Synthesis of Ti-Containing Pillared Montmorillonite Using a Trinuclear Acetatochlorohydroxo Titanium(III) Complex

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Synopsis. Trinuclear acetato-chloro-hydroxo titanium(III) chloride, $[Ti^{III}_3(OCOCH_3)_{6.4}Cl_{1.2}(OH)_{0.4}]Cl\cdot 11H_2O$, was prepared; its aqueous solution was reacted with Ca- and Cu-montmorillonites in air. Titanium(III) complex ions were mostly hydrolyzed, oxidized and condensed into their polynuclear forms, replacing the interlayer metal ions of montmorillonite. The calcined forms of both reaction products maintain large interlayer spacings of 22.2 and 21.3 Å, and have specific surface areas of 105 and 128 m^2g^{-1}, respectively.

Much attention has been paid to the pillaring of layered compounds by bulky inorganic or organic species,[1] including other host molecules, such as cyclodextrins.[2] Similar to zeolites, smectite clays may have micropores, thus affording another family of shape selective catalysts if they are pillared by polynuclear hydroxy metal cations. Titanium oxide is a typical photocatalyst which in combination with, for instance, platinum, is responsible for a variety of organic reactions, such as a one-step preparation of phenol from benzene.[3] These considerations have led to an expectation that smectite clays pillared with titanium oxide may act as a new type of photocatalyst possessing shape-selectivity.

In order to incorporate titanium oxide clusters into the interlayer space of montmorillonite, an attempt was made similar to a method applied to the synthesis of an iron oxide pillared montmorillonite.[4] Ca- and Cu-montmorillonites were reacted with aqueous solutions of a trinuclear acetato-chloro-hydroxotitanium(III) complex, resulting in the formation of titanium-containing pillared montmorillonites. After the present work was underway, Yamanaka, Nishihara, Hattori, and Suzuki[5] reported the synthesis of a titanium oxide pillared clay using montmorillonite and titanium hydoxide soll prepared by the hydrolysis of titanium alkoxide. This was followed by the report of Yoneyama, Haga, and Yamanaka[6] on the photocatalytic activities of the pillared materials.

Experimental

The Na-, Ca-, and Cu-montmorillonite samples used were the same as those used in previous studies.[7] An acetato complex of titanium(III) was prepared by a manner similar to that[8] reported for acetato complexes of iron(III), chromium(III), and aluminum with a general composition of $[M_3(OCOCH_3)_7(OH)\ (H_2O)_n]NO_3$(M=Fe(III), Cr(III), Al; n=0—4). Fifty cm³ of anhydrous acetic anhydride were slowly added to a mixed solution of 6.17 g of titanium trichloride, 10 cm³ of ethyl alcohol, and 5.8 cm³ of water.

