Synthesis of intercalated Al-hydroxy-montmorillonite

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Abstract. Montmorillonite from Durango, Mexico, of composition $(Si_{3.88}Al_{0.12})(Al_{1.41}Mg_{0.59})O_{10}(OH)_2(Ca_{0.07}Mg_{0.11}Na_{0.28}K_{0.06})$, surface area 42.07 m^2g^{-1}, d_{001} spacing 12.50 Å, and pore volume 0.002 cm^3g^{-1}, was intercalated with Al-hydroxy oligomer. The modified clay developed a surface area of 287.86 m^2g^{-1}, pore volume of 0.103 cm^3g^{-1}, and d_{001} spacing of 18.70 Å. Dehydration to 70 °C shift the d_{001} spacing to 17.29 Å; dehydroxylation started at 150 °C and by 300 °C had lost 1.92 w% and reduced the d_{001} spacing to 17.34 Å.

Keywords: Intercalated aluminum montmorillonite, clays, silicates, oligomer.

Resumen- Montmorillonita procedente de Durango, México, de composición $(Si_{3.88}Al_{0.12})(Al_{1.41}Mg_{0.59})O_{10}(OH)_2(Ca_{0.07}Mg_{0.11}Na_{0.28}K_{0.06})$, área superficial 42.07 m^2g^{-1}, espaciamiento d_{001} 12.50 Å, y volumen de poro 0.002 cm^3g^{-1}, fue intercalada con el oligómero de Al. La arcilla modificada desarrolló un área superficial de 287.86 m^2g^{-1}, volumen de poro 0.103 cm^3g^{-1}, y espaciamiento d_{001} 18.70 Å. Se deshidrata a 70 °C reduciendo el espaciamiento d_{001} a 17.29 Å; su deshidroxilación se inicia a 150 °C y a 300 °C perdió 1.92 % en peso, modificando d_{001} a 17.34 Å.

Palabras clave: Montmorillonita intercalada con aluminio, arcillas, silicatos, oligómero.

Introduction

Intercalated clays have interest as adsorbents, catalysts, and nanoporous materials in potential industrial and environmental applications [1-4]. Their applications as sorbents [2], in fluid separation [5], and in catalysis [1, 6, 7] have been studied. The intercalated Al-oxy-montmorillonites (AlO-m) prepared from Al-hydroxy-montmorillonites (AlOH-m) are strong and selective adsorbents of organic compounds [8]; they have been successfully applied to the separation of non-polar to highly polar eluents [9]. The development of thermally stable microporous and mesoporous interlayer structures continues to be an important objective in the preparation of cracking catalysts [10- 12].

Clays intercalated with oxy-ions and their uncalcined hydroxy-ions are characterized by high porosity, thermal stability, and residual exchange properties [1, 3, 13]. The intercalated clays can be synthesized by exchanging montmorillonite with polyhydroxy metal ions of distinct size and charge [14]. Their characteristics are related to the size of the ions [15]; the cations normally used are Al^{3+} [6, 7, 16], Zr^{4+} [8, 17, 18], Cr^{3+} [19], Ti^{4+} [20], Fe^{2+} [21], Si^{4+} [22], Ga^{3+} [23], rare earths [13, 24, 25], and others [26, 27]. The corresponding intercalated clays show d_{001} spacings of 18 Å and above, high surface areas of 200-300 m^2g^{-1} [22], and Brönsted and Lewis-type acidity [28]. Calcination of the hydroxy-intercalated clays to 300-500 °C develops intercalated fixed or pillared oxy-complex ion clays [6]. These hydroxy-intercalated precursors and their oxy-complexes may have specific chemical sorption, high selectivity for heavy metal cations in solutions of high salinity, and retention of the metal-intercalated complexes in a non-exchangeable form [3].

