

A study of hydroxy-chromium montmorillonites and the form of the hydroxy-chromium polymers

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Abstract

Polymeric hydroxy-chromium cations are prepared from chromium nitrate solutions by addition of NaOH to yield OH/Cr ratios 0, 0.5, 1.0, 1.5, 2.0. Hydroxy-chromium montmorillonites are obtained by ion-exchange reactions, and the compositions of the interlayer hydroxy complexes are derived from chemical analyses of the products. Even without addition of NaOH to the chromium nitrate solution, the exchanged Cr ions are partially hydrolyzed within the clay and have a composition near $[\text{Cr}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$. As the ratio OH/Cr in the nitrate solution is increased, polymeric cations are formed in the clay with increasing numbers of Cr ions and with a higher ratio of OH/Cr than in the external solution. With increasing polymerization of the interlayer material, the basal spacings of the montmorillonites increase to about 16.8Å and are stable to about 200°C. Surface areas of the 200°C heated montmorillonites, determined by N₂ absorption, increase linearly with the basal spacing up to about 280 m²/g when the spacing is near 16.8Å.

Introduction

Two methods have been used for preparing hydroxy-metal interlayers in expanding layer silicates: (i) a direct cation-exchange method, and (ii) a titration procedure. In previous studies, hydroxy-aluminum beidellite (Brindley and Sempels, 1977) and hydroxy-zirconium montmorillonite (Yamanaka and Brindley, 1979) were prepared by method (i). Polymeric cations of hydroxy-aluminum were obtained by adding NaOH solution to AlCl₃ solutions to provide desired ratios of OH/Al, and tetrameric cations of hydroxy-zirconium were obtained from a zirconyl chloride solution (Muha and Vaughan, 1960). The hydroxy cations were incorporated in the interlayer spaces probably in the form $[\text{Al}_6(\text{OH})_{16}\cdot n\text{H}_2\text{O}]^{2+}$ and $[\text{Zr}_4(\text{OH})_{14}\cdot n\text{H}_2\text{O}]^{2+}$ respectively.

Hydroxy-nickel montmorillonite (Yamanaka and Brindley, 1978) was prepared by method (ii). Hydroxy-nickel was precipitated preferentially in the interlayers of montmorillonite when Ni(NO₃)₂ solution was titrated in the presence of montmorillonite. A mechanism for the preferential precipitation has been proposed on the basis of the acidic properties of the interlayer water.

In continuation of these studies, an investigation of hydroxy-chromium montmorillonite has been made. Chromium is one of the few cations which can be hydrolyzed extensively to form polynuclear cations. Hydroxy-chromium montmorillonites have been prepared by method (i), using chromium nitrate-NaOH solutions with a range of basicities.

Experimental procedures

Hydroxy-chromium solutions with basicities OH/Cr = 0, 0.5, 1.0, 1.5, 2.0, were prepared by titrating 50 ml of 0.1M Cr(NO₃)₃ solutions with appropriate volumes of 0.1N NaOH. The titrations were made slowly and with frequent stirring to avoid formation of hydroxy precipitates by local concentrations of NaOH. After titration, each solution was diluted to 150 ml with distilled water and was allowed to stand for 10 days. It was assumed that equilibrium was attained in this period. The solutions thus prepared have the same total concentration of chromium.

Separate samples of 300 mg of Na-montmorillonite (a Wyoming montmorillonite supplied by the American Colloid Company under the name "Volclay," as used in our previous studies) were dispersed in 10.0 ml of distilled water, and 50.0 ml of hydroxy-chromium solution was added. After stand-

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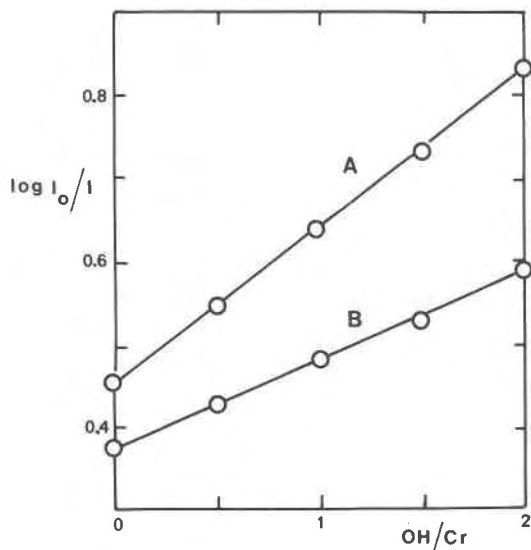