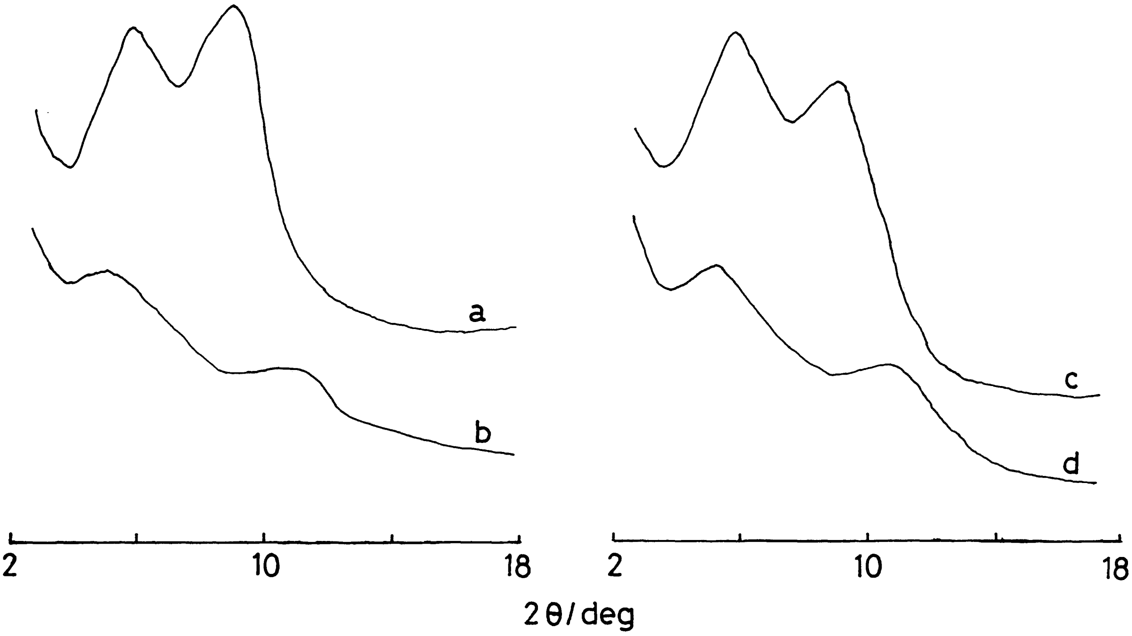

Fig. 1. X-Ray diffraction patterns of the reaction products of (left) Ca- and (right) Cu-montmorillonites heated at 40 °C (a, c) and 400 °C (b, d).

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After stirring for 12 h, the resulting solid, black in color and ca. 2.9 g in weight, was separated by filtration. A part of the solid was washed with acetic anhydride and diethylether, allowed to stand in a stream of nitrogen for 2 h, and used for a microanalysis. The other part of the solid was used without washing for a reaction with montmorillonite.

The montmorillonite sample (1 g) was weighed in a flask containing 100 cm^3 of an aqueous solution of the acetato titanium(III) complex (10 g), and kept at 25 °C for 24 h with stirring while the flask was unstoppered in air. The final products were centrifuged, fully washed with water, and dried in air at 40 °C, followed by calcination at 400 °C. When the Ca- and Cu-montmorlllonites were reacted with the acetato titanium complex solution in a stoppered flask, no significant indication of interlayer expansion was observed in the X-ray diffraction patterns of the resulting solids.

X-Ray diffraction measurements were carried out using Fe-$K\alpha$ radiation. The contents of C, H, and metal cations in the resulting materials were determined by a combined use of ICP or atomic absorption, C, H, N elemental and thermogravimetric analyses. A part of the purified acetatotitanium(III) sample was dissolved in water, hydrolyzed with sodium hydroxide, and centrifuged; the chlorine concentration of the supernatant was measured by a Dionex 2000i ion chromatograph. The surface area was measured by a conventional BET method using nitrogen at −196 °C.

Results and Discussion

The composition analysis of the acetatotitanium complex yielded: Ti, 17.7; C, 18.9; H, 3.7; Cl, 9.7 in wt%. This corresponded to a composition of $[\mathrm{Ti^{III}}_3(\mathrm{OCOCH_3})_{6.4}(\mathrm{OH})_{0.4}\mathrm{Cl}_{1.2}]\mathrm{Cl}\cdot 11\mathrm{H_2O}$, indicating that the acetatotitanium(III) complex prepared in this work is a trinuclear complex of titanium(III) isotypic with known trivalent metal acetato complexs, but partly including chlorine atoms as a ligand. It was also observed that the complex is gradually oxidized in air accompanying a weight loss and a change in color from black to white.

Table 1. Chemical Analyses of the Ca- and Cu-Montmorillonites Reacted with An Aqueous Solution of Trinuclear Acetato-Chloro-Hydroxo Titanium(III) Complex in Air

	Ca-Product	Cu-Product
	wt%	
Mg	1.9	1.7
Ti	10.8	15.8
Ca	0.1	—
Cu	—	0.04
C	0.36	0.59
Ignit. loss[a]	16.7	22.0
Molar content based on $O_{10}(OH)_2$ anion		
Silicate layer composition		
Si	3.83	3.83
Al(O)	0.17	0.17
Al(T)	1.60	1.60
Fe	0.10	0.10
Mg	0.32	0.32
Interlayer composition[b]		
Ti	0.92	1.51
Ca	0.01	—
Cu	—	0.005
OH	3.22	5.51
H_2O	1.46	4.0
Acetoxy	0.061	0.11

a) Total weight loss observed by heating up to 1000 °C in air. b) Tentative values for the OH and H_2O contents were determined by assuming y=0 in $\mathrm{Ti}_x\mathrm{O}_y(\mathrm{OH})_z(\mathrm{Acetoxy})_w$ for the incorporated titanium complex ions.