Polymers prepared from aluminous aqueous solutions are among the best known used for the synthesis of intercalated clays. The polymer, or so called Keggin structure, of formula $(AlO_4Al_{12}(OH)_{24}(H_2O_{12})^{7+}$ [16] contains twelve ^{VI}Al, one ^{IV}Al, and has a OH/Al molar ratio smaller than 2.5. It has four layers of superimposed oxygen atoms, required to expand the montmorillonite d_{001} spacing above 18 Å. The $[Al_{13}O_4(OH)_{24}(H_2O_{12})]^{7+}$ polyoxycation formed by hydrolysis of $(Al(H_2O)_6)^{3+}$ produces catalytically active pillared clays [11]. Several publications have commented on the synthesis of aluminum hydroxide polymers, hydrolysis [29], aging processes [30], mechanisms and structure rearrangements, and exchange properties of the intercalated phases [13]. Recent studies on the sorption of metals [5] and organic compounds [8, 31] by uncalcined hydroxy-intercalated precursor of aluminum have concluded that Al-hydroxy-interlayered and Al-oxy-clays are potential sorbents.

Distinct physicochemical characteristics such as cation exchange capacity, surface area, and basal spacing d_{001} depend on the nature of the 2:1 clay mineral substrate [14]. Thus, Al-OH-beidellite prepared from hydroxy-aluminum polymeric cations in solution with OH/Al ratios of 1.8 - 2.5 [6], develops a 17 Å basal spacing that persists to 500 ºC and a surface area in the range between 200 and 500 m^2g^{-1} [17]**.** Expanded smectite and vermiculite, stable to 550 ºC, may adsorb hydrocarbons [32]; several studies on intercalated Al-saponite and hectorite have been published [22, 33]. Al-hydroxy intercalated montmorillonites from various homoionic precursors namely Cs-, Ba-, Fe-, Cu-, and Ce-montmorillonite, different from Na-montmorillonite, have been used to investigate the interactions between oligomers and Al-hydroxy montmorillonite surface layers, showing dependence of the basal spacing on the thermal treatment and the cation in the precursor clay [35].

In this work we present and discuss the synthesis, ion exchange, and sorption behavior of an Al-hydroxy-montmoril-

lonite (AlOH-m). The clay used is a high-swelling montmorillonite from Durango, Mexico [34]. This study is part of a broader analysis on Mexican clay minerals.

Intercalated montmorillonite synthesis

The intercalated complexes were prepared on montmorillonite from Cuencamé, Durango, Mexico. This montmorillonite occurs in the Late Oligocene-Miocene tuffs of the Vizcarra Formation. The bentonitic tuff is about 70 % of montmorillonitic composition $(Si_{3.88}Al_{0.12})(Al_{1.41}Mg_{0.59})O_{10}(OH)_2$ $(Ca_{0.07}Mg_{0.11}Na_{0.28}K_{0.06})$, plus additional chalcedony, feldspar, quartz, sanidine, quartz, oxybiotite, glass shards, and clastic fragments that make up to 100 %. A detailed characterization has been previously reported [34].

The bulk tuff was used without any treatment to separate the montmorillonite from its associated minerals, essentially because the non-clay components were non reactive through the preparation of the clay complexes and because the surface characteristics of the clay were intended not to be altered. In any case, the non-clay components settle in the process of preparing the clay complexes [8]. The mineralogy and the characteristic basal spacing of the clays were established by X-ray diffraction using a Siemens D5000 diffractometer provided with filtered Cu Ka radiation. The aluminum oligomers and their attachment to the montmorillonite clay were identified by infrared spectroscopy studies in a Nicolet Fourier Transformation Instrument. Their thermal stability was determined using a Mettler Toledo Star System. The surface area was estimated by nitrogen adsorption and desorption on samples outgassed at 423 K and 1.33×10^{-3} Pa, submerged in liquid nitrogen at p/p_0 0.05-1.00, in a Micromeritics Gemini 2370 Surface Area Analyzer. The cation exchange capacity (CEC) was measured by the ammonium displacement technique. The aqueous leachates were analyzed by flame spectrophotometry in a Jenway PFP7 photometer.

Preparation of the oligomer

The Al-hydroxy oligomer was prepared by gradual addition of 0.2 M NaOH to 0.2 M $AlCl_3.6H_2O$, at the rate of 1 to 3 ml min^{-1} while stirring vigorously at 25 °C [6]. The resulting Al-polyhydroxy solution was kept at 25 °C for periods of 3, 7, 15, and 30 days. To accelerate the aging process of the oligomer, the solution was refluxed at 60 – 90 °C, 6 to 12 h [24]. The optimum OH/Al ratio to form the aluminum hydroxy precursor was 1.85.

