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HYDROXY-CHROMIUM SMECTITE: INFLUENCE OF CR ADDED

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Abstract—OH-Cr smectites were prepared with different mmol Cr/g smectite: 0.5, 1.5, 3.5, 5, 10 and 20 by treatment with hydroxy-chromium solution prepared at 60°C and one day of hydrolysis with OH/Cr = 2. The samples were characterized by X-ray diffraction (XRD), differential thermal analyses (DTA) and N_2 adsorption-desorption isotherms.

The d(001) spacings of OH-Cr-smectite were different according to Cr added/g smectite. Larger d(001) spacings: 1.95, 2.05 and 2.07 nm were obtained with 5, 10 and 20 mmol Cr per gram of sample. DTA diagrams of smectite treated with OH-Cr solution showed exothermic peak at 420°C corresponding to Cr_2O_3 (confirmed by XRD). N_2 adsorption-desorption isotherms of smectite treated with different amounts of Cr preserved the same slit-shaped pores than original sample, but with different micropore volume. This behavior was maintained until treatment temperature of 380°C. The specific area of smectite was increased from 36 to 175 m²/g after treatment with OH-Cr solution. The textural characteristics of OH-Cr smectite heated up to 420°C were changed. The specific area decreased and mesopore volume was produced. The different Cr added modified the structural and textural behavior.

Key Words—DTA, Pillared clays, Smectite, XRD.

INTRODUCTION

Pillared clays (PILC) or cross linked smectite (CLS) have potential interest for catalysts and adsorbents. Rengasamy and Oades (1978), Brindley and Yamanaka (1979), Vaughan and Lussier (1980), Carr (1985), Pinnavaia *et al* (1988), Vaughan (1988), Tzou and Pinnavaia (1988), Drljaca *et al* (1992), Volzone *et al* (1993) wrote papers referred to OH-Cr-clay study. Species present in hydrolyzed chromium solution on preparation of OH-Cr smectite were observed by Drljaca *et al* 1992, Volzone *et al* 1993, but there are no references about amount of Cr added to smectite to obtain this one good textural and structural characteristic.

This paper studies the influence of the amount of Cr added to sample from hydroxy-chromium solution on textural and structural OH-Cr smectite.

EXPERIMENTAL

Hydroxy-chromium solutions were prepared from a 0.1 M chromium nitrate solution by the addition of 0.2 M NaOH (OH/Cr = 2). The addition was done slowly with continuous stirring at 60°C with hydrolysis time of one day (1/60).

Polymeric species in hydrolyzed chromium solutions were analyzed by pH measurement and absorption within the visible range (325–750 nm) in a Beckman DU 65 spectrophotometer.

The smectitic material (E) was supplied by Georgia Kaolin, Co. and was characterized in previous work (Volzone *et al* 1993). It corresponds to dioctahedral smectite with impurities of quartz and cristobalite in low proportions. The smectite species present were Cheto-type-montmorillonite (95%) and beidellite (5%).

Different E samples were dispersed in distilled water (2% w/w) and the fresh hydroxy-chromium solutions were added slowly with stirring. After two hours in contact with continuous stirring, the solids were separated. The 0.5, 1.5, 3.5, 5, 10 and 20 mmol Cr/g samples were prepared (E-0.5, E-1.5, E-3.5, E-5, E-10 and E-20). The supernatants S-0.5, S-1.5, S-3.5, S-5, S-10 and S-20 corresponding to the different treatments with 0.5, 1.5, 3.5, 5, 10 and 20 mmolCr/g of sample respectively were analyzed by spectrophotometer. The solids were washed several times with distilled water in order to remove the electrolyte excess. The differential thermal analyses (DTA) diagrams were carried out with a Netzsch apparatus using α-Al_2O_3 as a reference and a heating rate of 10°C/min.

