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PILLARED CLAYS PREPARED FROM THE REACTION OF CHROMIUM ACETATE WITH MONTMORILLONITE

ANTONIO JIMENEZ-LOPEZ, JOSE MAZA-RODRIGUEZ, PASCUAL OLIVERA-PASTOR, PEDRO MAIRELES-TORRES AND ENRIQUE RODRIGUEZ-CASTELLON

Departamento de Química Inorgánica Cristalografía y Mineralogía, Facultad de Ciencias
Universidad de Málaga, Apartado 59, 29071-Málaga, España

Abstract—Refluxing chromium (III) acetate with a Na^+-montmorillonite suspension gives rise to the intercalation of linear Cr(III) polyhydroxo-acetate oligomers. Thermally stable chromia pillared montmorillonite materials are obtained upon calcination under ammonia up to 625°C, and basal expansions up to 6 Å are maintained. The porous materials retain high surface areas (366–464 $m^2\ g^{-1}$), a micropore volume of 0.1 $cm^3\ g^{-1}$ and narrow pore size distributions centered between 7.5 and 12 Å. The most thermally stable materials in air were those prepared under ammonia at 625°C, containing NH_4^+ as the exchangeable ion.

Key Words—Chromia, Montmorillonite, Pillaring.

INTRODUCTION

Pillared layered compounds are porous, thermally stable materials with attractive catalytic properties (Mitchell, 1990). In particular, smectite clays pillared by metal oxides have been used successfully as acid catalysts in several organic reactions (Adams, 1987). Chromia pillared materials are of particular interest because the interlayer pillaring agent itself is catalytically active.

Various polycationic species of Cr(III) have been intercalated in clays (Brindley and Yamanaka, 1979; Carr, 1985; Pinnavaia *et al.*, 1985) leading to a variety of materials with high basal expansions and specific surface areas. The type of polynuclear metal unit intercalated in the interlayers determines the characteristics of the pillared materials—i.e., surface area, porosity, and acidity—and, hence, the catalytic properties. Recently, the oligomeric chromium species from solutions of chromium nitrate partially hydrolyzed with Na_2CO_3 at 95°C (Pinnavaia *et al.*, 1985; Tzou and Pinnavaia, 1988) have been identified via EXAFS studies (Bornholdt *et al.*, 1991). For a CO_3^{2-}/Cr^{3+} molar ratio 0.5, the pillaring solution contains tetranuclear species with *cis*-linked edge-bridged octahedral units, which are retained on incorporation into montmorillonite. The catalytic activity of some chromia pillared clays prepared using these pillaring solutions has been reported (Pinnavaia *et al.*, 1985; Tzou and Pinnavaia, 1988).

In previous work, we reported the preparation and characterization of porous chromia pillared layered phosphates obtained from the reaction of $Cr(CH_3CO_2)_3$ ($Cr(OAc)_3$) with colloidal layered phosphates (Maireles-Torres *et al.*, 1991a, 1991b). The resulting intercalation compounds, with well defined Cr^{3+}-polyhydroxyacetato species inserted within the phosphate matrix, leads to a series of chromia pillared materials with basal expansions of 5–20.5 Å and surface areas of 250–330 $m^2\ g^{-1}$, after calcination under N_2. This procedure provides a buffered medium (pH = 4) without any competitive cation in solution, permitting *in situ* growth of linear oligomeric chromium species on the host surface. The acidity of layered phosphates is strongly increased by the incorporation of chromia pillars, which catalyze the dehydration of isopropyl alcohol. In addition, selectivity can be controlled according to the chromium content (Guerrero-Ruiz *et al.*, 1992). This method is now extended to a smectite clay (montmorillonite) with the objective of obtaining new acid porous materials with potential catalytic uses.

EXPERIMENTAL METHODS

The montmorillonite used came from Tidinit, Morocco. A Na^+-exchanged sample with particle size <2 μm was used as the starting material. The structural formula calculated from the chemical analysis is

$$(Si_{7.94}Al_{0.06})(Al_{2.90}Fe^{3+}_{0.20}Mg_{0.98})O_{20}(OH)_4 \quad (1)$$

and the cation exchange capacity (CEC) is 1.25 meq/g, based on the weight of the sample heated at 900°C.

