Intercalation of Montmorillonite with Individual Chromium(III) Hydrolytic Oligomers

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Introduction

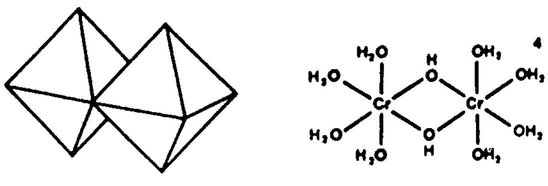
Renewed interest in the application of pillared clays has resulted from the synthesis of expanded clays, in which clay layers are held apart by robust metal oxide pillars.[1,2] These pillared clays can mimic the sorptive and some of the catalytic properties of zeolites. Unlike zeolites, however, their pore size can, in principle, be adjusted to suit the steric requirements of guest molecules.[2]

Pillared clays are generally prepared by incorporation of soluble polynuclear species into the clay layers, followed by heat treatment to generate the metal oxide pillars. Recent work on Al(III),[3] Ti(IV),[4] and Zr(IV)[5] pillared clays has resulted in materials with d_{001} spacings of 16–20 Å. Chromium pillared clays are of great interest because the chromia pillars could provide catalytically active sites additional to those inherent in the clay. Cr(III) pillared clays have been previously synthesized with d_{001} spacings of 17–28 Å and have been found to catalyze the dehydrogenation of cyclohexane to benzene and decane hydrocracking.[6] Chromium K-edge EXAFS studies[7] have probed the gross structural features of intercalated Cr(III) species and have provided evidence for the partial oxidation of Cr(III) during heat treatment. In all these studies, intercalation solutions were prepared by aging of partially neutralized Cr(III) solutions at temperatures up to 100 °C, a process which generates a range of polynuclear species.[8] On intercalation, a mixture of species is likely to be incorporated between the clay layers.

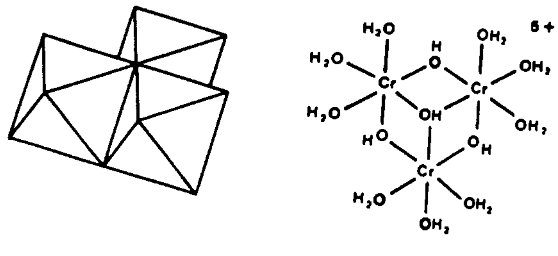
Recently, the separation and characterization of several Cr(III) oligomers have been reported.[8-10] The preparation of Cr(III) pillared clays by intercalation of individual Cr(III) oligomers into, for example, montmorillonite should generate products with reproducible properties. Since the structure (size) and charge of the oligomers are known, it should be possible to define the pillaring process more precisely. Thus, it becomes possible to study the variation in d_{001} spacing with oligomer nuclearity, to assess the orientation of the oligomer within the clay layer, and to compare the observed pillar density with that expected from the charge density on the clay surface. The results of studies on the intercalation of the Cr(III) hydrolytic dimer (**1**), trimer (**2**), and tetramer (**3**) (Chart I) are reported here.

