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HYDROXY-CHROMIUM SMECTITE

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Abstract—Hydroxy-chromium solutions were prepared from chromium nitrate solutions by adding NaOH with OH/Cr = 2.

The solutions were treated at 20°C and 60°C. The hydrolysis times were from 1 to 100 days. Polymeric species in hydrolyzed chromium solutions were followed by visible absorption spectra within the range 325–800 nm and by pH measurement. OH-Cr-smectite with high d(001) spacing (2.07 nm) was obtained when hydroxy-chromium solution was prepared at 60°C and with 1-day hydrolysis. When this sample was heated up to 350°C, the basal spacing collapsed at 1.8 nm.

The samples were characterized by X-ray diffraction and N_2 adsorption-desorption isotherms.

Key Words—Cross-linked smectites, Pillared smectites, Polymeric Cr species.

INTRODUCTION

For more than one decade, a new class of porous materials with high specific surface that are of potential interest for catalysts and adsorbents have appeared by means of pillared clays (PILC) or cross-linked smetite (CLS) (Vaughan, 1988). These pillared smectites are produced by a cation exchange of the interlamellar cations of the clays with poly- or oligomeric hydroxy cations, which are then stabilized by calcination. These materials develop a thermal stability higher than that observed in those materials obtained by cation-exchange (Rengasamy and Oades, 1978; Brindley and Yamanaka, 1979; Vaughan and Lussier,1980; Carr, 1985; Pinnavaia *et al.*, 1985; Vaughan, 1988; Tzou and Pinnavaia, 1988).

Vaughan (1988) reported that the structures of pillared species with Cr have not yet been identified. The present paper deals with the influence of temperature and hydrolysis time on the species formed in hydroxy-chromium solutions and their effects on the synthesis of OH-Cr-smectites.

EXPERIMENTAL MATERIALS AND METHODS

Hydroxy-chromium solutions

Hydroxy-chromium solutions were prepared from a 0.1 M-chromium nitrate solution by the addition of 0.2 N NaOH (OH/Cr = 2). The addition was done slowly with continuous stirring. Several hydroxy-chromium-solutions were prepared at 20°C and 60°C with hydrolysis times of 1, 2, 6.5, 8, 17, 30, 36, 67, and 100 days. The solutions were called A/B, where A is the hydrolysis time in days and B is the temperature in °C.

Polymeric species in hydrolyzed chromium solutions were analyzed by pH measurement and absorption within the visible range (325–800 nm) in a Beckman DU 65 spectrophotometer.

For quantitative chromium analysis, the washing solutions and the solids were converted to alkaline pH and oxidized to form $CrO_4^{=}$. The total Cr concentrations were determined spectrophotometrically at ϵ 374 = 4830 m^{-1} cm^{-1} (Stünzi *et al.*, 1983).

Preparation of hydroxy-chromium smectite

The smectitic material (E) was supplied by Georgia Kaolin Co. An XRD diffractogram from the total sample revealed an essentially dioctahedral smectite as the d(060) was less than 0.150 nm. Quartz impurities and cristobalite in low proportions were detected in the sample. The d(001) reflection of the sample from an oriented slide after air-drying, glycol treatment, and calcination at 600°C for 2 hr showed a typical behavior of smectite with 1.60, 1.70, and 0.90 nm, respectively. The smectitic species present were montmorillonite (95%) and beidellite (5%). This was calculated from the separation of the d(001) reflection by the Li-250°C-glycerol treatment. The X-ray diffraction (XRD) of the samples with KCl and after ethylene glycol solvatation confirmed the presence of Cheto-type montmorillonite.

The unit cell formula of the purified Na-smectite was derived from chemical analyses on the basis of anion charge of −44, and the Si content so determined was used to calculate the unit cell for the hydroxy-chromium smectite.