The X-ray diffraction (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 powder aggregates samples were measured by scanning at 2° (2θ)/min between 3 and 70° (2θ). The d(001) were measured on oriented slide specimens by scanning at ½° (2θ)/min between 3 and 10° (2θ).

Adsorption-desorption isotherms were obtained at liquid nitrogen temperature with N_2, in a Micromeritics Accusorb equipment. Specific surface area (S_{BET}) was calculated from the first part of the isotherm ($P/P_o < 0.3$) using 0.162 nm² 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). In the t-plot method was plotting, the volume of nitrogen adsorbed/g solid adsorbent against the corresponding statistical thickness,

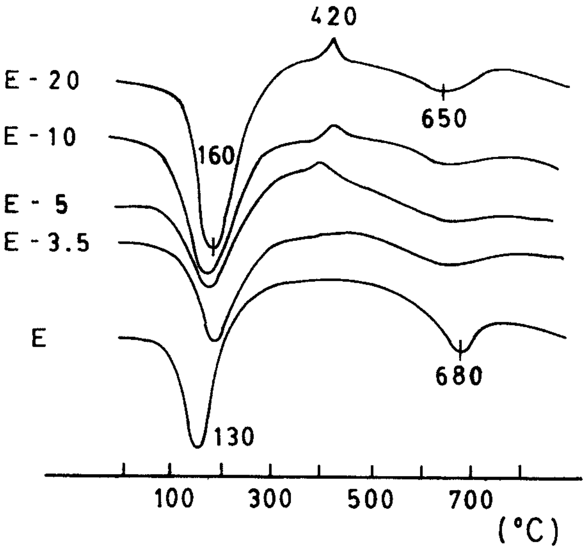

Figure 1. DTA diagrams of E and E treated with OH-Cr solution and with different mmol Cr/g of samples.

t, of the adsorbed layer of nitrogen on a nonporous reference solid.

RESULTS AND DISCUSSION

Figure 1 shows the thermograms (DTA) of the E and E treated with different mmol Cr/g sample. The large endothermic peak around 130°C for E sample was produced by dehydration of the clay (water intercalated between layers) (Grim and Kulbicki 1961). This peak shifted at 150–160°C when species OH-Cr were present. It was attributed to dehydration of oligomerics species (Spiccia 1988). The exothermic peak presented around 420°C corresponded to the dehydration of hydroxy-Cr species and then crystallization of Cr_2O_3 occurred. This was checked with XRD. The endothermic peak at 680°C was produced by OH loss of smectite structure(E). Such peak was shifted 680°C to 650°C when the OH-Cr species were intercalated into smectites, with broading peak. This peak would depend among others, on perfection of stacking of the layers and gross substitution. Loeppert and Mortland (1979) noted that the presence of Ni^{+2} intercalate into smectites had marked influence in increasing the rate of the dehydroxylation reaction.

Table 1. Sample structural characteristics with thermal treatment.

	Temperature(°C)				
Sample	25	160	380	420	1000
E	Smectite; d(001): nm				Anorthite
	1.49	1.20	1.20	1.00	Cordierite
	← α-quartz (impuritie) → ← α-Cristobalite (impuritie) →				β-Cristobalite
E-10	Cr-Smectite; d(001): nm				Cordierite
	2.05	1.90	1.84	1.40	β-Cristobalite
	← α-quartz (impuritie) → ← α-cristobalite (impuritie) →				Cr_2O_3
				Cr_2O_3	

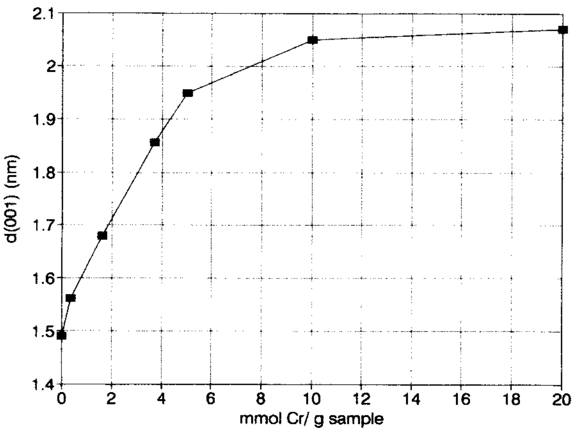

Figure 2. d(001) spacings of E and E treated with OH-Cr solution and with different mmol Cr/g of samples.

