fixed during the intercalation process, substituting the exchange cations of the sample. In the case of aluminum, a maximum value of about 9.5% of Al_2O_3 was fixed. The amount fixed was very similar in the series $Al_{1.0}$, $Al_{0.9}Cr_{0.1}$, and $Al_{0.8}Cr_{0.2}$ and decreased in the other series, in which the amount of aluminum in the intercalating solution was lower. In the case of chromium, the amount fixed by the intercalated solids increased parallel to the content of this element in the intercalating solution, reaching a maximum value of 13.22% of Cr_2O_3 in the $Cr_{1.0}$ series.

Table 4. Number of $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ and $[Cr_3(OH)_4(H_2O)_9]^{5+}$ Pillars per Saponite Unit Cell in the Different Solids

sample	$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$	$[Cr_3(OH)_4(H_2O)_9]^{5+}$
$Al_{1.0}$	0.1356	
$Al_{0.9}Cr_{0.1}$	0.1392	
$Al_{0.8}Cr_{0.2}$	0.1314	
$Al_{0.5}Cr_{0.5}$	0.0618	0.408
$Al_{0.2}Cr_{0.8}$	0.0260	0.492
$Al_{0.1}Cr_{0.9}$	0.0166	0.478
$Cr_{1.0}$		0.548

The amounts of aluminum and chromium fixed by the different solids may be expressed as the number of pillars per unit cell; the results are given in Table 4. Pillars of Al_{13} and $[Cr_3(OH)_4(H_2O)_9]^{5+}$ were considered, and the values given were calculated with the supposition that all aluminum and chromium polymerize forming these oligomers. In the case of the solids of the series $Al_{0.9}Cr_{0.1}$ and $Al_{0.8}Cr_{0.2}$, the amount of chromium is not expressed as a number of pillars, because all the data indicate that chromium does not polymerize in these series. The content of chromium in the solids may be due to its adsorption on the surface of the saponite and of the Al_{13} pillars.

The number of Al_{13} pillars increased with the content of this element in the intercalating solutions, up to values of about 0.13−0.14 pillars/saponite unit cell, almost constant in the series $Al_{1.0}$, $Al_{0.9}Cr_{0.1}$, and $Al_{0.8}Cr_{0.2}$, and which correspond to 1 pillar/7.2−7.6 saponite unit cells. This is a high pillar density, considering that Bergaoui et al.,[12,13] studying the intercalation with Al_{13} polycations of a large series of variable-charge synthetic saponites, calculated that the maximum density permitted by steric constraints is 1 pillar/5.9 saponite unit cells.

The amount of $[Cr_3(OH)_4(H_2O)_9]^{5+}$ pillars in the solids increased with the content of chromium in the intercalating solution, reaching a maximum value of 0.548 pillars/unit cell in the series $Cr_{1.0}$. That is, there is 1 $[Cr_3(OH)_4(H_2O)_9]^{5+}$ pillar for each 1.8 saponite unit cells, a very high pillar density. Brindley and Yamanaka[1] referred to a maximum fixation of 13.8% of Cr_2O_3 when pillaring montmorillonite with chromium polycations. Volzone et al. found a density of 1.24 $[Cr(OH)_{3-q}]^{q+}$ pillars per montmorillonite unit cell.[15] Pinnavaia et al.,[40,41] studying the pillaring of montmorillonite and using a modified method for the synthesis of the chromium polycations, found higher values of Cr fixed, with a maximum pillar density of 3.53 $[Cr(OH)_{3-q}]^{q+}$ pillars/unit cell. The smaller size and the lower polymerization degree of $[Cr_3(OH)_4(H_2O)_9]^{5+}$ polycation, compared to that of Al_{13} oligomer, justify the higher density of Cr-pillars in the interlayer space of saponite. The only data found regarding the size of these oligomers

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(55) Joint Committee on Powder Diffraction Standards, JCPDS File, International Center for Diffraction Data, Philadelphia, 1977.

(56) Mackenzie, R. C. Simple phyllosilicates based on gibbsite- and brucite-like sheets. In *Differential Thermal Analysis*; Mackenzie, R. C., Ed.; Academic Press: London, 1970.

are those reported by Volzone,[15] referring to the depth of these polycations.