Intercalating process

To intercalate the oligomer on the clay substrate, the clay was dispersed in demineralized water, settling the non-clay components and centrifuging the suspended < 2 microns fraction. The homoionic Na-montmorillonite was prepared by repeated washings with 1N NaCl until chloride free (AgNO$_3$ test).

Intercalation of the Al-hydroxy oligomer on the montmorillonite required its dropwise addition to the suspended clay at a rate of 1 ml/min while stirring vigorously at 25 °C. The newly formed intercalated clay sediment was filtered, washed to chloride-free (AgNO$_3$), air-dried at 50-60 °C, finely ground, and calcined at different temperatures.

Sorption behavior

The sorption behaviors of bulk montmorillonite and of the Al-hydroxy intercalated montmorillonite were determined by initial saturation with 1 M NaCl for 24 h at room temperature, followed by washing out the chlorides, filtration, and drying to 50 °C. Afterwards, the clays were separated in five 1 g fractions, reacted with 20, 40, 60, 80, and 100 mL of 0.01 M $CaCl_2.2H_2O$ for 6 h while constantly stirred, filtered, and the solutions analyzed for exchanged Na$^+$ by flame photometry.

Restore cation exchange capacity

The cation exchange capacity (CEC) of the Al-hydroxy intercalated montmorillonite was restored by stirring in 1M NaCl, with the pH adjusted to 10 with 1M NaOH. As the pH decreased with time, it needed adjustment with additional alkali; the pH would normally stabilize to 10 after a 30 hr period. The intercalated clay was filtered and washed to eliminate Cl$^-$, no change of pH being observed; final drying was at 80 °C during 15 h, [13].

Results and discussion

Intercalation and X-ray diffraction data

The data shown in Table 1 indicate that clay dispersions A, B, C and D reacted with the oligomer at different mass ratios. With the oligomer aged for periods from 3 to 15 days and added to the clay at distinct rates, were developed d_{001} spacings from 15.13 to 15.68 Å that indicate retention of the oligomer by the montmorillonite. When the oligomer was aged for 30 days a substantial increase of the d_{001} spacing to 17.11 Å occurs (sample *E*). However, the developed complex is thermally unstable and decomposes at about 100 °C. In test O and P the clay was reacted with refluxed oligomer prepared by refluxing at 60-90 °C during 6 h, the d_{001} spacing was 18.70 Å. Heating the *Al-hydroxy mon*tmorillonite above 100 °C (sample F) and below 300 °C (sample G), shifted the basal spacing to 17.34 Å while the diffraction peaks became shorter and broader (Fig. 1), presumably due to the transformation of the aluminum-hydroxy-montmorillonite to stable oxy-aluminum-montmorillonite. The intercalated montmorillonite is stable to 700ºC (sample H) for short periods of time (usually 5 h); at this temperature, the d_{001} spacing decreases to 16.5 Å and the reflection becomes broader, indicating structural degradation (Fig. 1). Longer heating for up to 12 h shows lost of structural integrity, even at 500 °C.

Table 1. Intercalation conditions of montmorillonite

Sample	Oligomer		Clay suspension (g ml⁻¹)	Rate of oligomer addition (ml min⁻¹)	d_{001} (Å)
	Aging (day)	Vol (ml)			
Montmorillonite	-	-	-	-	12.50
A	3	100	150	0.5	15.13
B	7	63	126	2	15.36
C	15	63	136	1	15.68
D	15	125	187	2	15.26
E	30	93	185	1 – 4	17.11
O and P	Refluxing	70	140	1	18.70

This highest d_{001} spacing of 18.70 Å, corresponds to the complete hydroxylation of the aluminum or Keggin ion (Table 1, samples O and P; Fig. 1). This is consistent with the reported 8.6 Å dimension of the oligomer [30], which was hydrolyzed prior to its placement in the montmorillonite interlayer, reducing charge and associated water [30]. In turn, the control in the synthesis route is critical on pH, OH/Al ratio, temperature, and time, to get the right conditions to modify the clay, avoid loss of octahedral ^{VI}Al, decomposition of Al_{13} to AlOOH or $Al(OH)_3$, or formation of defect Keggin species: recombination of two incomplete Al_{13} to dimmers $Al_{24}O_{72}$ or other compounds [6, 14].