Chart I

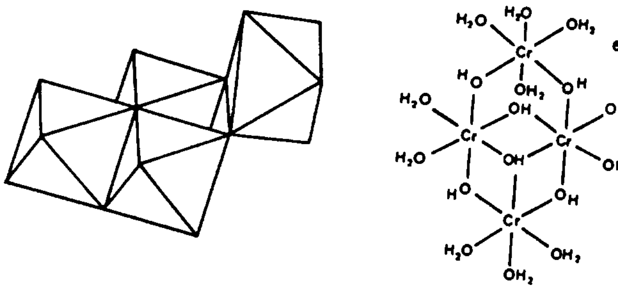
1. DIMER



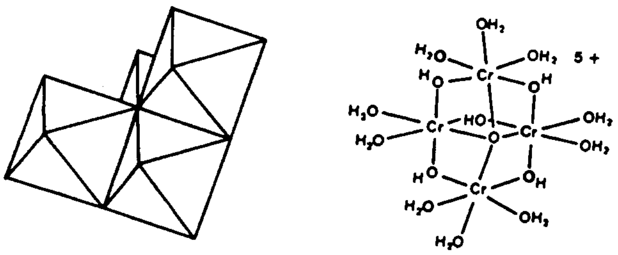
2. TRIMER



3a. OPEN TETRAMER



3b. CLOSED TETRAMER



Experimental Section

Synthesis. Cr(III) dimer mesitylate $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4]\{(CH_3)_3C_6H_2SO_3\}\cdot 4H_2O$ was prepared as described in the literature.[11] Solutions of dimer $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4]^{4+}$, trimer $[Cr_3(\mu\text{-}OH)_4(OH_2)_9]^{5+}$, and tetramer $[Cr_4(\mu\text{-}OH)_6(OH_2)_{11}]^{6+}$ were prepared by literature methods[8-10] with the exception that they were eluted from ion-exchange columns with acidified $Ba(ClO_4)_2$ (0.2–1.0 M, $[H^+] \sim 0.01$ M), desalted by the addition of stoichiometric amounts of K_2SO_4, and filtered at 273 K to remove the precipitated $KClO_4$ and $BaSO_4$. This procedure gave solutions with [oligomer] ~ 0.01 M and reduced the eluent concentration to levels where it could no longer compete with the highly charged oligomer for intercalation within the clay layers.

Na^+–montmorillonite was prepared from "Volclay", a Wyoming montmorillonite, using literature methods.[6b] Its composition and cation-exchange capacity (1.01 mequiv/g) matched those reported previously.[6a,b,e] Intercalation of Cr(III) oligomers was achieved by adding an acidified, ice-cold suspension of Na^+–montmorillonite (3% by weight slurry, pH ~ 2) to an ice-cold solution containing an excess of the desired oligomer (pH ~ 2) over 10 min, and the mixture was stirred at 273 K for 1 h to complete the intercalation. The temperature and time period were chosen to minimize acid cleavage of the oligomers and the deterioration of the clay structure in acid. The suspension was centrifuged, the supernatant removed, and the green clay material repeatedly resuspended (ca. 4 times)

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Table I. Analytical Data for the Cr(III) Monomer, Dimer, Trimer, and Tetramer Intercalated Montmorillonite

	intercalated oligomer				
				tetramer	
	monomer	dimer	trimer	open	closed
Chromatography					
starting oligomer (%)		97.5	96.1	95.4	
higher oligomers (%)		2.5	3.9	4.6	
Chromium Analyses					
Cr content (mmol/g)	0.335	0.396	0.463	0.513	0.608
charge balanced by oligomer (mequiv/g)	1.005	0.792	0.772	0.770	0.76
Sodium Analyses					
Na^+ content (mmol/g)	0.01	0.22	0.23	0.24	0.23
charge balanced by oligomer (from Na^+ content) (mequiv/g)	1.00	0.79	0.78	0.77	0.78
Powder XRD					
d_{001} spacing (Å)	13.8	15.2	14.5	15.7	15.5

in distilled water and recentrifuged until the conductivity of the suspension was below 5 mS/m.

Glycolation of Cr(III)-intercalated montmorillonite was achieved by mixing dry clay samples with ethylene glycol and allowing them to remain in contact with glycol for at least 1 h.

Characterization Studies. Powder X-ray diffraction patterns were recorded on either a Siemens D500 or a Scintag PAD 5 diffractometer using Ni-filtered Cu Kα radiation. Samples of the wet gel were smeared onto microscope slides, dried overnight at room temperature, and where necessary heated at the desired temperatures for 1 h prior to X-ray analysis. The Cr contents of oligomer solutions and Cr(III) pillared clays were determined[8] spectrophotometrically as CrO_4^{2-}. Solutions or solid clay samples were treated with excess NaOH and H_2O_2 and heated on a steam bath for ca. 1 h to ensure conversion to Cr(VI). Suspended clay particles were removed by filtration prior to analysis. Tests for the presence of CrO_3 in heated clays were made by suspending a sample of clay in base to convert any CrO_3 into CrO_4^{2-}, which could be determined spectrophotometrically. Sodium and other metals were determined by AAS on a Varian Spectr AA-400 spectrometer.

To establish the distribution of oligomers within the clay layers, the Cr(III) species were extracted twice from the wet gel with $NaClO_4$ solution (4 M, $[H]^+ \sim 0.01$ M) and analyzed chromatographically. After elution, Cr(III) oligomers were identified from their UV–vis spectra,[8] and the amount of each was determined by chromate analysis. This analysis was also used to established the % Cr in the clay after exchange. The Cr(III) species could no longer be exchanged from the clay layers with concentrated solutions of $Ba(ClO_4)_2$ and $La(ClO_4)_3$ (>1 M) after the gels had been dried at room or higher temperatures.

