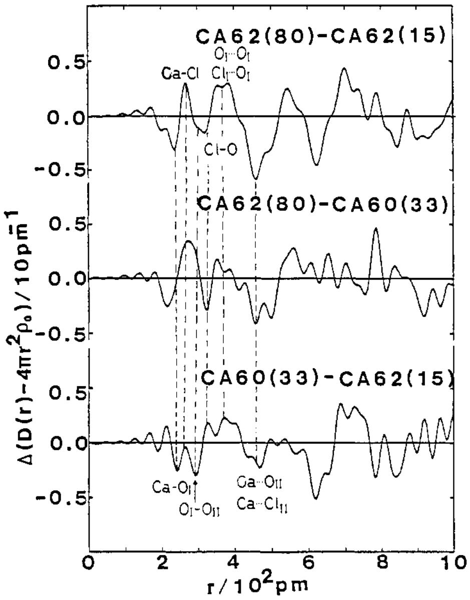

Figure 8. Difference radial distribution functions in the form of $\Delta(D(r) - 4\pi r^2\rho_0)$ between two of hydrate melts CA62 (15 °C), CA60 (33 °C), and CA62 (80 °C).

the positive one, and the second neighbor $Ca\cdots O_{II}$ and $Ca\cdots Cl_{II}$ peaks at 470 pm appear in the negative one. These trends are also found in the difference function between CA62(80) and CA60(33). These changes in the peaks are similar to those observed in Figure 6, in which we compared the solutions with different concentrations, and the results are interpreted in terms of exchange of bound water molecules with Cl^- ions in the first coordination sphere of Ca^{2+} ion.

On the basis of the above considerations, the model fitting was performed for the structure functions of CA62 at 15 and 80 °C. Models were employed along the same guideline mentioned in the previous section. The final results thus obtained are given in Table II. An increase in temperature resulted in a decrease in the $Ca-O_I$ interactions, an increase in the $Ca-Cl_I$ ones, and a decrease in the second-neighbor $Ca\cdots O_{II}$ and $Ca\cdots Cl_{II}$ interactions; the results indicate that water molecules bound to a Ca^{2+} ion are gradually exchanged with Cl^- ions to form contact $Ca^{2+}-Cl^-$ ion pairs. On the other hand, the structure parameter (n) obtained for CA62(15) suggests that aquated Ca^{2+} ions are more stable in the supercooled state. From a comparison between the structures of CA62(15) and solids $CaCl_2\cdot 4H_2O$ and $CaCl_2\cdot 6H_2O$ we can conclude that there is no structural similarity between the supercooled solution and the tetra- and hexahydrates of $CaCl_2$. This structural difference will cause the supercooling of the hexahydrate. The position of the solution CA62 at 80 °C is near that of CA56 at 72 °C in the phase diagram (see Figure 1b); correspondingly, both structures are similar, as seen from the results in Table II.

Acknowledgment. This work has been financially supported, in part, by the Ministry of Education, Science, and Culture of Japan (Grant-in-Aid for Scientific Research on Priority Area of Macromolecular Complexes No. 63612005). All the calculations were performed at the Computer Centers of Tokyo Institute of Technology and Fukuoka University.

Registry No. $CaCl_2$, 10043-52-4; H_2O, 7732-18-5; Ca, 7440-70-2.

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Pillaring of Montmorillonite by Organotin Cationic Complexes

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Received November 8, 1988

The intercalation of dimethyltin(IV) cationic clusters in montmorillonite leads to an organotin–clay complex exhibiting a basal spacing of 1.66 ± 0.02 nm. The maximum cluster loading is larger than expected on the basis of the cation-exchange capacity of the clay and the formal charge of monomeric tin complexes, indicating intercalation of organotin oligomers. The thermal transformation of the intercalated montmorillonite to pillared clay was studied via XRD, ^{119}Sn Mössbauer, and IR spectroscopies. Calcination above 250 °C leads to a collapsed interlayer space. However, calcination after glycerol solvation of the precursor at 240 °C leads to a tin oxide pillared clay that is stable up to about 500 °C. This result is attributed to a lower interlayer acidity upon displacing interlayer water with glycerol. The above treatment of the precursor opens a new route to the synthesis of pillared clays.