These data confirm previous indications on the influence of aging the oligomer to increase the d_{001} spacing [6]. However the oligomer clay complexes formed with aged oligomer are not as stable and do not develop d_{001} spacings as high as those prepared from refluxed oligomers solutions [24]. Keeping in mind that anhydrous montmorillonite has a 10-10.40 Å d_{001} spacing, one-water layer montmorillonite 12.50 Å, and the two-water layer phase 15.20 Å, higher spacings would depend on the nature of the adsorbed specie. Spacings as those developed for the Al-intercalated montmorillonite are substantially higher and confirm the large porous interlayer structure developed.

Thermal analysis

Gravimetric thermal analysis of the bulk montmorillonite in the 20 to 800 °C range, heating rate of 10 °/min, indicates dehydration at 95 °C with loss of 1.87 w% and dehydroxylation at 676 °C with loss of 0.56 w%. The intercalated clay (Fig. 2) dehydrates at 70 °C losing 8.03 w%, possibly of water adsorbed between the layers and on the surface of the clay. Between 150 °C and 280 °C the intercalated clay losses 1.92 w% that is attributed to the transformation of Al-OH- to AlO-montmorillonite The endothermic reaction starting at 400 °C and maximum at 645 °C, is associated with lost of structural OH⁻, and structural disruption. There is an additional endotherm starting at 280 °C and prolonged to 400 °C of 1.92 w% lost, attributed to the dehydration of the Al_{13} polymer and transformation to an oxy-aluminum intercalate.

Textural data

Intercalation of montmorillonite increases the surface area of 42.07 m²g⁻¹ of the bulk clay to 286.87 m²g⁻¹ of the intercalated montmorillonite (Table 2). The total pore volume changes from 0.00205 to 0.1029 cm³g⁻¹. The data confirm a three-fold increase in the BET surface area of the intercalated phase rela-
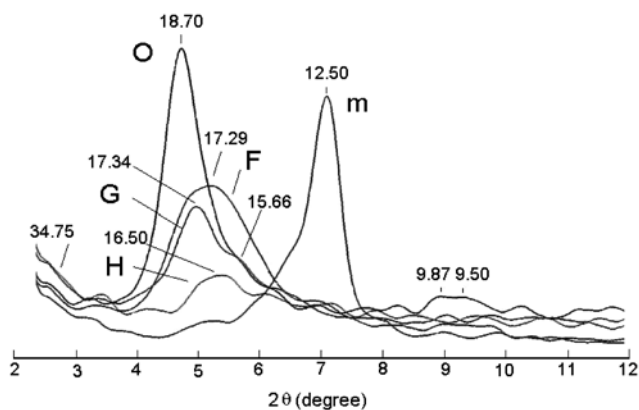

Fig. 1. X-ray diffraction patterns and basal spacing, in angstrom units, of: (m) bulk montmorillonite; (O) AlOH-montmorillonite at 22 °C; (F) AlOH-m heated to 100 °C; (G) AlO-m heated to 300 °C; (H) AlO-m heated to 700 °C.
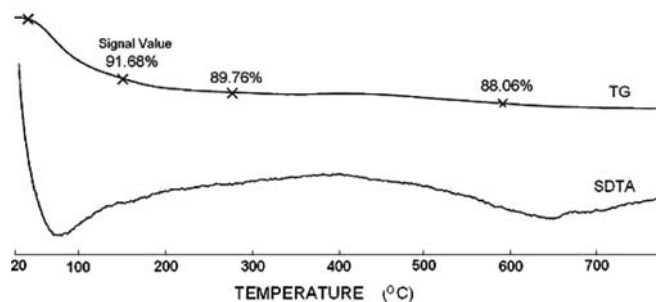