An aqueous suspension of 1 g of Na^+-montmorillonite was contacted with increasing quantities of $Cr(OAc)_3$, varying the Cr^{3+} concentrations from 9–366 $mmol/dm^3$ (final volume, 200 ml). In other series of experiments, the final volume was reduced to 100 ml in order to study the effect of the chromium concentration in solution for a given Cr^{3+}/clay ratio. In all cases, each suspension was refluxed for 10 days, cooled, centrifuged, washed with deionized water to a conductance of washing waters <40 μS, then air-dried, and analyzed (C, H, N, TG, Cr analyses).

XRD of cast films obtained by dropping and drying

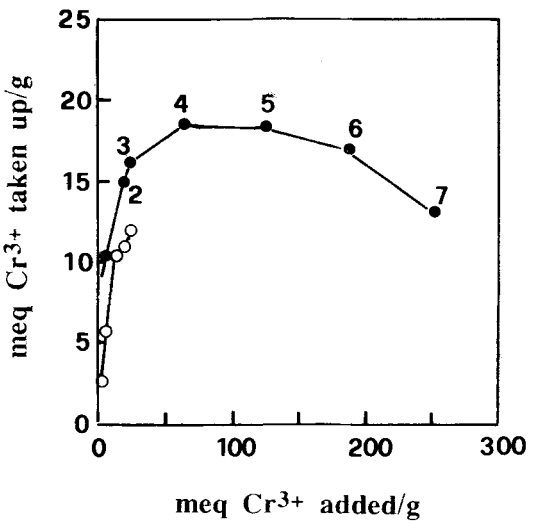

Figure 1. Uptake of hydrolyzed $Cr(OAc)_3$ species by Na^+-montmorillonite, (o) obtained using twice concentrated Cr^{3+} solutions at the same Cr/clay ratio.

the clay suspension on a glass slide were recorded on a Siemens D501 diffractometer (CuKα radiation). TG and DTA were measured on a Rigaku Thermoflex instrument (calcined Al_2O_3 as reference; 10°C min^{-1} heating rate). Cr^{3+} was analyzed colorimetrically using the chromate method (λ = 372 nm) on alkaline solutions after treatment with $NaOH-H_2O_2$. Optical spectra (diffuse reflectance) were registered on a Shimadzu MPC 3100 spectrophotometer ($BaSO_4$ as reference) and IR spectra on a Perkin-Elmer 883 spectrophotometer as KBr disks. Adsorption-desorption of N_2 was measured on a conventional volumetric apparatus (77K; degassing at 200°C; 10^{-4} mbar overnight).

RESULTS AND DISCUSSION

Previous studies have showed that polymeric species of Cr^{3+}-hydroxoacetate may be intercalated into layered phosphates by refluxing $Cr(OAc)_3$ aqueous solutions with colloidal suspensions of these ion exchangers. In most cases, the oligomeric chromium species intercalated were well-defined, single linear trinuclear, tetranuclear, pentanuclear or hexanuclear species (Maireles-Torres *et al.*, 1991a, 1991b).

The uptake of chromium acetate by montmorillonite occurs in a fashion similar to that in layered phosphates (Figure 1). Initially, Cr^{3+} uptake increases with increasing concentrations of Cr^{3+} in solution, but additions higher than 120 meq/g lead to materials with lower Cr^{3+} loadings. This uptake curve is typical for processes in which species association takes place in solution (Giles *et al.*, 1960). Thus, larger oligomers formed at high Cr^{3+} concentration are increasingly difficult to accommodate into the matrix. Montmorillonite takes up large amounts of Cr^{3+}, in excess of the theoretical exchange capacity. This is attributable to the significant reduction of the charge per cation ratio in oligomeric species, the maximum uptake being 18.5 meq Cr^{3+}/g (900°C). When the concentration of Cr^{3+} is increased by reducing the final volume to 100 ml, intercalation compounds with lower Cr^{3+} loadings are obtained (Figure 1). Table 1 lists the chemical analyses of Cr^{3+} exchanged montmorillonite samples. The OAc^-/Cr^{3+} ratio in these materials increases with the Cr^{3+} concentration in solution from 0.18 to 0.72; therefore, the oligomers intercalated in montmorillonite are polyhydroxy acetate Cr^{3+} moieties. In addition, the interlayer water contents are quite high.