Figure 2 shows the d(001) spacings of OH-Cr-smectite treated with 1/60 solutions according to different added mmol Cr/g of smectite. The mother liquid (1/60) contained abundant trimeric species and tetra-, mono-, and dimer (Volzone *et al* 1993). Small amount of Cr added did not produce higher spacings and it was possible that the amount of suitable species present in solution were not sufficient. The d(001) spacings of 2.05, 2.07 for 10 and 20 mmol Cr added/g of sample respectively would correspond to gallery heights of 1.09–1.11 nm. According to Spiccia (1987, 1988) and Stünzi (1983) dimer, trimer and tetramer have depth 0.4, 0.5 and 0.65 nm respectively, then perhaps two layers of species were intercalated between montmorillonite layer. It was demonstrated that smectite treated with 20 mmol Cr monomeric species/g sample gave spacing 1.5 nm, whereas with same 20 mmol Cr added/g of sample, but from hydrolysis solution 1/60, the spacing was 2.07 nm (Volzone *et al* 1993).

Table 1 shows the structural characteristics of E and E-10 samples and after thermal treatment heated through DTA(160, 380, 420 and 1000°C). The α-quartz and α-cristobalite were impurities of the samples. The smectite structure was preserved with thermal treatment until about 800°C. The montmorillonite heated within the range of 25° to 420°C showed a decreasing and shifting in the intensity of the (001) reflection from 1.49 nm to 1.00 nm for original sample (E) and from 2.05 nm to 1.40 nm for E-10, respectively. In sample, treated with OH-Cr-solution (E-10) and after 380°C it was not possible to observe Cr-species by XRD, but at 420°C, the spacings of 0.266, 0.248, 0.167, 0.363,

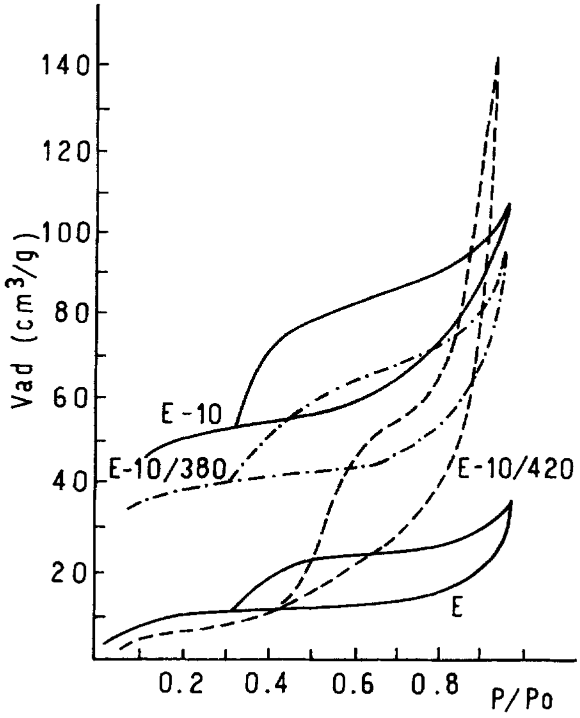

Figure 3. Nitrogen adsorption-desorption isotherms of E, E-10, E-10/380°C and E-10/420°C samples.