Results and Discussion

Room-Temperature Properties of Cr(III)-Intercalated Montmorillonite. Intercalation of montmorillonite with discrete Cr(III) oligomers, viz. dimer, trimer, and tetramer, has been achieved by mixing pure solutions of each oligomer with a montmorillonite slurry (Na^+ form) at pH ~ 2 and 273 K. Comparative data for monomer, Cr^{3+}, intercalated montmorillonite is also reported. The presence of Cr(III) species in the interlayer region was evident from the light green color of the products and from an increase in d_{001} spacing (Table I). The ability to intercalate individual oligomers coupled with the inertness of Cr(III) has allowed us to probe the chemical and physical processes associated with the pillaring of polyoxocations. These are difficult to disentagle when the intercalating agents are mixtures of polynuclear species or polynuclear species of labile metal centers.

Ion-exchange techniques showed that the integrity of individual oligomers is preserved during intercalation. For the wet gels (and even glycolated wet gels), all of the intercalated species (≥99%) were readily exchanged from the clay layers, indicating that extensive polymerization had not occurred. Moreover, the original oligomer was the predominant species present in the clay layers (95–98%) and only small amounts (2–5%) of oligomers with higher nuclearity had formed (Table I). In contrast, the species in the clay layers could not be exchanged immediately after the gels were dried in air, at ambient or elevated temperature, even after leaving clay samples in concentrated electrolyte solutions for days. This suggests that on drying the intercalating species are strongly, probably covalently, bound to the clay surface or that the clay did not reexpand to allow exchange to occur. Even in concentrated $HClO_4$ solution (>1 M) many hours are needed to leach the oligomers from the clay, but under these conditions the clay structure is also destroyed and a different extraction mechanism is likely. Chromatographic analysis of the solutions extracted by acid treatment of clay samples returned the starting oligomers (>95% of Cr_T). If extensive polymerization was responsible for difficulties in extracting the oligomers, then a range of products would be expected. Dried clay samples were found to expand on exposure to water and glycol, as indicated by the d_{001} spacings (see later), which eliminates this as a reason for the lack of exchange. Even for glycolated dry gels the intercalated species could only be extracted with concentrated acids. All of these observations point to the covalent attachment of oligomers to the clay surface. This feature of the intercalation process would be difficult to pinpoint when the intercalating agents are mixtures or are derived from labile metal ions which rearrange or cleave easily in acid.

Sodium analyses established the degree of exchange of Na^+ by each oligomer (Table I). Na^+-exchanged montmorillonite was found to contain 1.01 mmol of Na^+/g of dry clay (CEC = 1.01 mequiv/g), while Cr(III) oligomer intercalated clays contained 0.23 (±0.02) mmol Na^+/g, regardless of the intercalating oligomer. These data suggest that 0.78 mmol/g of Na^+ has been replaced by the oligomer. This result was unexpected since if all the Na^+ is present in the interlayer space, it should either be totally replaced by the oligomer or, alternatively, the proportion replaced should increase with oligomer nuclearity in keeping with the increase in overall charge of the oligomers from 4+ (dimer) to 6+ (open tetramer). The constant Na^+ content suggests that the oligomers displace all of the accessible Na^+ from the clay layer and that they cannot exchange the remaining 23%. In contrast, almost all of the Na^+ is replaced when monomeric $[Cr(OH_2)_6]^{3+}$ is used as an intercalating agent. A plausible explanation is that some Na^+ ions occupy the hexagonal cavities formed by the silicate tetrahedra. The size of the cavities appears to be such that Na^+ can be directly displaced by the Cr(III) monomer but not by the oligomers. Since the charge on the clay may not be localized, the oligomers can still displace Na^+ if the stability constant for intercalation of the oligomer is greater than that for the binding of Na^+ within the cavities. It worth emphasizing here that macrocyclic polyethers which bind the alkali metals strongly have an arrangement of oxygens which is not dissimilar to these cavities.[12]

The chromium content of intercalated clays (Table I) increases with oligomer nuclearity from 0.396 mmol/g for the dimer (**1**) to 0.513 mmol/g for the open tetramer (**3a**) and 0.608 mmol/g for the closed tetramer (**3b**). The clay surface charge counterbalanced by each oligomer is calculated by multiplying the Cr content (in mmol/g) by the charge per Cr of each oligomer. For example, the Cr content of dimer-intercalated clay (0.396 mmol/g) by the dimer charge density (2+ per Cr) gives 0.792 mmol/g (=mequiv/g), while for the closed tetramer the Cr content (0.608 mmol/g) by the charge density (1.25+ per Cr) gives 0.760 mmol/g. The complete set of results (Table I) suggest that the oligomers counterbalance 0.78 (±0.02) mmol of charge/g of intercalated montomorillonite, a value which is independent of the Cr(III) oligomer. It is in total agreement with that predicted from sodium