I. Introduction

During the last decade a novel class of microporous materials has emerged from the intercalation of swelling clays, i.e. smectites, with oligo- or polymeric cationic complexes of metals.[1] By calcination of the intercalates, the complexes inserted in the clay interlayer space transform into metal oxide pillars, which support the silicate sheets and keep them apart even at elevated temperatures (up to about 600 °C). Thus, the structure of pillared layered clays (PILC's) consists of a labyrinth of pores with sizes in the 1–10-nm range with a total surface area between 200 and 500 m^2/g, while a pronounced Brønsted and Lewis acidity prevails in the interlayer space. Therefore, PILC's offer a novel host material for molecular sorption, chemical synthesis, and catalysis under conditions of high selectivity, imposed by steric and electronic constraints of this super-zeolitic structure. The early recognition that PILC's have important potential applications (e.g. in petroleum cracking[2]) has stimulated research on the synthesis of new PILC's, on the understanding of the transformations occurring upon firing the PILC precursor, and on the elucidation of the role that the pillars play in the physicochemical processes in the interlayer space.

The list of metal oxides used in pillaring various smectites is rapidly expanding and comprises already quite a few metals, e.g. aluminum, zirconium, silicon, chromium, iron, titanium, niobium,

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molybdenum, and tantalum.[3] Furthermore, the spectrum of analytical techniques applied for the characterization of PILC's is already quite extensive, including e.g. magic-angle spinning NMR,[4] IR,[4] EPR,[5] neutron scattering,[6] and Mössbauer spectroscopies.[7]

In this paper we present (i) a route for the synthesis of montmorillonite pillared by tin oxide and (ii) the results of our study of the transformation of the PILC precursor of PILC along this route. The main analytical techniques used in this study are XRD, ^{119}Sn Mössbauer, and IR spectroscopies.

Our results show that the intercalated organotin(IV) complexes when heated in air above 250 °C disintegrate and thus the interlayer space collapses. However, upon glycerol solvation of the intercalated species, heat-stable SnO_2 pillars are formed, which keep the clay lamellas apart up to about 600 °C.

II. Experimental Section

Materials. Wyoming montmorillonite (Ward's International; Catalogue No. 46W0439) was sodium-saturated by reacting the clay overnight with an excess of aqueous 1 N NaCl and then washing the solid phase, gained by centrifugation, two times with aqueous 1 N NaCl. The material was then dispersed in distilled water, and the <2 μm clay fraction was collected and subjected to dialysis with frequent changes of water until the dialysate was free from chloride ions as detected with a 4.2% $AgNO_3$ solution. Finally, the clay was dried at 50 °C. Its cation-exchange capacity (CEC) equals 80 mequiv/g of clay. This was measured by converting first the Na^+–montmorillonite to its $(CH_3)_4N^+$ or $BuNH_3^+$ form and then determining by microanalysis the carbon and nitrogen contents of the organoclay product.

Pillaring Agent. The pillaring agent consisted of oligonuclear hydroxodimethyltin(IV) complexes prepared by hydrolysis of dimethyltin(IV) chloride. The hydrolysis of the dimethyltin(IV) cation has been examined in detail by Tobias et al.[8] over $(CH_3)_2SnCl_2$ concentrations varying from 1 to 80 mM. The results of their study indicate that in the pH region 1.0 < pH < 8.0 the main stable hydroxo complexes are $[(CH_3)_2Sn(H_2O)_2]^{2+}$, $[(CH_3)_2Sn(OH)]_2^{2+}$, and $[\{(CH_3)_2Sn\}_3(OH)_4]^{2+}$. The trinuclear complex predominates at pH 5.5, whereas it appears that in more concentrated starting solutions and at pH values slightly less than 5.5 even larger complexes exist in small amounts. On account of these observations and in order to achieve maximum loading of the clay, the intercalation was conducted at a pH between 5.0 and 5.5 in the following manner.

Intercalation. Thirty milliliters of a 40 mM solution of $(CH_3)_2SnCl_2$—pH adjusted with 1 N NaOH between 5.2 and 5.3—was slowly added with stirring to 1 g of Na^+–montmorillonite dispersed in 50 mL of water. Flocculation took place immediately, and after the mixture was allowed to stand for 30 min the supernatant liquid was discarded and the centrifuged solid washed twice with 50 mL of distilled water. The product was then redispersed in 50 mL of distilled water and the above intercalation procedure repeated twice. Thereafter, the solid was centrifuge-washed with distilled water until the supernatant was free of Cl^- ions.