One g samples of E were dispersed in 50 ml distilled water, and the different fresh A/B hydroxy-chromium solutions were added slowly with stirring. After 2 hr of contact with continuous stirring at 40°C, the solid was washed several times with distilled water in order to remove the excess electrolyte. After three wash cycles, the solution was free of hydroxy-chromium, as determined by the loss of absorbance of the washing solutions. The Cr retained in the samples was determined by the chemical analysis of solids and by the difference between the initial solution and the total washing solution. Another E sample was treated using

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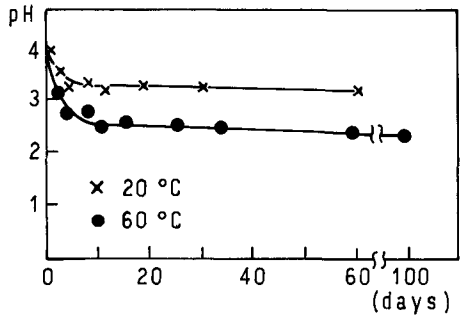


Figure 1. pH of polymeric solutions *vs.* hydrolysis time.

0.1 M-chromium nitrate solution (E–Cr). In all the cases, the amount of Cr/g sample was constant at 20 mmol Cr/g sample.

The XRD patterns were obtained with a Philips PW 1140/00 instrument, using Cu K_α radiation ($\lambda = 0.15405$ nm) and Ni-filter at 40 kV and 20 mA. The d(001) of all samples was measured on oriented slide specimens by scanning at ½°2Θ/min between the interval, 3° to 10° (2Θ).

Adsorption-desorption isotherms were obtained at liquid nitrogen temperature, with N_2, in a Micromeritics equipment Accusorb. Samples were outgassed at 100°C and 10^{-3} torr before nitrogen treatment for 12 hr. Specific surface area (S_{BET}) was calculated from the first part of the isotherm ($P/P_o < 0.3$) using 0.162 nm^2 as the molecular area of adsorbed N_2 molecule. Pore-size distribution was obtained taking into account considerations of Wheeler (1955), Barret *et al.* (1951), Pierce (1953), and Orr and Dalla Valle (1953). The t-plot was made according to Lippens and De Boer (1965).

RESULTS AND DISCUSSION

Figure 1 shows the pH of polymeric solutions OH/Cr = 2 *vs.* the hydrolysis time at 20°C and 60°C. The equilibrium pH is 3.23 at 20°C and 2.45 at 60°C. Absorption spectrophotometric analyses of these solutions show different species according to the variation of hydrolysis time.

Table 1 shows the pH, maximum absorption value (λ max_1, λ max_2), and the ratio between maximum intensity ($Imax_1/Imax_2$) bands of chromium nitrate and the polymeric solutions obtained at different temperatures and hydrolysis times.

Dimeric species of Cr in solution were thoroughly studied by Ardon and Plane (1959), Laswick and Plane (1959), and Thompson and Connick (1981). Two possible stoichiometric formulas—$[H_2O)_5CrOCr(H_2O)_9]^{+4}$ or $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{+4}$—were established by Kolaczkowski and Plane (1964). The trimeric complex, $Cr_3(OH)_4^{+5}$, was obtained by Laswick and Plane (1959) and Finholt *et al.* (1981) by ion exchange. Stünzi and Marty (1983) and Stünzi *et al.* (1989) also obtained oligomeric Cr (III) species by ion exchange on Sephadex SPC-25 gel, and they found in this way several new polymeric complexes (tetrameric, pentamer, and hexamer, although the last two complexes have not been studied in detail).

Table 1. pH, maximum absorption values (λ max_1/λ max_2), and ratio between intensity maximum bands ($Imax_1/Imax_2$).

Polymeric solution t (day)/T (°C)	pH	λ max_1 (nm)	λ max_2 (nm)	$Imax_1/Imax_2$
$(NO_3)_3Cr$				
0.1 M	2.10	408	575	1.17
1/20	3.90	424	583	1.34
2/20	3.52	424	583	1.36
8/20	3.34	424	583	1.38
17/20	3.30	423	584	1.39
30/20	3.23	423	584	1.45
1/60	3.08	424	585	1.39
6.5/60	2.81	423	586	1.33
36/60	2.50	422	586	1.36
67/60	2.49	420	586	1.32
100/60	2.45	419	586	1.32

Two bands were characteristic of each pure species. The first band shifted from 408 to 426 nm and the second band from 575 to 586 nm from monomer up to higher polymers (Stünzi and Marty, 1983). The ratio between maximum bands provided an easy check on the purity of the oligomers. Thus, 1.17, 1.18, 1.60, 1.95, and 1.5–1.56 correspond to mono, di, tri, tetra, and penta-hexamer, respectively (Thompson and Connick, 1981; Finholt *et al.*, 1981; and Stünzi and Marty, 1983). In our 0.1 M-chromium nitrate solution, the existence of the monomeric species, $Cr(H_2O)_6^{+3}$, was confirmed by the ratio of 1.17 between the maximum absorption at 408 and 575 nm (Table 1).