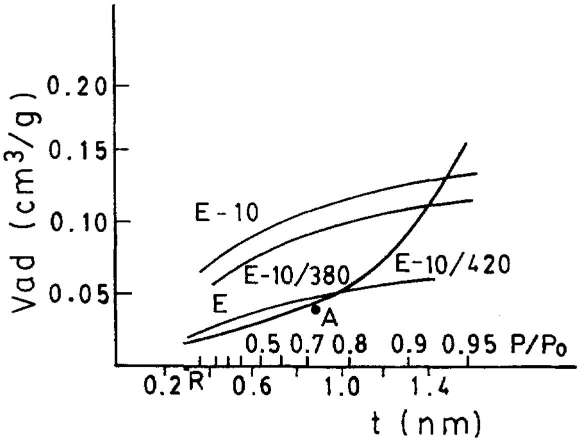

Figure 4. t-plot of E, E-10, E-10/380°C and E-10/420°C samples.

0.143, 0.181, 0.216 and 0.205 nm confirmed the Cr_2O_3 specie present with simultaneously exothermic peak in DTA. Cordierite, β cristobalite and anorthite phases were developed in E sample at 1000°C. In E-10 sample also Cr_2O_3 remained. Only anorthite phase ($Ca.Al_2Si_2O_8$) was not present. This could be attributed to the fact that the exchangeable Ca present in original sample (E) was replaced during treatment with OH-Cr solution by Cr, (E-10), and then anorthite phase was not possible at higher temperatures. The structural behavior with the thermal treatment in E-5 and E-20 samples was similar to E-10 sample.

N_2 adsorption-desorption isotherms of E treated with different hydrolysis mmol Cr/g of sample in natural and heated up to 380°C had the same shape as those measured before adsorption of hydroxy-chromium solutions indicating that the texture of the smectite was preserved. Those isotherm shapes were H3 type and corresponded to the system formed by slit-shaped pores (Gregg and Sing 1991). In Figure 3, N_2 adsorption-desorption isotherms for E, E-10 and E-10/380 and E-10/420 are shown. The treatment with OH-Cr solution (E-10) introduced micropores into the solid. The uptake was enhanced in the low pressure region. When the solid was heated up to 380°C the micropores slightly diminished. The E-10/420 isotherm showed a sharp decreasing in surface area and an important change in the shape of the isotherms occurred but it was not easy to ascribe the type of hysteresis to the loops, perhaps because of the tubular though short pores with widened parts were present (similar H1 type, Gregg and Sing 1991). The material took up more adsorbate than the corresponding to the volume of the multilayer.

The t-plot for E, E-10 and E-10/380 samples (Figure 4) indicated that the capillary condensation was not possible except at very high relative pressure (>0.95). Those curves result when narrow pores were filled at low relative pressures by multilayer adsorption there by reducing the available surface for continued adsorption. In E-10/420 the condensation into pores commences where the slope starts to increase (point A, Figure 4) at $P/P_0 \simeq 0.73$ (pore radius: 4 nm). Such sample showed mesopore systems with condensation of N_2 in very small pores at low relative pressure where

Table 2. Surface area calculated with the BET equation and from t-plot. (*) from Kelvin equation.

	Specific area (m²/g)			
	E	E-10	E-10/380	E-10/420
BET	36	175	141	50*
Sme	38	170	135	35
Se	25	32	30	—
Sm	7	138	105	—

Table 3. Sample textural characteristics. Vad: adsorbed volume; Vp: pore volume; Vmic: micropore volume.

Sample	Vad (cm³/g)	Vp (cm³/g)	Vmic(t) (cm³/g)	Vp/Vad (%)	Vmic/Vad (%)
E	0.070	0.039	0.010	56	14
E-10	0.178	0.087	0.090	49	54
E-10/380	0.157	0.091	0.064	58	41
E-10/420	0.25	0.238	0.015	95	6