The intercalated clay (IC) was obtained in powder form after drying the above washed solid first at room temperature and then at 50 °C. The dried mass was finally hand-ground. Oriented films of IC were obtained by spreading a water dispersion of the material over glass plates that were first dried in air at room temperature and then at 50 °C.

Powder as well as oriented-film samples of IC were calcined for 4 h at different temperatures up to 600 °C.

Glycerol Solvation. Samples of IC were placed in glass jars together with an open glass bottle containing sufficient amounts of glycerol and then heated according to either of the following two procedures: (a) first for 24 h at 80 °C and then at 240 °C for 4 h, designated thereafter as sample G80/240; (b) completely at either 220 or 240 °C, designated hereafter as G220 and G250. Finally, the glycerol-solvated samples were fired in air for 4 h at different temperatures (see section III).

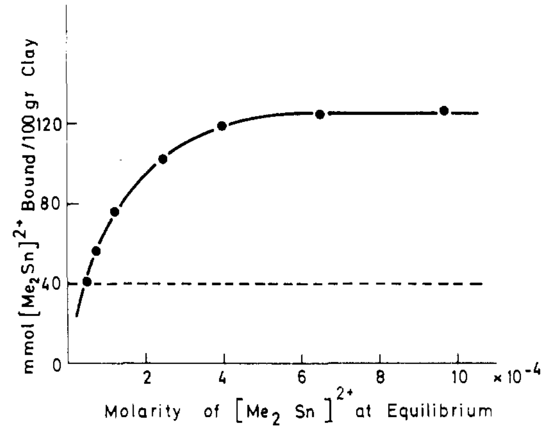

Figure 1. Binding at 25 °C of dimethyltin(IV) complexes by Na^+–montmorillonite. The dashed line indicates the binding limit expected for the displacement of 80 mequiv of Na^+/100 g of clay by complexes of formal charge +2.

$[(CH_3)_2Sn]^{2+}$ Binding Curve. The extent of binding of the oligonuclear cationic tin(IV) complexes to the clay was determined in the following way: $^1/_2$ g of Na^+—montmorillonite was first dispersed in 50 mL of water and then reacted with 50 mL of a pH 5.2 solution containing a known amount of $(CH_3)_2SnCl_2$. The pH of the resulting mixture of clay and intercalate was readjusted to 5.2, if necessary. The mixture was left to equilibrate for 5 h, and then the intercalated clay was separated by centrifugation and washed two times with 20 mL of water. The pH of the combined filtrates was adjusted to 2.5, and the amount of tin remaining in the solution was determined by precipitation with a solution of sodiumd diethyldithiocarbamate as $(CH_3)_2Sn[S_2CN(C_2H_5)_2]_2$.

Physical Methods. A Philips X-ray diffractometer with Cu Kα radiation was used for determining the d_{001} basal spacing in the intercalated clay structures. Powder samples and oriented films were used to this end. The films were prepared by drying at room temperature aliquots of the clay suspensions spread over glass slides. Infrared spectra (4000–600 cm^{-1}) of thin clay films as well as of powder samples in the form of KBr pellets were recorded with a Perkin-Elmer 257 spectrophotometer. Tin-119 Mössbauer spectra of powder samples were obtained in the temperature range 80–300 K with a constant-acceleration spectrometer and a 10-mCi source of calcium stannate kept at room temperature.

III. Results and Discussion

Binding Curve. Aqueous solutions of dimethyltin chloride, hydrolyzed at pH 5.2, reacted readily with the Na^+–montmorillonite water suspension, affording a gray-white clay complex. Figure 1 presents a plot of the amount of organotin cations sorbed by the clay versus their equilibrium concentration in the solution. Since the exact composition of the organotin moieties present either in the solution or in the clay is not known, the mass of organotin in the clay or in the solution is expressed in terms of the unit $[(CH_3)_2Sn]^{2+}$. After the initial steep rise, which shows the high affinity of these tin cations for the clay surface, the binding curve saturates at a loading of about 122 mmol of $[(CH_3)_2Sn]^{2+}$/100 g of clay. On the basis, however, of the CEC of the clay (80 mequiv/100 g of clay), the maximum amount of a divalent cationic moiety that could be intercalated in the clay is only 40 mmol/100 g of clay (dashed line in Figure 1). Therefore, the experimental value of 122 mmol/100 g of clay reveals that the charge carried into the clay by the intercalated complexes is on the average $+^2/_3$ per tin of the complex; i.e., the intercalated tin complexes are not mononuclear in tin but rather trinuclear, expected on the basis of the preparative conditions (see section II).