The addition of NaOH solution to the nitrate chromium solution changed the spectrum by the appearance of polymeric forms (Table 1). Consequently, the band width increased and shifted to higher wavelengths.

The solution spectrum from a hydrolysis temperature of 20°C and different hydrolysis times showed characteristics similar to tri- and tetrameric species, but there were differences in pH (3.90 to 3.23) and $Imax_1/Imax_2$ (1.34–1.45) values (Table 1).

Solutions from a hydrolysis temperature of 60°C mainly showed spectral characteristics of tri- and tetrameric species. At a longer hydrolysis time (36–100 days), the λmax_1 changed, giving rise to spectral characteristics of dimeric species. The pH changed from 3.08 to 2.45 and the $Imax_1/Imax_2$ from 1.39 to 1.32 for hydrolysis times from 1 to 100 days.

Stünzi *et al.* (1989) utilized pH measurement, chromatographic separation, and determination of the Cr content for each oligomer fraction. On the basis of similar results, we estimated the species content according to the pH values. Thus, in the 1/20 solution

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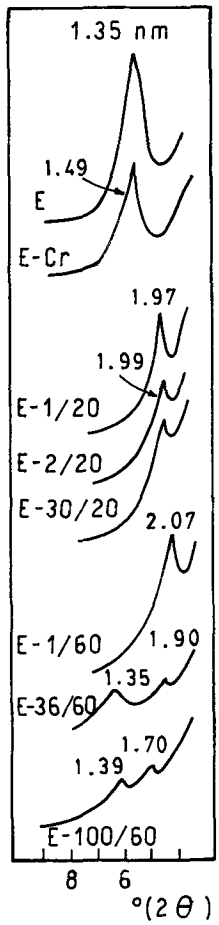


Figure 2. d(001) spacings of E samples before and after treatment with chromium nitrate (E–Cr) and polymeric solutions (E-A/B).

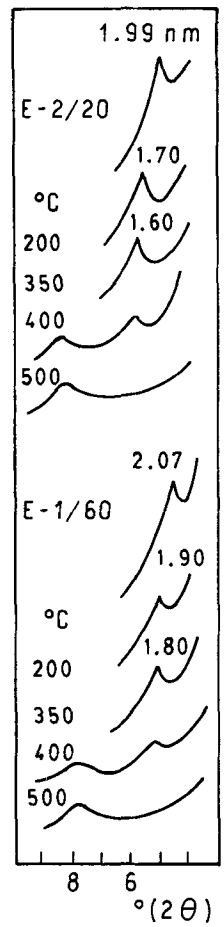


Figure 3. Thermal stability for E-2/20 and E-1/60 samples.

with pH 3.90, the tetramer species was in higher proportion with a lower content of trimer and pentamer species and a trace quantity of dimer and monomer. Upon variations of pH within the range of 3.52–3.23 that correspond to solutions 2/20 to 30/20 (Table 1), the trimeric and tetrameric species were significant. In the 1/60 solution with pH 3.08, trimeric species were the principal ones, followed by tetra-, mono-, and dimer. The pH decreased when the hydrolysis time increased. In the 36/60 and 100/60 solutions with pH 2.50 and 2.45, respectively, the monomeric species was the major one, although small amounts of tri- and dimer species were also found. The different $Imax_1/Imax_2$ could be correlated with the contribution of the species present with their characteristic ratio.