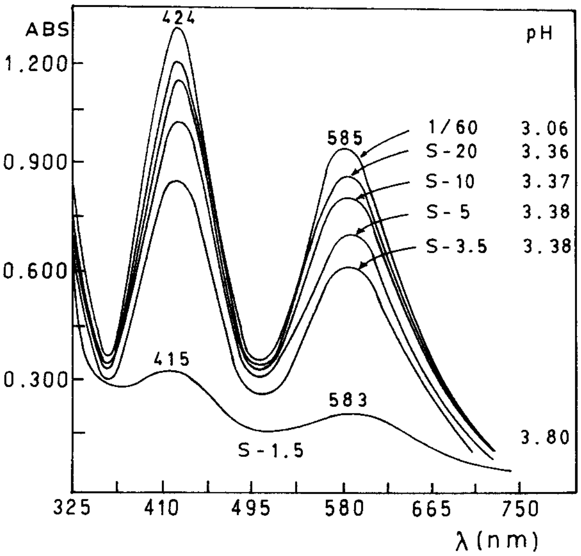

Figure 5. Absorption in visible spectra and pH of OH-Cr solution: 1/60, and supernatant after treatment with different mmol Cr per gram of sample.

the BET method assumes only multilayer adsorption. It was convenient to apply Kelvin law which is not related to the energies of adsorption but to the pore radius. The accumulative surface of the pores appears then as more satisfactory than the BET surface area (Figueras 1988).

Information concerning the micropore system and the external surface of solids which is not obtainable by methods such as the BET method, could be obtained by the t-plot. The slope of the linear branch at high pressure can be used to calculate the external surface area of the solid, Se (Gregg and Sing 1991). The slope of the line drawn from the origin to the "monolayer point" ($t = 0.35$ nm, point R, Figure 4), could be used to calculate the surface area of the micropores and the external surface, Sme (Dandy and Nadiye-Tabbiruka 1975). The Table 2 shows the surface area calculated with the BET equation and from t-plot. The smectite treatment with OH-Cr solution (1/60) and 10 mmol Cr/g of sample (E-10) produced a BET surface increased of 175 m^2/g from 36 for untreated smectite (E). When the sample was heated up to 380°C (E-10/380) the characteristics changed slightly with decreased surface to 141 m^2/g. The surface area corresponding to E-10/420 was calculated according to Kelvin law. Micropore surface, Sm, was obtained by differences between Sme and Se. The treatment with OH-Cr solution origined higher micropore surface (Sm:138 m^2/g) and after heated up to 380°C yet its contributions were important (Sm: 105 m^2/g).

The similar Se values for E, E-10 and E-10/380 (25, 32 and 30 respectively) indicated that the greater differences between these samples were attributed to the micropores contribution.

The high-pressure branch extrapolated to the adsorption axis in t-plot gives a positive intercept which is equivalent to the micropore volume (Vmic). The pore volume and adsorption volume ratio (Vp/Vad), for E-10, indicated that the treatment generated a microporous system (Table 3). The micropore volume from t-plot and adsorption volume ratio (Vmic/Vad) increased with respect to the original sample E indicating that the micropore contribution was four times major. The pore volume (Vp) of E-10/420 increased but textural characteristics changed largely and then the higher contribution was produced by the mesopores. Though Vmic of E-10/420 was similar to the original sample E, the Vad was very higher and then Vmic/Vad ratio was smaller (6 respect to 14, Table 3). Then mesoporous in E-10/420 system was created.

Figure 5 shows the characteristic spectra in the visible zone of fresh OH-Cr solutions at 60°C and one day of hydrolysis (1/60) and supernatants corresponding to treatment with different mmol Cr/g of sample (S-1.5, S-3.5, S-5, S-10 and S-20). The supernatant corresponding to treatment to 0.5 mmol Cr/g of sample (S-0.5) was colorless and then not shown bands in the spectrum. The 1/60 solution had one band at 424 nm and other band at 585 nm. In that solution trimeric species were the principal ones followed by tetra-, mono-, and dimer. The spectra to supernatant solutions had two bands in the same positions but with different intensity.