X-ray Data. The XRD spectrum of IC, i.e. of the as-prepared dried organotin-intercalated montmorillonite, shows an interlayer distance d_{001} = 1.66 nm and a series of rational higher orders d_{00n} (only two of which are shown in Figure 2a). The as-prepared material is thus made of aggregates containing several silicate layers having a separation of about 0.7 nm. When IC is heated in air at different temperatures (Figure 2b–d) it is found that the

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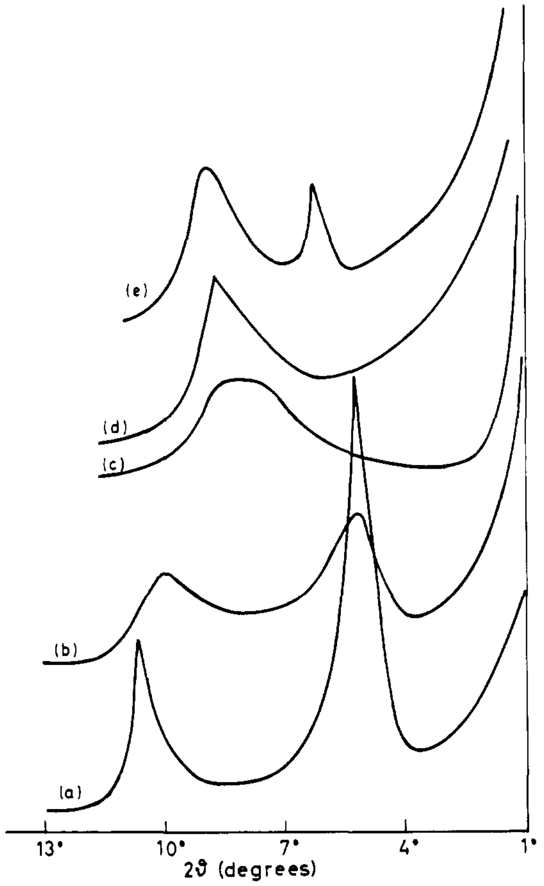

Figure 2. XRD spectra of (a) the intercalated clay and of samples thereof calcined at (b) 200 °C, (c) 250 °C, and (d) 300 °C. Spectrum e corresponds to a sample calcined at 300 °C after it was heated in air first at 80 °C and then at 240 °C.

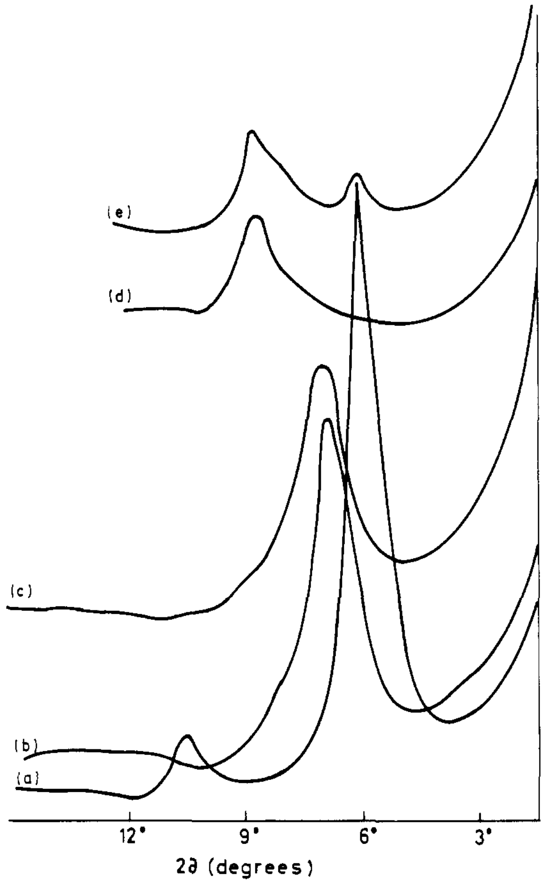

Figure 3. XRD spectra of sample G80/240 after its successive calcination of (a) 50 °C, (b) 400 °C, (c) 500 °C and (d) 600 °C. Spectrum e corresponds to a sample calcined at 600 °C after it was heated in air first at 50 °C and then at 100 °C.

intercalated tin moieties start to disintegrate around 250 °C and at 300 °C have migrated out of the interlayer space, leaving the silicate layers practically in contact, i.e. $\Delta d < 0.1$ nm. The spectrum (Figure 2e) corresponds to intercalated clay which was first further dried at 80 °C for 24 h before calcining it at successively higher temperatures up to 300 °C. This spectrum indicates that a more thorough dehydration of the material leads to the formation of stable pillars in some clay aggregates.

