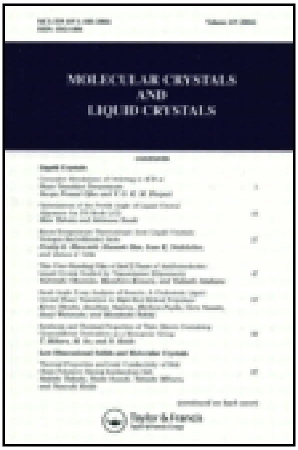

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INCORPORATING $SnO_2.xH_2O$ INTO THE INTERLAYER SPACINGS OF MONTMORILLONITE

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Abstract $SnO_2.xH_2O$ was incorporated into the silicate layers of Na-montmorillonite ($SnO_2.xH_2O$-Mont) via the hydrolysis of $(NH_4)_2SnCl_6$ in an aqueous slurry of Na-montmorillonite (Mont). The air-dried material and samples treated at various temperatures were characterized by X-ray diffractometry, X-ray fluorescence and infrared spectroscopies, derivatography and BET measurements. It was found that partially hydrated SnO_2 was precipitated inside the silicate layers. Upon heat treatment dehydration/dehydroxylation occurred, thus, the strength of hydrogen bonding holding the introduced substance in the layered structure decreased. From 393 K the SnO_2 started to migrate onto the outer surface and above 673 K finely dispersed, clay-supported SnO_2 was formed.

INTRODUCTION

Recently, there has been a growing interest in preparing structures, where a large variety of host materials accommodates various substances. They have the promise of novel physical, chemical as well as biological properties. They range from structures holding the intercalated species with strong primary bonds (e.g. anionic[1] or cationic[2] pillared layer clays) to those where the incorporated species are just weakly bonded to the parent structure (e.g. metal containing graphimets[3]).

In this work, we describe a system of the latter kind where partially hydrated tin oxide species are held with secondary forces (presumably mostly with hydrogen bonds) within a sheet silicate structure.

EXPERIMENTAL

Materials and synthesis

$(NH_4)_2SnCl_6$ was prepared, by dissolving $SnCl_4$ and NH_4Cl (products of Reanal) in double-distilled water. This solution was added dropwise under vigorous stirring to a suspension of Na-montmorillonite (Mont). After two hours of reflux, the suspension was cooled to room temperature, the clay was separated and washed free of chloride and finally, it was air-dried.

Methods of characterization

The composition of the air-dried substance was measured by X-ray fluorescence (XRF) spectroscopy. The Sn content was determined quantitatively with the help of analytical standard. Spectra were taken in the 1-8 keV range.

X-ray diffractions (XRD) were measured on a DRON 3 diffractometer using Cu-K_α radiation. Interlayer distance and its variation with heat treatment were determined from the position of the (001) reflection. Qualitative identification of the incorporated species was done by taking and comparing the XRD spectra of the parent Na-montmorillonite, the modified montmorillonite ($SnO_2.xH_2O$-Mont) and an SnO_2 mineral, the cassiterite (heat treatment at 373 K for 2 hours).

KBr pellet technique was applied for infrared (IR) measurements. IR spectra were taken in the range of 400-4000 cm^{-1} for Na-montmorillonite and between 400 and 1800 cm^{-1} for $SnO_2.xH_2O$-montmorillonite. Measurements were done with a Specord 75 spectrometer.

Thermal behavior of the samples were investigated by thermogravimetry (TG) with a Derivatograph-Q instrument. The powdered samples were placed on a platinum sample holder and studied under the following conditions: mass of sample 100 mg, heating rate 10 degree/min, temperature range 300 to 1270 K, N_2

atmosphere. Before measurements the samples were kept under saturated NH_4Cl solution.

BET measurements were performed in a conventional volumetric adsorption apparatus at the temperature of liquid N_2 (77 K). Prior to measurements the samples were heat treated for 2 hours under evacuation at 298 K, 333 K, 353 K, 373 K, 393 K, 473 K, 573 K, 673 K or 773 K, respectively. Results are given in m^2/g.

RESULTS

XRF measurements disclosed that the parent sample contains Si, Ca, Ti as well as Fe (FIGURE 1, lower curve).