Fig. 1. Increase of intensity of the two absorption bands of chromium nitrate solutions, A at 425 nm and B at 587 nm, with increase in basicity of the solutions, OH/Cr.

ing for 3 days with occasional shaking, the supernatant liquids were separated by centrifugation, and the visible absorption spectra were recorded. The spectra were compared with those of the mixtures of 50.0 ml of initial hydroxy-chromium solutions and 10.0 ml of distilled water to determine the amount of chromium taken up by the montmorillonite. To ensure completeness of reaction, the exchange procedure was repeated and the resulting solids were washed several times with distilled water to remove excess electrolyte. Total chemical analyses of the twice-treated samples were made by the atomic absorption method using a lithium borate fusion technique.

The expansion of the montmorillonite basal spacing by exchange of hydroxy-chromium ions and the subsequent collapse by heat treatment to 500°C were followed by X-ray diffraction of thin layers of the

Table 1. Uptake of Cr³⁺ ions from hydroxy-chromium solutions by Na-montmorillonite, in me/100g clay

OH/Cr, in Solution	Uptake of Cr ³⁺ ions	
	1st exchange	2nd exchange
0	111	119
0.5	280	295
1.0	327	420
1.5	420	560
2.0	590	750

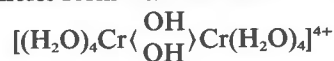
clay on glass slides. Usually only the first-order reflections corresponding to spacings in the range 10–18 Å were measurable. Higher orders were weak and broad and indicated variable basal spacings and possibly variable sorption between the layers.

Surface areas were determined by nitrogen sorption, using a Quantasorb surface area analyzer. Samples were degassed at 200°C for 2 hr by flowing dry N₂ gas prior to sorption measurements.

Results

Hydroxy-chromium complexes in solution

Chromium nitrate solution with no added base is red-purple with two optical absorption bands at 413 and 577 nm. The color is due mainly to monomeric Cr³⁺ ions. As the basicity of the solution increases, the absorption maxima shift to 425 and 587 nm and the color changes to blue-green and then to deep green until hydroxy-chromium precipitates begin to form near OH/Cr ≈ 2.3. Polymeric species in hydrolyzed chromium solutions were studied by Laswick and Plane (1959), who identified the blue-green species as a dimeric form with an olated link,



and the deep green species were attributed to higher polymeric forms. The intensities of the absorption bands increase linearly with the basicity of the solutions (Fig. 1). The absorption bands are probably related to the number of olated links, which increase with the basicities of the solutions.

Chemical analyses of products

The total chemical analyses of the products after two treatments showed that appreciably more chromium was taken up than after a single treatment, especially for solutions having OH/Cr > 1.0. The results are shown in Table 1.

The total chemical analyses and derived formulae are given in Table 2. The weight loss of samples from room conditions (20°C, 40–50 percent RH) to 110°C is recorded as H₂O–. The loss from 110–1000°C is given as H₂O+. Iron was determined wholly as Fe₂O₃ and chromium as Cr₂O₃. The formula of the initial Na-montmorillonite is derived on the basis of a total cation valence of +22 and anions O₁₀(OH)₂. The composition conforms closely to the usually-accepted formula for montmorillonite. The layer charge is +0.32 per formula unit. Formulae for the hydroxy-chromium montmorillonites are obtained by assum-

ing no change in the interlayer composition. The results lead directly to the composition of the interlayer material. The ratio OH/Cr in the interlayer material increases considerably more rapidly than the ratio in the solutions (Fig. 2).

X-ray diffraction data for hydroxy-chromium montmorillonites

With thin oriented layers of the hydroxy-chromium montmorillonites on glass slides, only the first-order basal reflections were clearly observed. The breadths of the diffraction maxima and the general absence of higher orders suggest irregular layer spacings. The measured spacings, therefore, must be regarded as average values. The complexes are stable to about 200°C, but at 300°C they collapse to about 10.4 Å and at 400°C reach a minimum value of 9.8 Å. The basal spacings for the different prepared samples are shown in Figure 3. The maximum spacing corresponding to $(\text{OH}/\text{Cr}) = 2.0$, *i.e.*, with the most highly polymerized interlayer material, is 16.8 Å.