It is known[4b,9] that when a smectite intercalated with metal ions of high ionic potential or with oligonuclear hydroxo complexes thereof is heated, a high Brønsted acidity develops in the interlayer space above 200 °C due to the dissociation of coordinated H_2O as well as to the condensation of OH's belonging to the intercalated species or to the clay lattice. This high interlayer acidity probably induces a dissolution of the intercalated oligomeric complexes to mononuclear ones. These then disperse in the interlayer in order to balance the clay layer charges, which are on the average 1 nm apart. Thus, no robust metal oxide pillars can be formed to prop the silicate layers apart. The above picture is supported by the finding reported by Christiano et al.[9b] that further dehydration of their PILC precursor at 130 °C under vacuum for 24 h led to the formation of pillars stable up to 350 °C, while direct calcination of 250 °C of the room-temperature-dried precursor resulted in a collapsed interlayer.

In view of the above a possible mechanism for heat-stable pillaring of smectites could be the in situ replacement of H_2O with other neutral molecules that would not produce such high interlayer acidity. To this end we heated samples of IC in an atmosphere saturated with glycerol vapors according to the procedure G80/240 described in section II. After this treatment the material exhibits a nonrational series of XRD lines (Figure 3a) giving a highest Δd value of about 0.5 nm, revealing that the tin moieties are now differently arranged in the clay galleries compared to the arrangement in the as-prepared state (Figure 2a). Furthermore, the series of XRD spectra in Figure 3b–d reveals that when the glycerol-solvated samples are calcined at successively higher temperatures up to 500 °C, the tin moieties do not disintegrate. At this temperature the interlayer opening is still about 0.3 nm, while it finally collapses at 600 °C (Figure 3e). It should be noted that glycerol complexes of montmorillonite having alkali or alkali-earth metals as balancing cations collapse when calcined up to 350 °C.[9]

These findings show that the insertion of glycerol molecules in the interlayer space has a marked effect not only on the structure of the intercalated tin complexes but also on their thermal stability. In order to further ascertain the role of the dehydration in connection with the 24 h long solvation step at 80 °C in procedure G80/240, we heated samples of IC directly at 220 °C or at 250 °C under an atmosphere saturated with glycerol vapors (samples G220 and G250). The XRD spectra in Figure 4 show that after these latter solvations a rational series of peaks emerges corresponding to an interlayer spacing d_{001} of about 1.8 nm. This value is practically equal to that of the known[10] glycerol–Na^+–montmorillonite complex and in any case indicates a different arrangement of the inserted glycerol molecules compared to that resulting from procedure G80/240. Furthermore, when the new material is calcined at 360 °C, the tin moieties transform to pillars 0.6 nm in height, i.e. 2 times as high as those formed in sample G80/240 calcined at the same temperature. However, in samples

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Table I. Hyperfine Parameters and Relative Absorption Areas (A) of the Spectral Components of the Dimethyltin–Montmorillonite Intercalation Compound after Various Treatments

heat	component I				component II				component III			
treatment	Γ, mm/s	δ, mm/s	ΔE_q, mm/s	A, %	Γ, mm/s	δ, mm/s	ΔE_a, mm/s	A, %	γ, mm/s	δ, mm/s	ΔE_q, mm/s	A, %
IC	0.94 (2)	0.96 (1)	3.24 (1)	36 (3)	1.12 (2)	1.36 (1)	3.37 (1)	64 (6)				
250 °C	1.34 (2)	0.86 (1)	2.18 (1)	46 (1)	1.10 (2)	2.20 (1)	3.88 (1)	19 (1)	1.21 (1)	0.09 (1)	0.79 (1)	35 (1)
300 °C	1.02 (4)	1.16 (1)	2.56 (1)	8 (1)	1.26 (4)	2.16 (1)	4.00 (1)	14 (1)	1.22 (2)	0.06 (1)	0.79 (1)	78 (1)
680/240	0.94 (2)	1.02 (1)	3.28 (1)	37 (2)	1.06 (2)	1.46 (1)	3.42 (1)	41 (2)	1.30 (4)	0.73 (3)	2.00 (4)	22 (2)
350 °C	1.02 (2)	0.90 (1)	3.10 (1)	9 (1)	1.26 (2)	2.14 (1)	4.10 (1)	16 (1)	1.38 (4)	0.18 (1)	0.86 (1)	75 (1)
400 °C	1.02 (2)	1.01 (2)	2.54 (4)	2 (1)	1.26 (2)	2.60 (1)	3.37 (1)	8 (1)	1.22 (2)	0.08 (1)	0.80 (1)	90 (1)