Figure 2 shows d(001) values of the E sample, E treated with 0.1 M chromium nitrate (E–Cr), and a third one treated with polymeric solutions at 20°C and 60°C at different hydrolysis times. The exchange with chromium nitrate scarcely affected the basal spacing of 1.49 nm with respect to the 1.35 nm of the original sample due to the fact that monomeric species were prevailing. On the other hand, when the E sample was treated with a solution with OH/Cr = 2, the d(001) increased. When the smectite was treated with hy-

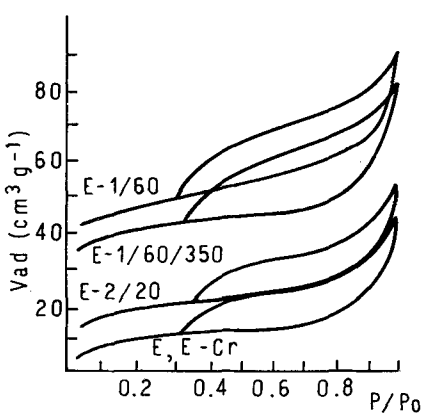


Figure 4. Nitrogen adsorption-desorption isotherms of E, E–Cr, E-2/20, and E-1/60 samples as well as E-1/60 heated at 350°C.

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Table 2. Hydroxy-chromium in unit-cell interlayer and d(001) spacing.

$Cr(OH)_{3-q}^{q+}$	d(001) (nm)
1.24	2.68 (1)
1.58	2.07 (2)
1.88	1.68 (3)
3.53	2.76 (4)

1 = Pinnavaia *et al.*, 1985. 2 = Present study. 3 = Brindley and Yamanaka, 1979. 4 = Pinnavaia *et al.*, 1985, and Tzou and Pinnavaia, 1988.

droxy-chromium solution at 60°C for 1 day of hydrolysis, the spacing obtained was 2.07 nm. Under this condition, the solution contained an abundance of trimeric species. Good basal spacings (1.99 nm) were also obtained with 2/20 polymeric solutions up to the maximum hydrolysis time studied. Longer hydrolysis times at a temperature of 60°C were not appropriate to obtain high basal spacings. Smectites treated with polymeric solution 36/60 developed a d(001)s of 1.34 and 1.98 nm. By scanning these solutions, it was found that there were more monomeric than trimeric species.

Rengasamy and Oades (1978), Brindley and Yamanaka (1979), Pinnavaia *et al.* (1985), and Tzou and Pinnavaia (1988) obtained a maximum of d(001) spacing of 1.40, 1.68, 2.70, and 2.76 nm, respectively, for OH–Cr-smectite with OH/Cr = 2. These differences could be attributed to different procedures followed by each author: i.e., preparation, hydroxy-chromium solution, hydroxy-chromium-smectite, and amount of Cr/sample.

Tzou and Pinnavaia (1988), using hydroxy-chromium solution from Na_2CO_3 with hydrolysis temperature 25°C for 3 weeks, obtained d(001) of 1.77 nm; whereas, our results were 1.99 nm. This could be attributed to a different preparation and pH. Carr (1985) obtained a basal spacing of approximately 1.47 nm using the solution OH/Cr = 1.

Figure 3 shows that E-2/20 and E-1/60 samples collapse at 500°C. It must be noted that E-1/60 sample was thermally more stable, and the d(001) shifted to 1.8 nm when reaching 350°C.

The following unit-cell formula corresponds to E-1/60 samples:

Table 3. Sample textural characteristics.

Sample	Surface BET (m^2/g)	V_{ad} (cm^3/g)	V_p (cm^3/g)	$V_{mic}(t)$ (cm^3/g)	V_p/V_{ad} (%)	V_{mic}/V_{ad} (%)
E	36	0.070	0.039	0.010	56	14
E-Cr	38	0.070	0.039	0.010	56	14
E-2/20	67	0.086	0.042	0.025	48	29
E-1/60	170	0.148	0.047	0.085	30	57
E-1/60 (350°C)	142	0.128	0.047	0.065	36	51

V_{ad} = adsorbed volume; V_p = pore volume; and V_{mic} = micropore volume.