The X-ray diffraction patterns of the reaction products are shown in Fig. 1. The dried forms of the Ca- and Cu-exchanged products show a strange XRD pattern, in that the d values of the first reflections are 18.2 and 18.8 Å and the second ones are 12.2 and 12.1 Å, respectively. Both apparently show no rational relation. One interpretation is that the first and the second reflection peaks are so broad that they partly overlap each other and, thus, their separation is apparently reduced. In the present case, however, it seems to be difficult to find two such elementary peaks. It is, therefore, much more likely that the dried forms comprise two phases or, more likely, two types of domains with interlayer spacings of 18.2 or 18.8 and 12.2 or 12.1 Å. On the other hand, the calcined forms show two orders of reflections corresponding to interlayer spacings of 22.2 and 21.3 Å, respectively. These observations suggest that during calcination two types of interlayer titanium complexes in the dried form are rearranged to form a single phase of titanium-containing intercalate with larger spacings.

When the acetatotitanium(III) complex had been partly oxidized before dissolving in water, the reaction products showed a distinct peak at 2θ=31.95° (d=3.52 Å) attributable to the 101 reflection of titanium dioxide (anatase). However, the above dried and the calcined samples showed no trace of the titanium oxide peak.

Analytical data for products dried at 40 °C are summarized in Table 1. Preliminary analyses of the reaction products indicated that the intralayer composition of the initial montmorillonites remained unexchanged in a reaction with the acetato-hydroxo titanium(III) complex. The chemical formulae of the dried products were, therefore, determined on the basis of the intralayer anion composition, $O_{10}(OH)_2$, as well as the observed content of magnesium ions in the intralayer octahedral sheets.

From the color (white) of the reaction products, the titanium ions incorporated between the silicate layers were assumed to be tetravalent. The amounts of the acetoxy groups were calculated from the carbon content. The total weight loss observed upon heating to 1000 °C in air was attributed to a loss of interlayer water and acetoxy groups, as well as the water produced by condensation of the intra- and inter-layer hydroxide groups. Although the incorporated titanium complex ions would have a composition of $\mathrm{Ti}_x\mathrm{O}_y(\mathrm{OH})_z(\mathrm{acetoxy})_w$, it is difficult to precisely determine the hydrogen content and the total weight loss for an evaluation of y and z. Tentative values for z and the water content were calculated by assuming y=0; the results are listed in Table 1.

Both of the initial Ca- and Cu-momtmorillonites contain 0.203 moles of interlayer Ca^{2+} and Cu^{2+} ions per formula weight.7) According to the composition data listed in Table 1, the interlayer cations are almost completely replaced by titanium complex ions. This exchange reaction is accompanied by a large decrease in the molar ratio of acetoxy to titanium for the exchanged ions, relative to an expected value of 7/3 for the initial acetatochlorohydroxo titanium(III) complex. The molar exchange ratios of titanium to the initial interlayer Ca^{2+} and Cu^{2+} ions are 4.8 and 7.4, respectively.

When the dried Ca- and Cu-samples were heated at 400 °C, the resulting solids were fully decarbonized, and decreased in weight by 13.5 and 18.7 wt%, respectively, due to a loss of interlayer water and acetoxy groups as well as the water produced by the interlayer condensation. This observations suggest that the interlayer species in calcined samples are formed from titanium(IV) complex ions, during which the molar ratio of intralayer cations to titanium remains unexchanged.

The thicknesses of the titanium complex ion layer for the calcined samples can be estimated by subtracting 9.5 Å for the silicate layer from the observed interlayer spacings of 22.2 and 21.3 Å, yielding 12.7 and 11.8 Å, respectively. The latter two values are in good agreement with a value of 12.1 Å for the van der Waals length of a HO–Ti–O–Ti–OH sequence. These facts suggest that the titanium complex ions taken up by Ca- and Cu-montmorillonites are polynuclear hydroxooxotitanium(IV) ions comprising mainly HO–Ti–O–Ti–OH units directed to the silicate layers. Such polynuclear ions would be formed by an incomplete hydrolysis of the initial acetato titanium complex ions and subsequent condensation. Specific surface areas of 105 and 128 $m^2 g^{-1}$ were obtained for the calcined forms of the Ca- and Cu-montmorillonite based products. These values are much smaller than 300 $m^2 g^{-1}$ for a titanium oxide pillared montmorillonite, obtained by the hydrolysis of titanium alkoxide.5) This is probably due to the polynuclear forms of titanium resulting from trinuclear acetatochlorohydroxo titanium(III) ions, which are smaller in size than those from titanium alkoxide.

The reaction product obtained from Na-montmorillonite showed a much smaller tendency to intercalate polynuclear titanium complex ions, presumably due to the higher population of interlayer Na^+ ions than that of Ca^{2+} or Cu^{2+} ions.

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