Table 2. Chemical analyses and structural formulae of Na-montmorillonite and hydroxy-Cr montmorillonites obtained with various initial OH/Cr solution ratios

	Na-mont.	Hydroxy-Cr montmorillonites				
		OH/Cr=0	0.5	1.0	1.5	2.0
SiO ₂	60.6	55.2	51.4	49.2	49.1	45.4
Al ₂ O ₃	21.2	19.6	18.3	17.6	17.5	16.2
Fe ₂ O ₃	4.10	3.63	3.41	3.27	3.27	3.06
MgO	2.59	2.22	2.08	2.00	1.99	1.87
CaO	0.00	n.d.	n.d.	n.d.	n.d.	n.d.
Na ₂ O	2.54	0.00	0.00	0.00	0.00	0.00
Cr ₂ O ₃	n.d.	2.6	6.2	8.4	11.1	13.8
H ₂ O(+)	6.04	7.73	8.98	9.38	9.68	10.76
H ₂ O(-)	2.81	9.15	10.54	10.42	8.59	9.76
Total	99.88	100.13	100.91	100.27	101.23	100.85
Compositions per formula unit containing 0 ₁₀ (OH) ₂						
Si	3.93	3.93	3.92	3.92	3.93	3.92
Al ^{IV}	0.07	0.07	0.08	0.08	0.07	0.07
Al	1.55	1.57	1.56	1.57	1.57	1.57
Fe	0.20	0.19	0.20	0.20	0.20	0.20
Mg	0.25	0.24	0.24	0.24	0.24	0.24
Interlayer compositions and ratios						
Na	0.32	-	-	-	-	-
Cr	-	0.15	0.37	0.53	0.70	0.94
OH	-	0.13	0.79	1.27	1.78	2.50
H ₂ O	0.31	0.77	0.89	0.86	0.70	0.85
OH/Cr	-	0.87	2.14	2.40	2.54	2.66
(OH + H ₂ O)/Cr	-	6.00	4.54	4.02	3.54	3.56

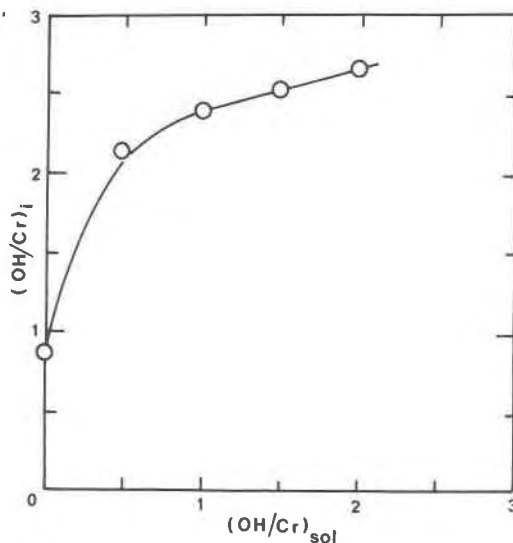


Fig. 2. Relation between $(\text{OH}/\text{Cr})_i$ in the interlayer material, and $(\text{OH}/\text{Cr})_{\text{sol}}$ in the initial chromium nitrate solution.

This value is appreciably greater than would be expected for a montmorillonite with a hydroxide interlayer which, as in chlorites, would give a basal spacing of about 14.2–14.4 Å.

Surface areas by N₂ absorption

Figure 4 shows the surface areas, *S*, in m²/g plotted against basal spacing for samples heated to 200°C. A nearly linear relation is obtained. The highest area obtained is about 280 m²/g or about 35

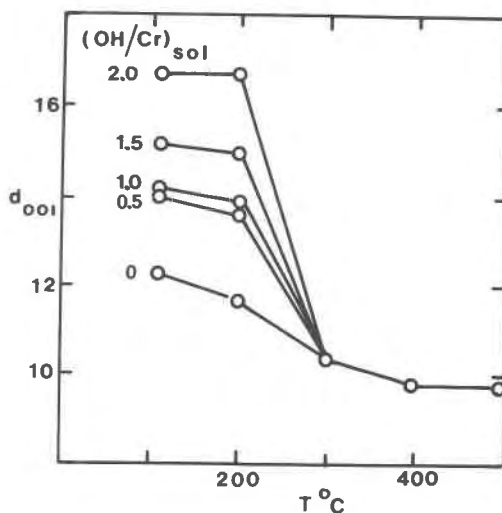


Fig. 3. Basal spacings, d_{001} in Å, of hydroxy-chromium montmorillonites prepared with different ratios (OH/Cr) in solutions, plotted against temperature T of heat treatment in °C.