It is seen from Figure 5 that the spectrum of S-1.5 differs from that of all supernatants. A shift of the peaks to smaller wavelength and decreased absorbancy was observed. Such trends could indicate that species in S-1.5 were less highly polymerized forms. Then, certain selectivity of the smectite to retain specific polymerized species could occur; though, if necessary, other species will be retained. It was demonstrated when 0.5 mmol Cr/g of sample were treated, its supernatant, S-0.5, did not show Cr species. The smectite retained all species.

In the same Figure 5, the pH of solution is indicated. The 1/60 solution had pH: 3.06. After the smectite treatment with OH-Cr solution, 1/60, the pH of supernatants increased with decreasing of mmol Cr/g of sample. The S-0.5 had pH: 6.80. The supernatants had Na, K and Ca exchangeable cation from smectite that were removed by treatment with OH-Cr solution, 1/60. The Na_2O, K_2O and CaO from original sample (E) were 2.52, 0.79 and 1.81% respectively. After treatment with OH-Cr solution, those cations were removed and 0.06, 0.28 and 0.05% were determined respectively. The different cations and pH of the supernatants did not permit to evaluate with certainty in such solutions the OH-Cr-species present.

The percentage of decreasing absorption of two bands in visible spectrum of 1/60 solution after treatment

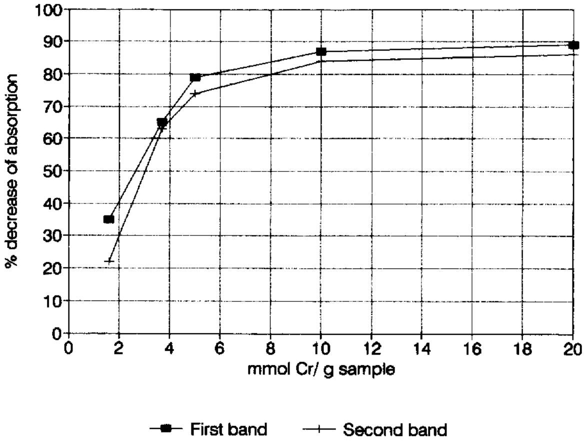

Figure 6. % decrease of absorption bands of OH-Cr solution 1/60 after treatment with different mmol Cr per gram of sample.

with different mmol Cr/g of sample, is shown in Figure 6. When the smectite was treated with solutions 1/60 in condition of minor 5 mmol Cr/g of sample, the absorption of two bands quickly decreased. The solution 1/60 after treatment according 0.5 mmol Cr/g of sample was colorless. That is the smectite retained all Cr species.

The structures of the mono, dimer, trimer and tetramer species have the composition Cr^{+3}, $Cr_2(OH)_2^{+4}$, $Cr_3(OH)_4^{+5}$, $Cr_4(OH)_6^{+5/+6}$, respectively (Stünzi 1989). According to the species present in solution 1/60, it was possible to estimate the average meq Cr added per gram of sample. When 0.9 meq of Cr was added/g of sample, the d(001) spacings were slightly higher (1.57 nm) than that of the original sample E (1.49 nm) and the sample retained all Cr because the supernatant was colorless. To produce d(001) spacing around to 2.00 nm it was necessary to add higher 10 meq Cr/g of sample. Then the amount and quality of species present were important to produce good characteristics.

CONCLUSIONS

Larger d(001) spacings of smectite, 1.95 to 2.07 nm, treated with OH-Cr solution prepared at 60°C during one day of hydrolysis were obtained with 5 to 20 mmol Cr added per gram of sample.

The smectite treated with different amount of Cr preserved the same textural characteristics than the original sample (slit shaped pores), but with different micropore volume. Such characteristics were conserved up to 380°C thermal treatment. Heating up to 420°C a new phase appeared: Cr_2O_3 specie, and textural properties changed with diminution of micropore volume.

The different Cr added modified the structural and textural behavior.

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