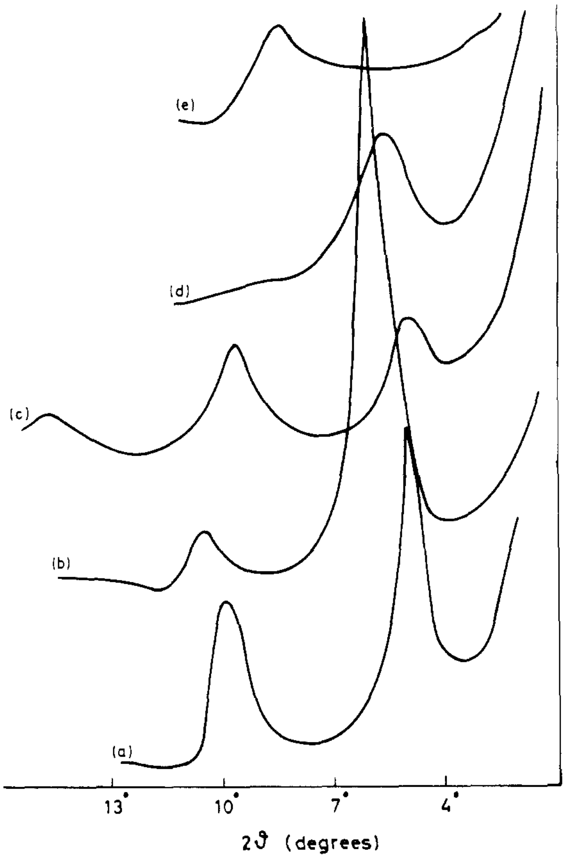

Figure 4. XRD spectra of samples (a) G200, (b) G80/240, and (c) G250. Spectrum d corresponds to sample G250 after its calcination at 360 °C and spectrum e to sample G220 after its calcination first at 360 °C and then at 470 °C.

G220 and G250 the interlayer opening collapses already at 470 °C (Figure 4e).

These results point out that the 24 h long solvation step at 80 °C is important for avoiding a disintegration of the intercalated tin moieties at low heating temperature. During this step dehydration in the interlayer is clearly extensive and the displacement of water molecules by glycerol results in a new arrangement of the intercalated species (see Figure 3a). The details, however, of this structure are not known.

Mössbauer Data. Figure 5 presents Mössbauer spectra obtained at liquid-nitrogen (LN) temperature of the as-prepared intercalated clay as well as the clay after calcination at various temperatures up to 300 °C. The spectrum of the starting material (Figure 5a) consists of a symmetric broad doublet while a pronounced asymmetry appears at spectra obtained at temperatures above 240 K. As discussed elsewhere[11] in detail, this asymmetry arises from a premature melting of the interlayer water. The LN spectrum can be fitted with two symmetry doublets having an area ratio of about 2:1 (Table I). This ratio is in agreement with the trimeric form of the intercalated organotin complex, whch has two equivalent terminal ions and one central Sn ion. A similar fit is achieved for the LN spectrum of a frozen solution of the intercalate. It should be noted, however, that fits of equal quality can be obtained for the same spectra with two symmetric doubelts of equal areas. In both cases the isomer shifts of these doublets correspond to Sn(IV).