Table 1. Composition data of air-dried Cr^{3+} polyhydroxoacetate montmorillonite intercalates.

Sample	$[Cr^{3+}]_{add.}$ (mol·liter^{-1})	meq. Cr^{3+} add./g (900°C)	meq. Cr^{3+} taken up/g (900°C)	% OAc^-	OAc^- : Cr ratio	% H_2O
1	0.009	6.2	10.5	1.21	0.18	12.5
2	0.027	18.7	15.1	2.09	0.24	11.7
3	0.037	25.0	16.2	2.80	0.28	9.57
4	0.091	62.5	18.5	3.91	0.38	16.6
5	0.183	125.0	18.4	4.39	0.42	13.5
6	0.274	187.5	17.1	4.67	0.48	12.5
7	0.366	250.0	13.2	5.70	0.72	10.6

Chemical compositions per unit cell $[O_{20}(OH)_4]$ are listed in Table 2. The Cr contents are in the range found by other authors (Brindley and Yamanaka, 1979; Tzou and Pinnavaia, 1988), but empirical formulae of single species, like those found for zirconium phosphate, cannot be established, suggesting the presence of more than one species in the interlayer region of montmorillonite. This agrees with broadening of bands in optical spectra and diffraction peaks in XRD patterns. The samples 2–7 present similar Cr^{3+} contents but different Cr/OAc ratios, water contents, and basal spacings, suggesting that the oligomeric species intercalated should possess different polymerization degree and charge. Polymerization increases with the concentration of Cr^{3+} in solution (Maireles-Torres *et al.*, 1991a, 1991b).

The diffuse reflectance spectra (Figure 2) are similar to those found for the chromium oligomers intercalated in α-tin and α-zirconium phosphates, i.e., they show

Table 2. Chemical composition per unit cell $[O_{20}(OH)_4]$ and d_{001} basal spacings of air-dried Cr^{3+} polyhydroxoacetate montmorillonite intercalates.

Sample	Empirical formulation	d_{001} (Å)
1	$Cr_{2.41}(OAc)_{0.45}(OH)_{5.98}(H_2O)_{6.25}$-Mont	16.5
2	$Cr_{3.46}(OAc)_{0.83}(OH)_{8.75}(H_2O)_{6.16}$-Mont	18.9
3	$Cr_{3.74}(OAc)_{1.04}(OH)_{9.38}(H_2O)_{4.76}$-Mont	20.4
4	$Cr_{4.26}(OAc)_{1.50}(OH)_{10.48}(H_2O)_{9.22}$-Mont	17.7
5	$Cr_{4.24}(OAc)_{1.68}(OH)_{10.24}(H_2O)_{7.42}$-Mont	17.1
6	$Cr_{3.94}(OAc)_{1.79}(OH)_{9.20}(H_2O)_{6.75}$-Mont	16.4
7	$Cr_{3.04}(OAc)_{2.18}(OH)_{6.14}(H_2O)_{5.42}$-Mont	16.3

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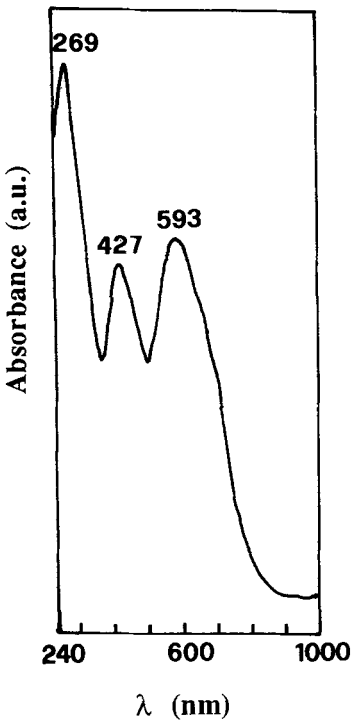

Figure 2. Optical spectrum of a Cr^{3+}-polyhydroxoacetate montmorillonite intercalate (Sample 2).