Fig. 2. Thermogravimetric and differential thermal analysis of AlOH-montmorillonite.
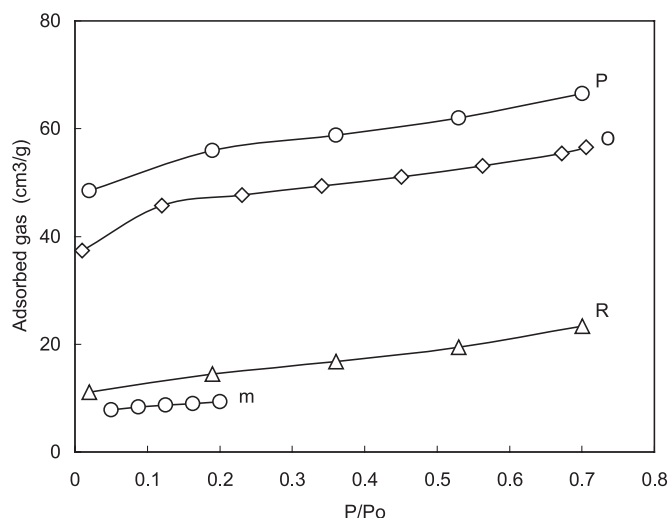
Table 2. Basal d_{001} spacing, cation exchange capacity, surface area, and micropore volume of bulk and intercalated Al-hydroxy montmorillonite

Concepts	Bulk montmorillonite	Al-hydroxy-montmorillonite AlOH-m (O)	Restored CEC AlOH-m (O)
d_{001} (Å)	12.5	18.7	-
CEC (meq g⁻¹)	1.37	No- restored 0.022	0.664
BET surface area (m²g⁻¹)	33.07	117.51	37.93
External surface area (m²g⁻¹)	42.07	286.87	104.51
Total pore volume (cm³g⁻¹)	0.00205	0.1029	0.0361

tive to the bulk and a six-fold increase in the external surface area. The fixation of aluminum on the Durango montmorillonite increases the surface area to 286.87 m²g⁻¹, with different possible distribution of the AlOH-intercalated. Samples O and P with similar basal d_{001} spacings (Fig. 1) and different N_2 adsorption (Fig. 3), suggest distinct accommodation of the oligomer in the interlayer.

IR spectroscopy

The Infrared absorption data show the characteristic OH⁻ stretching bands at 3628 and 3623 cm⁻¹ in the bulk (Fig. 4A) and intercalated montmorillonites, respectively (Fig. 4B). The 3443 and 3451 cm⁻¹ bands correspond to adsorbed water and the 1641 cm⁻¹ band to the OH deformation. The absorption at 468 cm⁻¹ indicates Si-O stretching, and that at 519 cm⁻¹ confirms the substitution of Si^{4+} by Al^{3+}. Bands at 1038-1088 cm⁻¹ in the bulk clay and at 1040-1086 cm⁻¹ in the intercalated montmorillonite are assigned respectively to Si-O-Al and Si-O bending.

CEC restoration

The cation exchange capacity of 1.37 meq g⁻¹ that characterizes the bulk montmorillonite is within the limits of 0.60-1.50 meq g⁻¹ commonly expected for montmorillonites (Table 2). The exchange capacity of 0.022 meq g⁻¹ of the AlOH-montmorillonite is attributed to the non-exchangeable character of the AlOH polymer, and confirms intercalation by the hydroxy aluminum in the clay. Restoration of the exchange capacity of the hydroxyl aluminum montmorillonite by the method described by Karamanis (1997) increases the exchange capacity to 0.664 meq g⁻¹, but some crystallinity is lost in the process.
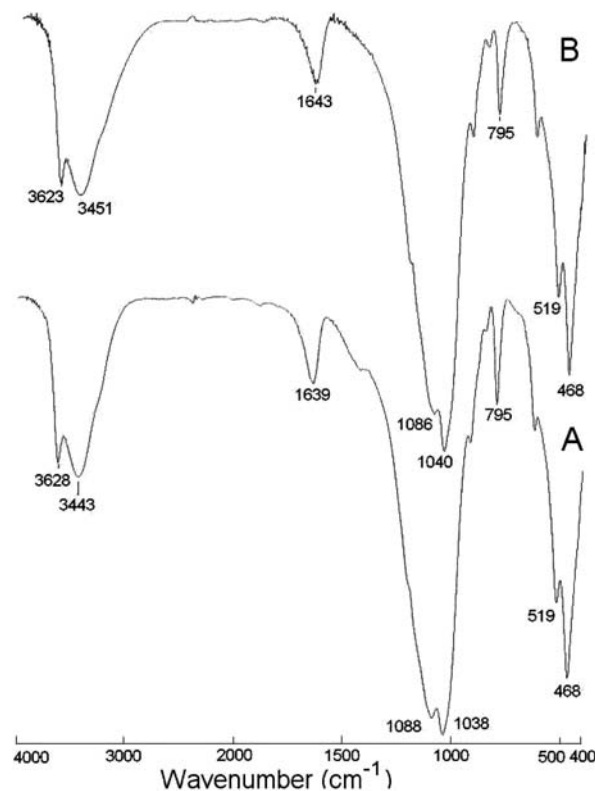