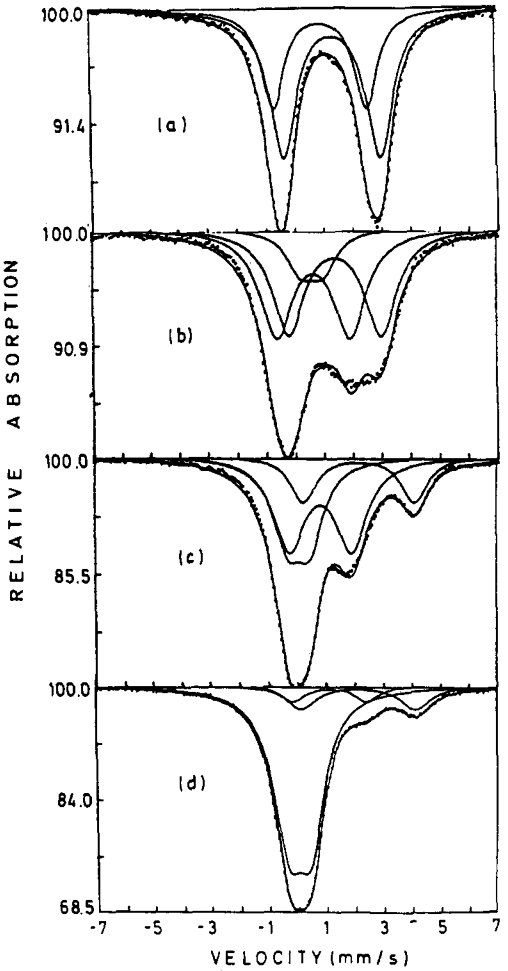

Figure 5. ^{119}Sn Mössbauer spectra obtained at LN temperature of (a) the intercalated clay and of samples thereof calcined at (b) 200 °C, (c) 250 °C, and (d) 300 °C.

The spectra of the intercalated clay after it is heated in air at 100 and 150 °C are essentially identical with the spectrum of the as-prepared IC. A dramatic change occurs, however, in the spectral features upon calcining the material at 200 °C (Figure 5b). Fitting of this spectrum cannot be achieved with two doublets, and even the introduction of a third doublet furnishes only a moderate reproduction.

Samples of IC calcined at 250 and 300 °C give spectra (Figure 5c,d) that can be reasonably fitted with three doublets, one of which has the isomer shift and quadrupole splitting corresponding to those of SnO_2 (Table I). This latter doublet increases at the expense of the other two doublets as the calcination temperature increases. Furthermore, this doublet becomes more enhanced compared to the other two doublets in spectra obtained at room temperature. This finding reveals a large Debye–Waller factor for this spectral component, as expected for SnO_2 formation. The

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[11] Simopoulos, A.; Petridis, D.; Kostikas, A.; Gangas, N. H. J. *Hyperfine Interactions* **1988**, *41*, 843.

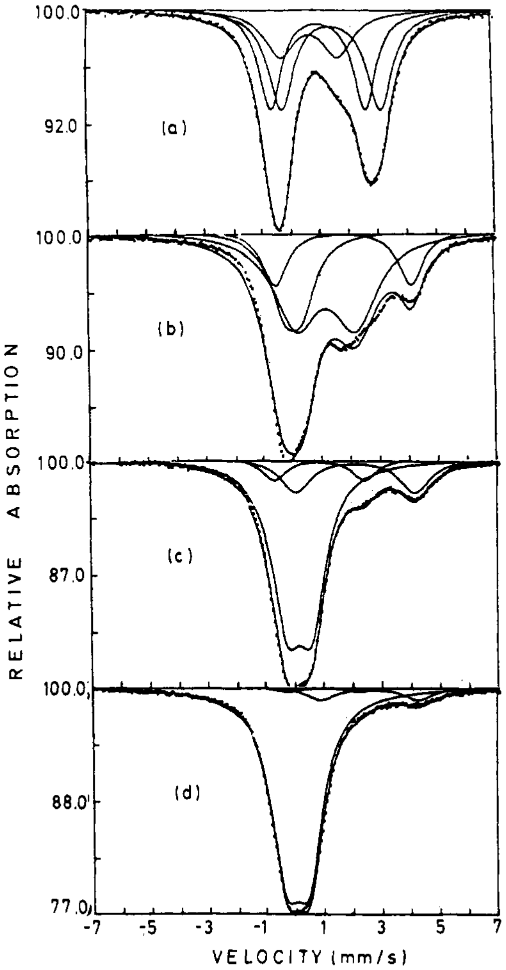

Figure 6. ^{119}Sn Mössbauer spectra obtained at LN temperature (a) of sample G80/240 as prepared and of the sample after its calcination of (b) 300 °C, (c) 350 °C, and (d) 400 °C.

hyperfine parameters of the remaining two components have changed compared to the values determined from the spectra of the samples heated below 200 °C, despite the fact that their area ratio continues to remain roughly equal to 2:1. The isomer shift of one of these components has increased to values close to the range of divalent tin.