(d) Thermal Analyses. Thermogravimetric and differential thermal analyses of the different intercalated solids were carried out, the curves obtained being compared to those of the raw saponite. Natural Yunclillos saponite has an initial weight loss due to interlayer water departure, with an associate endothermal effect centered at 145 °C. Subsequently, there is a very gentle weight loss between 200 and 800 °C and the final dehydroxylation and phase change (830−850 °C) to form $MgSiO_3$, enstatite.[45,46] The weight loss between 30 and 950 °C is about 20% of the weight of the solid.

Thermal curves of $Al_{1.0}$-intercalated saponite were very similar to that of natural saponite. The thermal effects attributable to the dehydration and dehydroxylation of Al_{13} oligomers did not appear as very important effects or else appeared masked by the effects corresponding to saponite, as occurs in the region of 70−150 °C. After calcination at high temperature, enstatite and alumina peaks were observed. The total weight loss was of 22% of the weight of the solid.

The thermal curves of $Cr_{1.0}$ intercalated saponite showed two exothermal effects at 320 and 530 °C and an endothermal effect at 385 °C, effects not observed in natural saponite and that may correspond to thermal processes in chromium oligomers. Between 825 and 850 °C, the dehydroxylation of the saponite and formation of enstatite were observed. The total weight loss was 20% of the initial weight of the solid. Volzone reported an exothermal effect at 420 °C and an endothermal one at 650 °C but did not assign them.[15] Krajcovic et al. observed an endothermal effect at 642 °C as the only thermal effect during calcination of chromium-intercalated montmorillonite, indicating that this effect corresponds to the dehydroxylation of the clay, not of the chromium polycations.[32] As observed, different thermal curves are reported in the literature, due to the preparation conditions employed, which makes the content in chromium and the chromium species in the clay interlayer different depending on the experimental procedure.

In the series containing both aluminum and chromium, the thermal behavior was intermediate between the two described before. The intensity of the thermal effects depends on the amount of each element in the intercalating solution.

(e) FT-IR Spectroscopy. The FT-IR spectra of the intercalated and pillared solids were very similar to those of the raw saponite. Only small differences were observed in the low wavenumber region. The band that appeared at 1011 cm^{-1} in natural saponite, characteristic of tetrahedral sheet Si−O−Si vibrations, remained at the same wavenumber in the intercalated solids, but shifted to 1024 cm^{-1} in the pillared samples. Similar behavior was observed for the bands corresponding to Mg−OH and Mg−O bending bands. The first appeared at 659 cm^{-1} in the natural saponite and intercalated samples and shifted to 671 cm^{-1} when calcined at increasing temperatures; the second appeared at 448 cm^{-1} in natural saponite and shifted to 460 and 466 cm^{-1} in intercalated and pillared solids, respectively. At the same time, a new band centered at 623 cm^{-1} was observed in the solid of $Cr_{1.0}$ series calcined at 500 °C, probably due to Cr−OH or Cr−O vibrations. All these changes indicate an interaction between the pillars and the clay layers during the intercalation and pillaring process.

Table 5. BET Surface Area of Raw Saponite and Intercalated and Pillared Solids

sample	BET surface area (m^2/g)			
raw saponite	161			
	intercalated	pil 500 °C	pil 600 °C	
$Al_{1.0}$	304	236	172	
$Al_{0.9}Cr_{0.1}$	231	164	157	
$Al_{0.8}Cr_{0.2}$	224	177	171	
	intercalated	pil 200 °C	pil 300 °C	pil 500 °C
$Al_{0.5}Cr_{0.5}$	369	332	301	181
$Al_{0.2}Cr_{0.8}$	310	314	180	
$Al_{0.1}Cr_{0.9}$	242	237	165	
$Cr_{1.0}$	239	222	155	131

(f) Texture Properties. Nitrogen adsorption−desorption isotherms of natural saponite and intercalated and pillared solids all correspond to type II of IUPAC classification, with a type H3 hysteresis loop in the same classification,[57] behavior characteristic of samples with slit-shaped pores and that can be expected considering the morphology of the clay particles. The specific surface area of intercalated and pillared solids was calculated by application of the BET method to these isotherms; the results obtained are summarized in Table 5, and the tendency of the surface area is illustrated in Figure 5.