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analysis and further supports the view that, with the exception of Cr^{3+}, total exchange of the Na^+ does not occur. These results also show that deprotonation of the oligomers either does not occur during intercalation or that it is accompanied by protonation of the clay surface. If this were not the case, more Cr would be present within the clay layers than expected on the basis of the oligomer charge. Under the influence of the negatively charged clay surface, deprotonation of the oligomers could be more difficult because of the strong attraction between the oligomers and the clay surface, i.e. their p*K*a's should increase, and it is well-known that the p*K*a's of metal ions increase with ionic strength.[13] Note that this does not exclude migration of surface hydroxyls to accommodate the charge of each oligomer.

The air-dried products exhibit sharp, symmetric powder XRD patterns, the line widths (fwhm) being 0.78° (dimer), 0.80° (trimer), and 1.10° (tetramer) for specimens air-dried, at room temperature. The instrumental line width of ca. 0.04° in the 2θ range 5–7° was too small to necessitate deconvolution from the observed line width. The sharpness of the XRD patterns for these Cr(III) oligomer-pillared montmorillonites indicates a degree of ordering comparable with that in the original Na^+ form (fwhm = 0.64°, air-dried at room temperature).

The d_{001} spacings for montomorillonite intercalated with dimer, trimer, and tetramer at pH = 2 of 15.2, 14.6, and 15.7 Å, respectively, are greater than for monomer-intercalated clay (13.8 Å) and correspond to gallery heights of 5–6 Å. These spacings were reproducible and did not vary with the conditions of washing and drying. The structure of the dimer is known (**1**)[10] and has a depth of 4 Å and length of 6.5 Å. In the extreme, the dimer can adopt orientations that are either perpendicular or parallel to the clay layer, which would give rise to d_{001} spacings of 13.5 and 16 Å, respectively. The intermediate experimental d_{001} spacing of 15.2 Å can be rationalized in terms of the dimer adopting the following: (i) a perpendicular orientation and the lower than expected spacing arising from covalent bonding of dimer to the clay layer on drying which releases coordinated water and reduces its effective size; (ii) a tilted orientation, while still attaching itself to the clay layer, for which there is literature precedent.[14] From the proposed structure of the trimer (**2**),[9] a depth of ca. 5 Å and length of 6.5 Å can be predicted corresponding to spacings of either 14.5 or 16 Å. The experimental d_{001} spacing of ca. 14.5 Å indicates that trimer adopts a flat orientation within the clay layer. Solution characterization studies have indicated that tetramer can adopt two structures (**3a**,**b**).[8] At pH = 2, the open form (**3a**) accounts for about 70% of all the tetramer and, since excess oligomer is used in the intercalation, this form can be preferentially incorporated into the clay (greater attraction to negatively charged clay surface because of its higher charge), while at pH = 4.5, the tetramer exists in the closed form (**3b**) and this form will be intercalated. From the proposed structures and Cr(III) dimer bond lengths, the shortest dimension of either form of tetramer is ca. 6.5–7 Å. The measured d_{001} spacings of 15.7 and 15.5 Å for intercalation at pH = 2 and 4.5, respectively, correspond to gallery heights (ca. 6 Å) which are in agreement with expectation, assuming that binding to the clay layers occurs on drying. The increase of ca. 1 Å over the gallery height of trimer-intercalated clay suggests that the tetramer is no longer flat and provides circumstantial support for the proposed structures (**3a**,**b**).[8]

Glycolation sharpens XRD patterns (fwhm = 0.5°), shifts peak positions to higher 2θ values, and enhances several higher order reflections which were not obvious in the unglycolated materials. The d_{001} spacings increase from 14.5 to 15.5 Å for unglycolated samples to 17.5 Å for glycolated samples of both wet and dry gels, consistent with the introduction of ethylene glycol into the interlayer region. Thus, the interlayer is accessible to glycol and is not blocked by polymerization products. In addition, it appears that on drying the oligomers attach themselves to only one silicate sheet. Attachment to both sheets would result in nonuniformity and broader XRD patterns, as there would be regions occupied by the oligomer which could not be expanded by glycol.