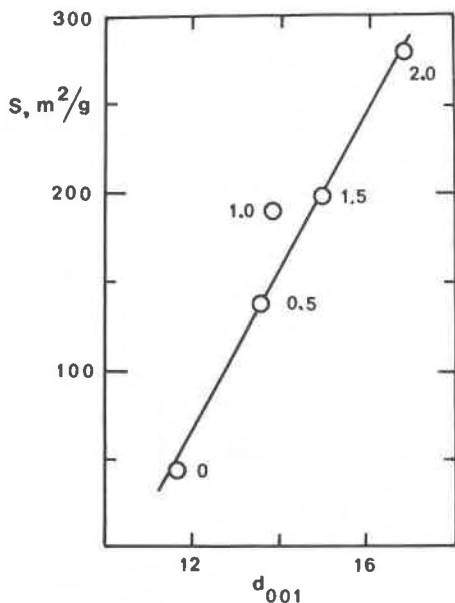


Fig. 4. Surface areas S , in m^2/g , of hydroxy-chromium montmorillonites after heating to 200°C . Numbers opposite each data point indicate the initial OH/Cr ratios in solution.

percent of the total layer surface, internal and external, of montmorillonite.

Discussion

Hydrolysis of chromium ions in montmorillonite

Figure 2 shows that the ratio OH/Cr of the interlayer material is greater, sometimes considerably greater, than the corresponding ratio in the solution. Although a cation-exchange reaction is involved, as shown by the complete removal of Na^+ ions from the montmorillonite, the interlayer conditions must greatly increase the hydrolysis of the Cr ions. Similar non-linear relations have been found in previous studies. In a study of hydroxy-aluminum smectites, Veith (1978) pointed out that the average basicity of the aluminum taken up by the smectites was higher than that of the hydroxy-aluminum solution. His finding is consistent with the previous work on hydroxy-aluminum beidellite (Brindley and Sempels, 1977). The species present in zirconyl chloride solution is $[\text{Zr}_4(\text{OH})_8 \cdot n\text{H}_2\text{O}]^{8+}$, but the species incorporated in montmorillonite is near $[\text{Zr}_4(\text{OH})_{14} \cdot n\text{H}_2\text{O}]^{2+}$ (Yamanaka and Brindley, 1979). A similar result was observed in the formation of $\text{Ni}(\text{OH})_2$ internally in montmorillonite without precipitation in the external solution until the interlayers became filled with $\text{Ni}(\text{OH})_2$ (Yamanaka and Brindley, 1978). The suggested explanation involved a partial dissociation of

H_2O adjacent to Ni^{2+} ions in the interlayers, so that $\text{Ni}^{2+} + \text{H}_2\text{O} \rightarrow [\text{Ni}(\text{OH})]^+ + \text{H}^+$ with concomitant exchange of 2H^+ by Ni^{2+} and a continued reaction.

A similar reaction with Cr^{3+} ions is even more likely to occur because of the three-fold charge. The analytical results show that before the addition of NaOH to the external solution, the interlayer composition (see Table 2) is $\text{Cr}_{0.15}(\text{OH})_{0.13}(\text{H}_2\text{O})_{0.87}$, or $[\text{Cr}(\text{OH})_{0.87}(\text{H}_2\text{O})_{5.13}]^{2.13+}$ which is close to $[\text{Cr}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$. In other words, Cr^{3+} ions in solution become divalent hydroxy ions when exchanged into montmorillonite. The composition suggests an octahedral coordinated group around each Cr ion, but the basal spacing of about 12A at 110°C indicates that the OH and H_2O are probably co-planar.

Interlayer polymeric complexes

The fact that the ratio OH/Cr in the interlayer material tends towards the value 3 as the external basicity increases suggests that the interlayer composition tends towards a trihydrate composition, $\text{Cr}(\text{OH})_3$, analogous to that in the gibbsite structure. However, at the highest external ratio of OH/Cr which can be used without precipitation occurring, the number of interlayer Cr ions per formula unit is less than one-half the number required for complete dioctahedral hydroxide interlayers. Therefore the polymeric species are by no means continuous hydroxy-interlayers but must be of relatively small extent and associated with the remaining water not removed at 110°C .

This situation is quite different from that obtained with hydroxy-nickel interlayers, where it was possible to form a nearly complete $\text{Ni}_3(\text{OH})_6$ interlayer, or more correctly an interlayer $[\text{Ni}_3(\text{OH})_{5.68}(\text{H}_2\text{O})_{0.32}]^{0.32+}$ where the resultant charge $+0.32$ balances the negative layer charge. By analogy, a similar hydroxy-chromium interlayer would have the composition $[\text{Cr}_2(\text{OH})_{5.68}(\text{H}_2\text{O})_{0.32}]^{0.32+}$, but in fact the highest hydroxy-Cr content is $[\text{Cr}_{0.94}(\text{OH})_{2.50}(\text{H}_2\text{O})_{0.85}]^{0.32+}$. Evidently there will be a distinctly porous structure in the hydroxy-chromium montmorillonite, which is reflected in the large surface area found by N_2 gas absorption.