The raw saponite had a large surface area, 161 m^2/g, larger than that usually reported for natural saponites, probably due to the sedimentary origin of the Yunclillos deposit. $Al_{1.0}$-intercalated saponite had a surface area of 304 m^2/g, which decreased to 236 m^2/g when calcined at 500 °C and to 172 m^2/g when calcined at 600 °C. The addition of Cr^{3+} to the intercalating solution resulted in lower values of surface area, in both the intercalated and pillared compounds. Thus, intercalated solids of series $Al_{0.9}Cr_{0.1}$ and $Al_{0.8}Cr_{0.2}$ had surface areas of 231 and 224 m^2/g, respectively. In both series, calcination at 500 or 600 °C made the surface area decrease to minimum values of 160−180 m^2/g.

$Cr_{1.0}$-intercalated saponite had a surface area of 239 m^2/g. When calcined at 200 °C, the surface area decreased to 222 m^2/g. At higher temperature, the layered pillared structure was destroyed and the surface area decreased greatly, 155 m^2/g when calcined at 300 °C and 131 m^2/g when calcined at 500 °C. When Al^{3+} was added during the preparation of the oligomers, the surface area of intercalated solids increased. Thus, the surface areas of intercalated solids of series $Al_{0.1}Cr_{0.9}$ and $Al_{0.2}Cr_{0.8}$ are 242 and 310 m^2/g, and the surface areas of solids in the same series calcined at 200 °C are 237 and 314 m^2/g, respectively. Calcination at 300 °C makes the surface area of the solids in all series have a minimum value of 160−180 m^2/g.

In the series $Al_{0.5}Cr_{0.5}$, the surface area of intercalated solid is very high, 369 m^2/g, decreasing to 332 m^2/g when calcined at 200 °C, to 301 m^2/g when calcined at 300 °C, and to 181 m^2/g when calcined at 500 °C. Comparing the above series with the series $Cr_{1.0}$, $Al_{0.1}Cr_{0.9}$, and $Al_{0.2}Cr_{0.8}$, the tendency to an increase in the surface area when increasing the amount of Al^{3+} in the intercalating solution is maintained. On the other hand, if the solids in $Al_{0.5}Cr_{0.5}$ series are compared to those in series $Al_{1.0}$, $Al_{0.9}Cr_{0.1}$, and $Al_{0.8}Cr_{0.2}$, it can be observed that the

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(57) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemienewska, T. *Pure Appl. Chem.* **1985**, *57*, 603.

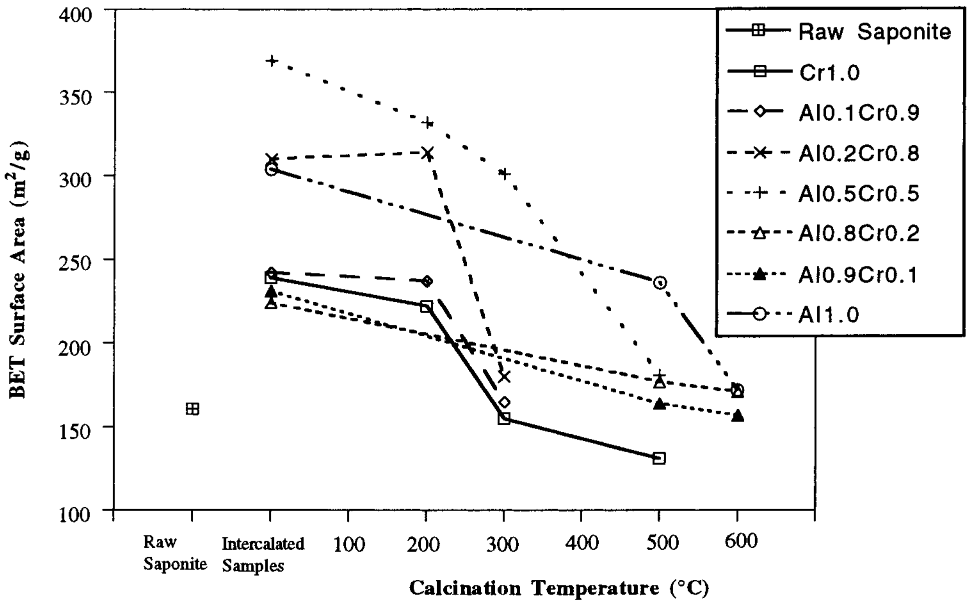

Figure 5. Effect of the calcination temperature, for each Al−Cr ratio, on the surface area of the solids.