Fig. 4. Infrared spectroscopy of (A), bulk montmorillonite, (B), AlOH-montmorillonite.

Fig. 3. Nitrogen adsorption isotherms of: (m), bulk montmorillonite; (P) and (O), AlOH-montmorillonite; (R), AlOH-m of restored CEC.

Table 3. Adsorption of Ca^{2+} by bulk montmorillonite and AlOH-montmorillonite (O)

Ca^{2+} in solution C$_s$	Ca^{2+} in bulk montmorillonite C$_m$	Separation factor $\alpha_{Ca/Na}$	Ca^{2+} in solution C$_s$	Ca^{2+} in AlOH-montmorillonite C$_{AlOH-m}$	Separation factor $\alpha_{Ca/Na}$
0.01134	0.2764	45.6800	0.14	0.0140	0.003409
0.14681	0.0225	3.4088	0.34	0.0225	0.016155
0.27661	0.5251	1.6452	0.53	0.0227	0.000725
0.44808	0.4762	0.7251	0.61	0.0690	0.042059
0.46794	0.5907	0.7251	0.67	0.0300	0.006534

$\alpha^{Ca/Na} = Ca_{(AlOH-m)} Na_{(s)} / Na_{(Al-m)} Ca_{(s)}$, where (AlOH-m) represents the Al-hydroxy- montmorillonite, (m) bulk montmoril-lonite, (s) solution. Adsorption of Ca^{2+} in number of equivalents.

Ca^{+2} adsorption

The absorption and retention of Ca^{+2} by the intercalated hydroxy Al-montmorillonite was studied to explore their application to the remediation of wastes and effluents [8]. It is known that strong competition between Ca, other alkaline-earths, and alkali cations prevents the absorption of calcium. The exchange data indicate that a minimum amount of calcium is sorbed by the AlOH-intercalated montmorillonite, relative to the bulk clay. This can be associated with the distribution of the pillars, that would prevent access of the ions (Table 3).

Conclusions

The addition of Al-oligomer to Na-montmorillonite forms an intercalated AlOH-montmorillonite with a d_{001} spacing of 18.7 Å and a BET surface area of 287.86 m^{2}g^{-1}, relative to the 42.07 m^{2}g^{-1} of the precursor montmorillonite 12.50 Å. This measured expansion presumes formation of a well-defined hydroxyalu-minum polymer, the so-called Al$_{13}$ specie or Keggin ion. A minor reduction is observed in the basal spacing when the material is heated to 700 °C to form oxy-aluminum-montmo-rillonite (samples G and H, Fig. 1). The d_{001} spacing, cation exchange capacity, surface area, and pore volume of the bulk and the intercalated clays are summarized in Table 2.

Our study corroborates that the structure of Al-hydroxy-montmorillonite can be modified to favor a fast uptake of cations from aqueous solutions. However, the exchange of calcium is less in the Al-hydroxy-montmorillonite than in the bulk montmorillonite, possibly due to the spatial organization of the interlayer.

The modification of swelling of this Mexican montmoril-lonite may be relevant to industrial processes where keeping an expanded layered silicate at high temperatures may be of interest for selective adsorption and catalytic applications.

Acknowledgements

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