The above results, together with the X-ray data, allow us to draw the following picture for the chemical and structural transformations occurring in the intercalated clay upon heating it in air: Calcination up to about 200 °C affects very little the intercalated tin moieties, which probably retain in the interlayer space their trimeric structure. Above this temperature the structure of these moieties starts to disintegrate gradually. The inserted species transform into SnO_2, most of which migrates out of the clay interlayer space. However, better dehydration of the starting material results in the formation of some clay aggregates with SnO_2 pillars that keep the layers apart up to 300 °C (Figure 2e).

Further evidence for the disintegration of the organotin clusters is provided by their infrared spectra. The bands at 2920 and 2860 cm^{-1} are due to the carbon-hydrogen vibrations and are clearly seen in the spectra of clay films dehydrated at 100 °C. Their intensities diminish, however, with increasing calcination temperature until finally around 250 °C these bands disappear.

The Mössbauer spectra of the samples solvated with glycerol show in general features similar to those of the nonsolvated IC. However, the LN spectrum of sample G80/240 (Figure 6a) resembles the spectrum of the 50 °C dried IC sample (Figure 5a), although the former corresponds to material heated already to 240 °C. We note further that the spectrum of Figure 6a can be fitted with three doublets, two of which are identical with those of the spectrum in Figure 5a.[12] It appears that the third doublet corresponds to a precursor of SnO_2, since calcination of G80/240 at higher temperatures leads to the formation of the component identified as SnO_2 in the calcined but not glycerol-solvated IC. A drastic spectral change appeared when sample G80/240 was heated in air at 300 °C (Figure 6b). Here too, as in the case of the IC sample calcined at 200 or 250 °C (Figure 5b,c), a poor fitting can be obtained with only three components. Thus, the only difference detected by the Mössbauer spectra before and after glycerol solvation is that formation of SnO_2 in the glycerol-solvated samples starts at 50–100 °C higher. This small retardation in the thermolysis of the intercalated tin moieties to tin oxide results, however, in thermally stable pillaring of the clay layers; while the Mössbauer spectrum of sample G80/240 calcined at 400 °C reveals that about 90% (Figure 5d) of the intercalated tin complexes have transformed to SnO_2, the X-ray data (Figure 3c) show that all the clay layers are propped apart by pillars of about 0.3 nm height.

IV. Conclusions

The binding curve for dimethyltin(IV) complexes shows that the intercalated tin moieties are further hydrolyzed in the clay interlayer, forming mainly trinuclear oligomers. The observed interlayer spacing of about 0.7 nm in the intercalated clay supports this conclusion since few of the tin and oxygen atoms are required to make up a molecular prop of that height.

When the as-prepared organotin–montmorillonite is calcined, the intercalated tin moieties start to disintegrate around 250 °C. At this temperature the infrared data show that the methyl groups have also disintegrated, while the formation of SnO_2 is detected in the Mössbauer spectra. Most of the tin oxide migrates out of the clay at 300 °C, leaving the silicate layers practically in contact.

The thermolysis of the intercalated molecular props is most probably due to the high interlayer protonic acidity developing upon dehydrating the intercalated clay above 150 °C. The results on samples of material subjected to different preheatings under a glycerol atmosphere support the above picture as the cause of the observed early decomposition. In particular, glycerol solvation at 80 °C for 24 h and at 240 °C for 4 h gave a product with interlayer props up to at least 500 °C. However, the pillars supporting the silicate layers at this high temperature were only about 0.3 nm high.

The understanding of the processes causing a low-temperature disintegration of intercalated complexes of metals in several cases[13] is of great importance in the synthesis of PILC's with high thermal stability. In this view the results of this work contribute to the elucidation of these processes and hint also at a suitable pretreatment of the PILC precursors.

It is finally noted that the synthesis of thermally stable SnO_2-pillared clays offers the possibility[11] of obtaining via ^{119}Sn Mössbauer spectroscopy dynamic information about the interactions between pillars and guest molecules inserted in the interlayer galleries.

Acknowledgment. We thank D. Morphis for helping with the XRD measurements.

Registry No. $(CH_3)_2SnCl_2$, 753-73-1; SnO_2, 18282-10-5; montmorillonite, 1318-93-0.

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[12] We present here the alternative fit with equal intensities for the two main doublets.

[13] (a) Brindley, G. W.; Yamanaka, S. *Am. Mineral.* **1979**, *64*, 830. (b) Yamanaka, S.; Numata, K.; Hattori, M. Presented at the International Clay Conference, Denver, CO, July–Aug 1985.