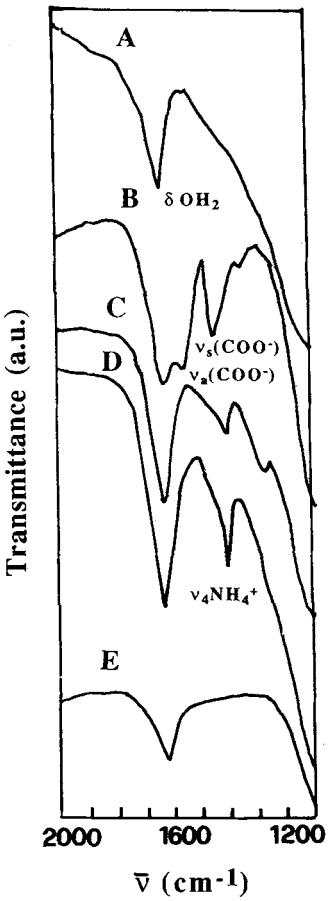

Figure 3. Infrared spectra of: (A) Na^+-montmorillonite; (B) material 3 freshly prepared; (C) material 3 calcined in NH_3 at 400°C; (D) material 3 calcined in NH_3 at 500°C; (E) Na^+-exchanged material (D).

the $4_{T_{2g}} \leftarrow 4_{A_{2g}}(\nu_1)$ and $4_{T_{1g}} \leftarrow 4_{A_{2g}}(\nu_2)$ transitions typical of a six-coordinate geometry for Cr^{3+}. The intensity ratios of these absorption bands for all intercalates were in the range 1.07–1.26, suggesting the presence of linear oligomers of chromium in the interlayer space of the silicate (Maireles-Torres *et al.*, 1991a, 1991b). It seems that requirements of charge neutralization in the sterically restricted interlamellar region preclude the formation of compact structures, such as those believed to exist in solution (Monsted *et al.*, 1985).

The d_{001} basal spacings of the Cr^{3+}-polyhydroxyacetate intercalates (Table 2) vary between 16.3 and 20.4 Å. These values do not correlate with chromium and interlayer water contents, which can be attributed to different arrangements of Cr^{3+} oligomers in the interlayer region depending on their charges and sizes. Cr^{3+}-polyhydroxoacetate oligomers are intercalated into layered phosphates in a more ordered way (narrower diffraction peaks) with higher interlayer distances. It appears that short (i.e., those with lower charge) oligomers tend to orient perpendicular to the layer, whereas larger ones (i.e., those with higher charge) preferentially adopt a slanted position. Moreover, the phosphates, which have a very high charge density, can intercalate bilayers of these oligomers (Maireles-Torres *et al.*, 1991a, 1991b). The montmorillonite surface, which has a much lower charge density than those of layered phosphates, allows the oligomers to lie in a more tilted position with respect to the layer; thus, materials with lower Cr^{3+} loadings are obtained. It is inferred, therefore, that the hydrolysis of Cr^{3+} is forced on the exchanger surface; thus, the products obtained depend on the surface characteristics. According to Tzou and Pinnavaia (1988), the X-ray basal spacing of the products depends on the extent of metal ion hydrolysis and the metal ion/clay ratio used in the pillaring reaction. For an optimum ratio of 50 mmol Cr added/meq clay, they reported basal spacings for air-dried samples between 16.3 and 27.6 Å corresponding to CO_3^{2-}/Cr^{3+} molar ratios between 0.0 and 1.25. The basal spacing values found here are similar to those reported by these authors for $CO_3^{2-}/Cr^{3+} < 0.75$. It is suggested that linear chromium oligomers, intercalated by *in situ* polymerization of $Cr(OAc)_3$ on the montmorillonite surface, gradually adopt a more slanted disposition as the polymerization degree and charge increase, i.e., as the Cr^{3+} concentration of the pillaring solution increases; the basal spacing of the intercalates thus decreases gradually for high chromium concen-

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Table 3. d_{001} basal spacings of Cr^{3+}-exchanged montmorillonite materials calcined under ammonia at different temperatures.