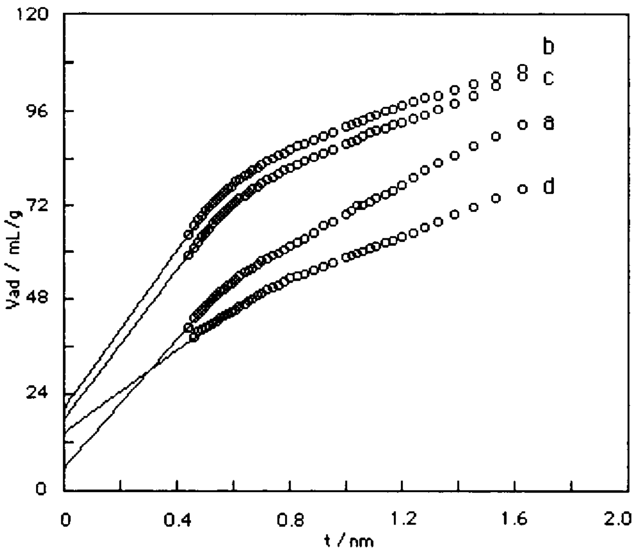

Figure 6. *t*-plot of raw saponite (a) and solids intercalated (b) and pillared at 200 (c) and 300 °C (d) in series $Cr_{1.0}$.

tendency to decrease in the surface area when increasing the content of Cr^{3+} in the intercalating solution is broken. That is, the surface area of the solids in $Al_{0.5}$-$Cr_{0.5}$ series is more conditioned by their content in aluminum than by their content in chromium, which indicates, in accordance with XRD data, that the Al_{13} pillars in these solids are able to maintain the clay sheets separated even when chromium oligomers collapse.

These surface area values are similar to those reported in the literature for intercalated and pillared samples. Numerous references can be found in which the surface areas of aluminum-intercalated and -pillared montmorillonites and saponites are given. Regarding chromium intercalated and pillared samples, Brindley and Yamanaka[1] reported a maximum value of 280 m²/g, Volzone et al.[15] of 175 m²/g, Krajcovic et al.[32] of 268 m²/g, and Sychev et al.[28,34] of 375 m²/g. Only Pinnavaia et al.[40,41] have reported values significantly higher, up to 433 m²/g. All of these values correspond to intercalated and pillared montmorillonites; no references have been found on the chromium pillaring of saponites.

Intercalation and pillaring treatments create a microporous system in the solids, with pore size below 10 Å. Raw saponite is an almost nonmicroporous solid. The extrapolation of its *t*-plot representation[58] to the axis of the volume adsorbed is very close to zero, and the microporosity is of about 10 mL/g (STP conditions). In intercalated and pillared solids, the extrapolation of *t*-plot does not pass through zero, and values up to 55 mL/g are obtained for the microporosity, indicating the creation of a microporous structure during the treatments (Figure 6). Calcination of intercalated solids produces a decrease in the amount of adsorbed nitrogen; the *f*-plot[59] comparing intercalated and pillared solids is parallel throughout the relative pressure range, that is, calcination does not produce a very important variation in the porous structure of the solids, but only a decrease in the amount of adsorbed nitrogen.

Conclusion

Saponite was intercalated with solutions containing different Al/Cr ratios. $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ and $[Cr_3(OH)_4(H_2O)_9]^{5+}$ polycations were the major pillaring oligomers. The solids obtained fixed up to 10% of Al_2O_3 and 13% of Cr_2O_3, thus leading to a high density of alumina and chromia pillars. Solids intercalated with Al solutions have basal spacings of about 19 Å, which decrease slightly when calcining at increasing temperatures, the clay layered structure being stable up to 600 °C. Solids intercalated with Cr solutions have basal spacings of about 19 Å, that significantly decrease when calcined at 200 °C, the clay lamellar structure disappearing when calcined at 300 °C. The addition of chromium impairs the thermal behavior of Al-pillared solids, but the addition of aluminum significantly increases the thermal stability of Cr-pillared solids. The surface area of intercalated and pillared solids reaches values of about 300 m²/g, with an important microporous structure.

Acknowledgment. Financial support from the Comisión Interministerial de Ciencia y Tecnología, CICYT (MAT96-0643 Project) is gratefully acknowledged.

CM970117V

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