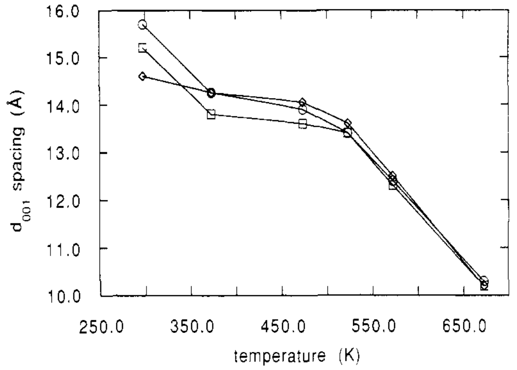

Figure 1. Temperature dependence of d_{001} spacings for dimer (□), trimer (◇), and tetramer (○) pillared montmorillonite samples heated in air.

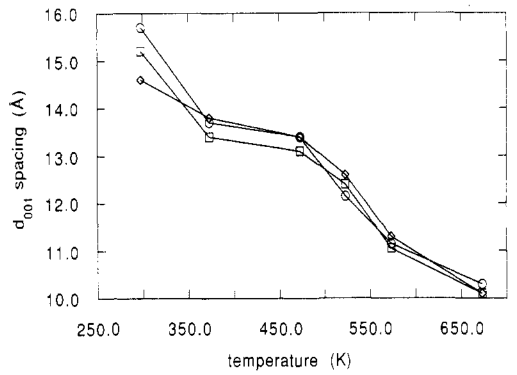

Figure 2. Temperature dependence of d_{001} spacings for dimer (□), trimer (◇), and tetramer (○) pillared montomorillonite samples heated under nitrogen.

Thermal Stability of Cr(III)-Intercalated Montmorillonite. Powder XRD was used to monitor the thermal stability of Cr(III) pillared clays in air and nitrogen. For samples heated in air, a small drop in d_{001} spacing of 0.5–1.5 Å is observed up to 573 K, but this is followed by collapse of the pillars which is complete at 673 K (Figure 1). Previous work on the dehydration of Cr(III) "active" hydroxides[9,10,15] and other Cr(III) pillared clays[6] suggests that this is caused by the following: (i) the removal of water trapped between the clay layers; (ii) dehydration of the oligomers; (iii) crystallization of α-Cr_2O_3, which can occur even at 673 K. TG/DTG analysis of Na^+ and oligomer-exchanged montmorillonite showed substantial weight losses in the same temperature range. However, weight losses (ca. 15%) were greater for Cr(III)-intercalated clay than for Na^+-montomorillonite (8%). This is to be expected since as the interlayer region is expanded by the oligomer more solvent would be trapped between the layers. Full glycolation of Cr(III) pillared montomorillonite has been possible after heating at 473 K (d_{001} spacing 17.5 Å). This indicates that although the pillaring species undergo structural changes on heating, glycol can still access the interlayer region.

It was first postulated that the collapse of Cr(III) pillars by heating in air may be due to partial or total oxidation of Cr(III) to Cr(VI) and that this could be restricted by heating under nitrogen. However, lower d_{001} spacings were found for clays heated under nitrogen compared with air (Figures 1 and 2). This result is difficult to rationalize although it is possible that oxygen

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may assist the formation of a mixed-valence oxide which might prevent the crystallization of α-Cr_2O_3. Recent EXAFS work[7] has suggested that mixed-valence oxides, possibly Cr(III)–Cr(VI) oxides, form on heating of Cr(III) pillared clays in air. The Cr content of clays heated in air up to 673 K was constant, indicating that Cr release through formation of volatile CrO_3 had not occurred. Free CrO_3 was not present in the heated clays since chromate did not develop on suspension of clays in basic solution, but this does not exclude the formation of a mixed-valence oxide.

Conclusion

A series of Cr(III) hydrolytic oligomers have been intercalated into montmorillonite for the first time and shown to retain their integrity between the clay layers. While the oligomers can be exchanged from the wet gel in their original form, this is no longer possible after drying, indicating covalent attachment to at least one silicate sheet in the clay interlayer. Polymerization of the oligomers was excluded because acid-leaching experiments have shown that the oligomer nuclearity is unchanged on drying of the clay. Not all of the sodium present in the Na^+ form of the clay is exchanged by the Cr(III) oligomers, but it is exchanged by Cr^{3+}. This suggests that some of it could be situated in hexagonal cavities formed by silicate tetrahedra. These oligomers do not produce d_{001} spacings as large as those reported by other methods, but they do give products with very reproducible properties and the spacings are entirely consistent with the known or proposed structures of the oligomers. The products have appreciable thermal stability to 573 K with gallery heights of about 4 Å and can be glycolated even after heating in air at 473 K.

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