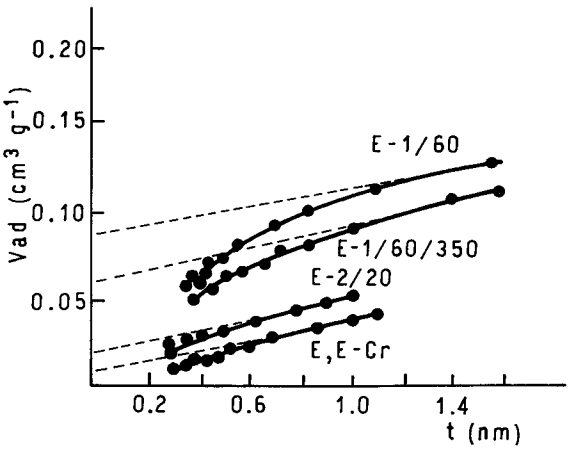


Figure 5. Vad-t plot of E, E–Cr, E-2/20, and E-1/60 samples as well as E-1/60 heated at 350°C.

$$(Cr(OH)_{2.48})_{1.58}(Si_{7.94}Al_{0.06})$$
$$(Al_{2.95}Fe_{0.18}Ti_{0.02}Mg_{0.8})O_{22}(OH)_4$$

where OH/Cr = 2.48 in the interlayer and OH/Cr = 2 in the solution hydroxy-chromium demonstrated that the Cr hydrolyzed in the clay was greater than in the solution. This was demonstrated by Brindley and Yamanaka (1979) and confirmed by Carr (1975) and Tzou and Pinnavaia (1988). The OH–Cr content in the interlayer could not at present be representative of the d(001) as shown in Table 2. However, this fact might be related to smectite selectivity for certain species.

The N_2 adsorption-desorption isotherms had the same shape as those measured before adsorption of hydroxy-chromium solutions. Although there was an increase in the initial volume adsorbed, this indicates that the texture of the smectite was preserved. The isotherm shapes corresponded to H3 type as shown in Figure 4. This type is a hysteresis loop with a vertical adsorption branch at a relative pressure very close to 1 and a desorption branch close to medium pressure. Such a hysteresis loop can be formed by very wide pores having narrow, short openings or by pores formed by parallel plates at the same distance from each other (slit-shaped pores) (Gregg and Sing, 1982).

The textural parameters resulting from the analysis of these isotherms are given in Table 3. An increase of the specific surface area of the smectite was observed with an increase of the hydrolysis temperature for the different hydroxy-chromium solutions. This value reached 170 m^2/g for E-1/60 samples. The total volume of adsorbed N_2, V_{ad}, increased to 0.148 cm^3/g from 0.070 cm^3/g. A decrease in the percentage of V_p/V_{ad} ratio indicates that the treatment brought about a microporous system. Table 3 and Figure 4 show that the original E and E–Cr samples have similar characteristics. The t-plot of all samples shows that the capillary condensation is not possible except at very high relative pressure (>0.86) since deviations occur from a straight

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line. The slope of the V_a-t-plot decreases (Figure 5). This indicates that they were formed by slit-shaped pores. On the other hand, the adsorption axis intercept of the extrapolated linear branch give the micropore contribution (Sing, 1970) and, when converted to a liquid volume, it may be considered as equal to the micropore volume itself. It is sometimes convenient to convert all the uptakes into liquid volumes before drawing the t-plots (Figure 5).

Table 3 shows the micropore contribution (V_{mic}) and the percentage of V_{mic}/V_{ad}. The last values indicate that, in the E-1/60 sample, more than 50% are micropores with a three-fold increase with respect to the original sample. Thermal stability of E-1/60 sample treated for 2 hr at 350°C yet maintains good textural characteristics (Figure 4 and Table 3).

CONCLUSIONS

OH–Cr smectites with different d(001)s were obtained by treating them with hydroxy-chromium solutions at different hydrolysis conditions (time and temperature). OH/Cr = 2 and Cr/g smectites remained unchanged in all the cases. The largest d(001) of 2.07 nm was obtained by treatment with a hydroxy-chromium solution prepared at 60°C with 1 day of hydrolysis. This solution had the maximum amount of trimeric species. The presence of monomeric species alone does not produce a high d(001) spacing.

The smectite texture was preserved after treatment with OH–Cr solutions, but treatment gives rise to a sample with a higher volume of micropores.