Sample	d_{001} (Å)		
	200°C	400°C	500°C
1	14.6	12.8	12.3
2	15.6	15.3	15.3
3	15.8	15.6	15.2
4	14.6	14.2	14.4
5	14.2	13.7	13.3
6	13.9	13.2	13.1
7	14.0	12.4	12.4

trations in solution. Conversely, oligomers prepared by partial hydrolysis of $Cr(NO_3)_3$ with carbonate are presumably high connectivity rigid structures, which do not change on incorporation into the clay (Bornholdt *et al.*, 1991).

IR spectra of all products (Figure 3) show the characteristic bands of the COO^- group at 1550 and 1450 cm^{-1}, corresponding to the asymmetrical (ν_{as}) and symmetrical (ν_s) stretching vibrations, respectively. The difference $\nu_{as(COO)} - \nu_{s(COO)}$ is 100 cm^{-1}, which is characteristic of the presence of bidentate OAc^- groups (Nakamoto, 1986). It has been suggested (Maireles-Torres *et al.*, 1991a, 1991b) that the presence of bidentate acetate ligands in intercalated Cr^{3+}-oligomers precludes formation of high connectivity clusters similar to those found in solution (Stunzi and Marty, 1983).

Calcination of these materials above 200°C in air or N_2 leads to collapsed structures with segregation of chromium oxide; this is detected in the XRD patterns of the samples heated at T > 400°C by the appearance of distinctive diffraction peaks at 3.6, 2.6 and 2.5 Å, which correspond to those of Cr_2O_3 (Powder Diffraction File, 1967).

The mechanism that operates in the formation of these collapsed structures by calcination in air is a triple process of oxidation-segregation-reduction. Oxidation of Cr(III) and organic matter occurs on calcination in air between 220° and 340°C (exothermic effect in DTA curves). The CrO_3 formed is subsequently segregated from the interlayer region and then is reduced at higher temperatures. The presence of Cr(VI) is detected by washing the samples calcined in air at 300°C: A yellow solution of $H_2Cr_2O_7$ immediately forms. Formation of collapsed structures upon calcination in inert atmosphere was not expected to occur (Pinnavaia *et al.*, 1985; Maireles-Torres *et al.*, 1991a, 1991b); however, all materials calcined under N_2 presented basal spacings lower than 10.5 Å. Although the mechanism is unclear, it is assumed that an abrupt release of protons is responsible for the segregation of chromium oxide from the interlayers. Protons can migrate toward the vacancies in the octahedral sites at high temperature, progressively reducing the negative charge of the montmorillonite layer (Poncelet and Schutz, 1986).

Table 4. Textural parameters for chromia-montmorillonite samples obtained under NH_3 at 500°C.

Sample	S_{BET}	C_{BET}	$S_{Lang.}$	$V_{microp.}$*	$S_{ext.}$*
1	274	596	366	0.10	51
2	333	401	424	0.12	120
3	353	567	464	0.14	79
4	349	541	446	0.14	121
5	344	533	390	0.11	85
6	328	535	391	0.12	81
7	291	557	388	0.12	70

* Calculated by the α-method.