To determine the possible form of the interlayer complexes, we will assume that the water remaining after drying at 110°C is associated with the hydroxy-chromium complexes, that each Cr ion is octahedrally coordinated with six (OH + H_2O), and that the coordination groups are linked by edges as in the hydroxide layer structures. The shared octahedral edges will involve pairs of OH ions linking adjacent Cr

ions, and the remaining OH and H₂O will occupy non-linking positions. Figure 5 shows some simple polymeric forms, and the (OH + H₂O)/Cr ratios for these models are compared with the values given in Table 2. The results suggest that, with increasing basicity of the external solutions, the internal polymeric complexes progress quickly toward ring-shaped groups with six or seven Cr ions. Similar results have been discussed for hydroxy-aluminum complexes by Pa Ho Hsu and Bates (1964), by Brindley and Sempels (1977), and other investigators mentioned by these authors.

In view of the complexity of the hydrolytic chemistry of Cr, however (see, for example, Earley and Cannon, 1965, p. 64 *et seq.*), it is certainly necessary to be cautious in the interpretation of the chemical analyses of the interlayer complexes, and this is particularly necessary as regards the hydroxy monomeric complex apparently formed prior to addition of NaOH to the external solution. It is noted that a dimer form predominates over a monomer at equilibrium in partially hydrolyzed solutions. The dimer form has a ratio (OH,H₂O)/Cr = 5, whereas the interlayer composition before addition of NaOH is close to Cr(OH)(H₂O)₅. If dimers were present to any appreciable extent, considerable additions of H₂O also would be required to bring the average ratio (OH,H₂O)/Cr from 5 to 6, and such an interpretation would be equivalent to regarding the observed ratio of 6 as being largely fortuitous; furthermore the additional water would have to be held in the interlayers at 110°C. As regards the more highly polymerized forms, it is reasonable to consider that various forms may be present.

Surface areas, basal spacings, and polymeric complexes

It remains to bring together these physical and chemical data into a single coherent picture. There are, however, serious difficulties. In the first place, if the hydroxy-chromium complexes are of the form shown in Figure 5, a basal spacing of the order of 14.5Å would be expected, similar to that in chlorites but slightly larger because of the weaker electrostatic attraction between the silicate layers and the hydroxy interlayers. In fact, the basal spacings after heating at 110° and 200°C are considerably larger, up to 16.8Å, as seen in Figure 3. The basal spacings are probably variable, because of the breadth of the first observed diffraction and the weakness or absence of higher orders. Therefore some spacings may be greater and






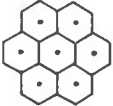
		(OH + H ₂ O)/Cr	
		model	obs.
		6.0	6.0
		5.0	
	}	4.67	4.54
		4.33	
		4.00	4.02
		3.43	3.56 3.54

Fig. 5. Possible polymeric forms of hydroxy-chromium complexes formed by edge-sharing octahedral groups of six (OH + H₂O) surrounding chromium ions. The full octahedral group is shown only in the uppermost diagram; in other diagrams it is indicated by the hexagonal outline. The chromium ion is indicated by the central dot in each occupied octahedron.

others less than 16.8Å in order to give an average value of 16.8Å. Conceivably the large surface area available to N₂ absorption may arise from the larger spacings. The linear decrease of surface area with decrease of the basal spacing, as shown in Figure 4, may be due to a diminishing proportion of wider spacings as the average spacing diminishes. Arguments along these lines imply an inhomogeneous model. That most montmorillonites have an inhomogeneous charge distribution is now well established from the work of Lagaly and Weiss (1970, 1975), and of Stul and Mortier (1974), and therefore the present argument is not disqualified because it suggests that inhomogeneity may be a significant feature of the hydroxy-chromium montmorillonites. However, it is still not obvious how a proportion of larger spacings may be developed from the hydroxy-chromium complexes, unless they arise from the way the complexes are distributed in order to balance the layer charges most effectively.

It is evident that more detailed studies will be required before we can show in detail how the lattice

spacings, the surface areas, and the hydroxy complexes are interrelated.

Acknowledgments

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