REFERENCES

Ardon, M. and Plane, R. A. (1959) The formation of a dinuclear Cr(III) species by oxidation of chromous solutions: *J. Am. Chem. Soc.* **81,** 3197–3200.

Barret. E. P., Joyner, L. G., and Halenda, P. H. (1961) The determination of pore volume and area distribution in porous substances. I. Computation from nitrogen isotherms: *J. Am. Chem. Soc.* **73,** 373–380.

Brindley, G. W. and Yamanaka, S. (1979) A study of hydroxy-chromium montmorillonites and the form of the hydroxy-chromium polymers: *Amer. Mineral.* **64,** 830–835.

Carr, M. R. (1985) Hydration states of interlamellar chromium ions in montmorillonite: *Clays & Clay Minerals* **33,** 357–361.

Finholt, J. E., Thompson, M. E., and Connick, R. E. (1981) Hydrolytic polymerization of Chromium(III). 2. A trimeric species: *Inorg. Chem.* **20,** 4151–4155.

Gregg, S. J. and Sing, K. S. W. (1982) *Adsorption Surface Area and Porosity:* Academic Press, London, 303 pp.

Kolaczkowski, R. W. and Plane, R. A. (1964) The characterization of $[Cr(H_2O)_4OH]_2^{+4}$ and its formation by oxygen oxidation of chromous solution: *Inorg. Chem.* **3,** 322–324.

Laswick, J. A. and Plane, R. A. (1959) Hydrolytic polymerization in boiled chromic solutions: *J. Am. Chem. Soc.* **81,** 3564–3567.

Lippens, B. C. and de Boer, J. H. 1965) Studies on pore systems in catalysts: *J. Catal.* **4,** 319–323.

Orr, C. and Dalla Valle, J. M. (1959) *Fine Particle Measurement Size, Surface, and Pore Volume:* The Macmillan Co., New York, 271 pp.

Pierce, C. (1953) Computation of pore size from physical adsorption data: *J. Phys. Chem.* **57,** 149–152.

Pinnavaia, T. J., Tzou, M. S., and Landau, S. D. (1985) New chromia pillared clay catalysts: *J. Am. Chem. Soc.* **107,** 4783–4785.

Rengasamy, P. and Oades, J. M. (1978) Interaction of monomeric and polymeric species of metal ions with clay surfaces. III. Aluminium (III) and Chromium (III): *Aust. J. Soil Res.* **16,** 53–66.

Sing, K. S. W. (1970) *Surface Area Determinations,* D. H. Everett and R. H. Ottewall, eds., Butterworths, London, 25 pp.

Stünzi, H. and Marty, W. (1983) Early stages of the hydrolysis of chromium(III) in aqueous solution. 1. Characterization of a tetrameric species: *Inorg. Chem.* **22,** 2145–2150.

Stünzi, H., Spiccia, L., Rotzinger, R. P., and Marty, W. (1989) Early stages of the hydrolysis of chromium (III) in aqueous solution. 4. Stability constant of the hydrolytic dimer, trimer, and tetramer at 25°C and I = 1.0 M: *Inorg. Chem.* **28,** 66–71.

Thompson, M. and Connick, R. E. (1981) Hydrolytic polymerization of chromium(III). 1. Two dimeric species: *Inorg. Chem.* **20,** 2279–2285.

Tzou, M. S. and Pinnavaia, T. J. (1988) Chromia pillared clays: *Cat. Today* **2,** 243–259.

Vaughan, D. E. W. and Lussier, R. J. (1980) (Preparation of molecular sieves on pillared interlayered clays(PILC)): Proceedings of the 5th International Zeolite Conference, L. V. C. Rees, ed., Heyden Press, London, 94–101.

Vaughan, D. E. W. (1988) Recent developments in pillared interlayered clays: in *Perspectives in Molecular Sieve Science,* W. H. Flank and T. E. Whyte, eds., American Chemical Society, Washington, D.C., 308–323.

Wheeler, A. (1955) Reaction rates and selectivity in catalysts pores: in *Catalysts, Vol. II,* P. H. Emmet, ed., Rainhold Publishing Corp., New York, p. 118.

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