Calcination under NH_3 instead leads to a series of expanded materials stable up to 625°C, with still recognizable basal spacings in the range of 12.3–15.3 Å (Table 3) and high specific surface areas (Table 4). Ammonia retains the protons released during calcination (Vaughan, 1988), and the presence of NH_4^+ ions stabilizes Cr(III) because NH_4^+ tends to reduce Cr(VI) to Cr(III) at high temperatures (Cotton and Wilkinson, 1988). Inasmuch as we have not detected the characteristic diffraction peaks of Cr_2O_3 during calcination of the samples under NH_3, we have concluded that no chromium oxide is precipitated on the external surface of the mineral. NH_4^+ ions are indicated in the interlayer region by the appearance of a new band in the IR spectra at 1400 cm^{-1} (Figure 3) attributed to the

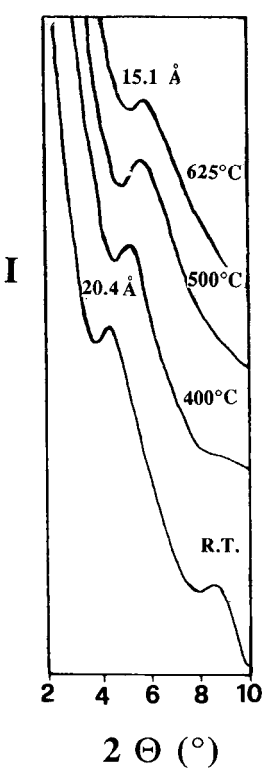

Figure 4. XRD patterns of material 3 freshly prepared and calcined in NH_3 at different temperatures.

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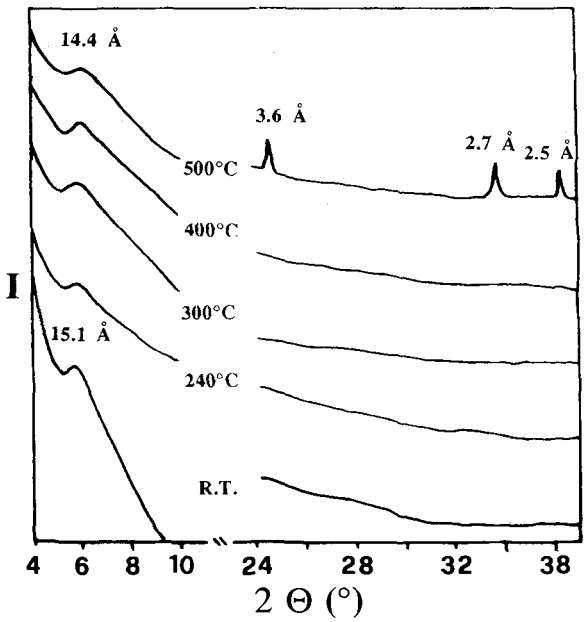

Figure 5. XRD patterns of material 3 prepared under NH_3 at 625°C and then treated at different temperatures in air.

vibration mode ν_4. This band disappears when the sample is treated with a 1 M NaCl solution (due to the replacement of NH_4^+ by Na^+).

The basal spacings of the samples calcined under NH_3 decrease by between 2 and 4.5 Å at 200°C, which is attributable to the loss of water with concomitant rearrangement of the oligomers in the interlayer space. Above this temperature, only a minor decrease is observed for Samples 2, 3, and 4, which retain basal spacing higher than 14 Å, a threshold value for considering a layered structure to be pillared (Vaughan, 1988). The maximum basal expansion reached is about 6 Å, assuming a layer thickness of 9.5 Å, for Samples 2 and 3. The basal spacings of these materials calcined in NH_3 at T > 400°C did not change after treatment with diluted HCl solution or with MCl_n solution (M^{n+} = metal ion), confirming that a true pillaring of chromia nanostructures within the interlayer of montmorillonite has occurred. Ammonium exchanged chromia pillared montmorillonite (Sample 3) has a cation exchange capacity of 0.34 meq/g, and the NH_4^+ ion is easily replaced by other metallic ions. Figure 4 shows the evolution of the d_{001} basal spacing of Sample 3 upon calcination under NH_3. Under these conditions the material is thermally stable up to 625°C and still maintains a basal expansion of 5.7 Å.

The thermal stability of the pillared products prepared in NH_3 atmosphere was tested by calcining these materials in air. The results obtained for Sample 3 are illustrated in Figure 5. The thermal stability of chromia pillared montmorillonite depends critically on the temperature at which the material was obtained under NH_3:

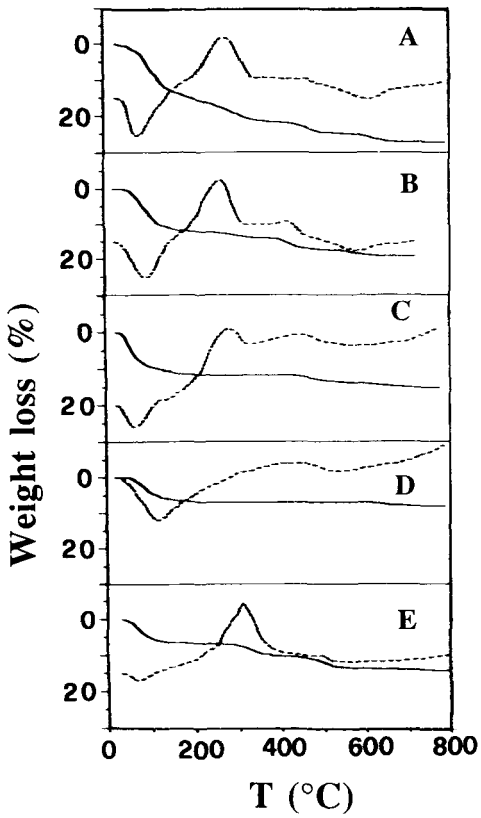

Figure 6. DTA-TG curves of material 3 at different conditions: (A) as prepared; (B) calcined in NH_3 at 400°C; (C) calcined in NH_3 at 500°C; (D) calcined in NH_3 at 600°C; (E) Na^+-exchanged material (C).

the higher the temperature, within the range 400°–625°C, the higher the stability in air. Thus, the sample calcined under NH_3 at 625°C is stable in air up to 500°C. Conversely, calcination below 600°C under NH_3 leads to materials less stable in air, with partial segregation of chromium oxide at T > 300°C; and this result increases when the temperature of calcination in NH_3 is decreased. The thermal stability of the pillared materials in air can also be appreciated by observing the corresponding TG-DTA curves (Figure 6). An exothermic effect centered at 270°C is apparent in DTA curves of the sample prepared at T < 600°C while it is absent for the sample obtained at 625°C. The intensity of the exothermic effect increases when the preparation temperature under NH_3 is decreased. This exothermic effect is associated with formation of CrO_3, which is segregated from the interlayer of montmorillonite and then reduced to Cr_2O_3, according to the reaction:

$$2\,Cr^{3+} + 4\,OH^- \xrightarrow{\%O_2} 2\,CrO_3 + H_2O + 2\,H^+$$
$$\downarrow -\%O_2$$
$$Cr_2O_3$$

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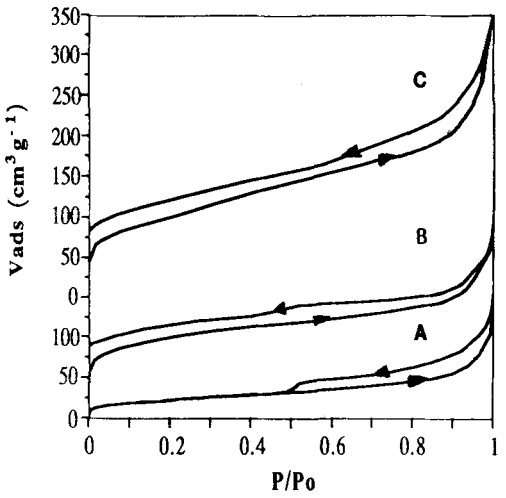

Figure 7. Adsorption-desorption isotherms of N_2 at 77 K on: (A) Na^+-montmorillonite; (B) material 3 calcined in NH_3 at 500°C; (C) material 4 calcined in NH_3 at 500°C.

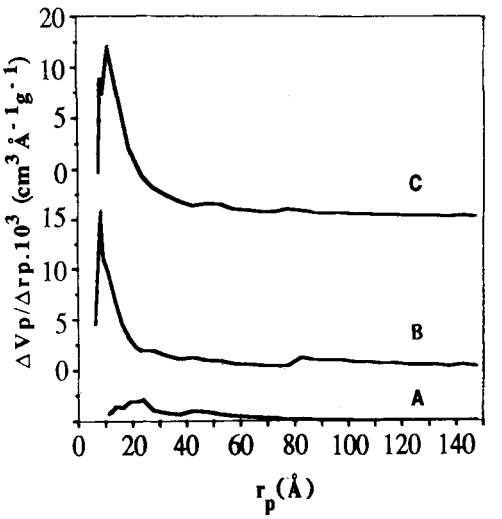

Figure 8. Pore size distributions of: (A) Na^+-montmorillonite; (B) material 3 calcined in NH_3 at 500°C; (C) material 4 calcined in NH_3 at 500°C.

although mixed-oxidation species, including Cr(IV) and Cr(V) may also be formed (Maireles-Torres *et al.*, 1991a, 1991b).

The OH^- groups must be involved in the oxidation process inasmuch as higher calcination temperatures under NH_3 (i.e., lower OH^- content) lead to less extensive oxidation. The weight loss of pillared materials between 270°–400°C, attributed to the removal of water, decreases when the calcination temperature under NH_3 increases from 400° to 625°C.

Oxidation of intercalated Cr(III)-oligomers occurred at higher temperature than that observed for chromia gels (Navarro-Martos, 1977) because of protection by the silicate matrix. Inversely, the structure of montmorillonite is stabilized by the presence of Cr_2O_3 pillars; thus, the possibility of condensation of structural OH^- groups is reduced: Only a slight weight loss is observed at $T > 600$°C, whereas the original Na-montmorillonite starts to lose structural water at 550°C. If the interlayer NH_4^+ ion is replaced by other ions, e.g., Na^+, the extent of oxidation of the interlayer Cr(III) increases (Figures 6C and 6E).

The adsorption-desorption isotherms of N_2 at 77 K were measured on the sodium-montmorillonite samples at 200°C and on chromia montmorillonite samples prepared under NH_3 at 500°C. As shown in Figure 7, insertion of Cr_2O_3 in the interlayer of montmorillonite causes noticeable changes on the silicate surface. The isotherms of the pillared samples are characteristic of microporous solids, but with a contribution of mesopores (Gregg and Sing, 1982), which is more evident in the samples with lower basal spacings. The microporous nature of the samples is confirmed by the high values of the C_{BET} parameter (Table 4) and the existence of low pressure hysteresis, as is characteristic of ultramicropores, i.e., pores with sizes between 3 and 7 Å (Gregg and Sing, 1982). The isotherm corresponding to the original sample is of type IV, characteristic of a mesoporous material.

The values of the specific surface areas (Langmuir and BET), C_{BET} parameters, micropore volumes, and external surfaces are listed in Table 4. The micropore volumes and external surfaces were calculated by the α-method, using a hydroxylated silica as standard (Gregg and Sing, 1982). Similar values of micropore volumes are obtained by the Dubinin method (Dubinin, 1966).

The specific surface areas of the chromia-montmorillonite samples are increased substantially with respect to the Na-montmorillonite (62 m^2/g). Since the external surfaces are of the order of the initial clay, it is inferred that the increase in the specific surface area of chromia-montmorillonite samples is due to the presence of micropores created by chromia pillars in the interlayer region. Although the basal spacings of these chromia-pillared materials are lower than those reported by Pinnavaia *et al.* (1985), the specific surface areas are quite similar.

The micropore volume values are of the order of 0.12 cm^3/g, which are close to those of other pillared montmorillonites (Pesquera *et al.*, 1991).

Pore size distributions, determined by the Cranston method (Cranston and Inkley, 1957), are shown in Figure 8. The majority of pores in chromia-montmorillonite samples are in a narrow radius range between 7.5 and 20 Å, which supports the presence of a true pillaring model. Pore size distribution is more dependent on the type of Cr^{3+}-oligomer intercalated than on the interlayer distance of the calcined product.

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