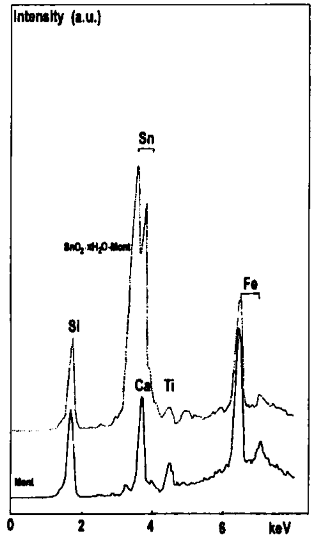

FIGURE 1 XRF spectra of Mont and $SnO_2.xH_2O$-Mont

TABLE I BET surface areas of Mont (B) and $SnO_2.xH_2O$-Mont (A) after pretreatment at various temperatures

Temp. of pretreat./K	BET surface area $/m^2/g$ A	B
298	91.5	-
333	119.0	-
353	119.8	-
373	127.0	75.9
393	182.7	-
473	135.3	87.1
573	119.8	88.9
673	109.1	88.1
773	90.5	88.1

After the synthesis, the XRF spectrum of the air-dried sample showed a very intense doublet typical of Sn (FIGURE 1, upper curve). Quantitative analysis revealed that Sn could be introduced into the clay structure in 27.2%.

BET measurements (TABLE I) verified that partially hydrated SnO_2 precipitated between the layers, since there was a substantial increase in BET surface area as soon as physisorbed water was removed from and among the silicate layers. The surface of the clay increased with increasing the temperature of heat treatment up to 393 K. Upon further increase in the temperature of pretreatment the BET surface area decreased gradually, nevertheless, the value typical of the host Na-montmorillonite sample was only obtained after heat treatment above 673 K.

IR spectroscopic measurements revealed that the solid samples are crystalline (XRD results gave further evidence). The $SnO_2.xH_2O$-montmorillonite practically showed the same bands in the range of framework vibrations as Na-montmorillonite. There were no sign of SnO_2 up to heat treatment at 673 K, but a band started to develop near 600 cm^{-1} at this temperature and above, showing that now there was a larger amount and to a small extent agglomerated SnO_2 on the outer surface.

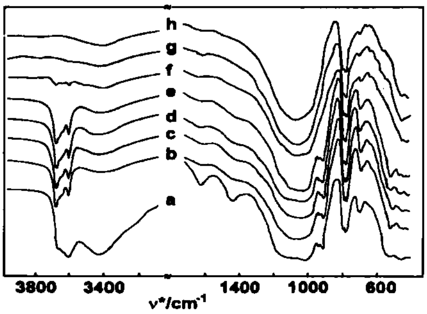

FIGURE 2 Framework IR of Mont treated at (a) room temperature, (b) 373 K, (c) 473 K, (d) 573 K, (e) 673 K, (f) 773 K, (g) 873 K, (h) 973 K

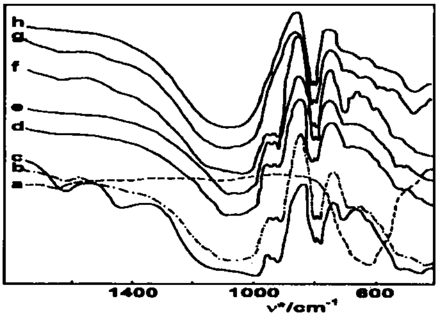

FIGURE 3 Framework IR of (a) SnO_2, (b) Mont; $SnO_2.xH_2O$-Mont: (c) room temperature, (d) 473 K, (e) 573 K, (f) 673 K, (g) 773 K, (h) 873 K

Thermogravimetric results showed the $SnO_2.xH_2O$-montmorillonite, just like Na-montmorillonite had a weight-loss practically at the same temperature (378 K and 383 K, respectively). Here, adsorbed water was removed. As the temperature was raised $SnO_2.xH_2O$-montmorillonite sample was loosing weight continuously due to the dehydration/dehydroxylation of the partially hydrated tin oxide guest. A similar but much less significant weight-loss could be observed with the host Na-montmorillonite as well due to a slow dehydroxylation of the silicate structure. There was a step-like second weight-loss too, but its temperature was significantly higher for Na-montmorillonite (963 K) than for $SnO_2.xH_2O$-montmorillonite (863 K). This means that the sheet-silicate structure collapses easier when SnO_2 is introduced into the system.

X-ray diffractometry gave 1.48 nm as $d_{(001)}$ interlayer spacing for the air-dried sample. It is 21% higher than that of the air-dried Na-montmorillonite (1.28 nm). The change in interlayer spacings and intensities of the (001) reflection on heat treatment was also studied (FIGUREs 4 and 5).

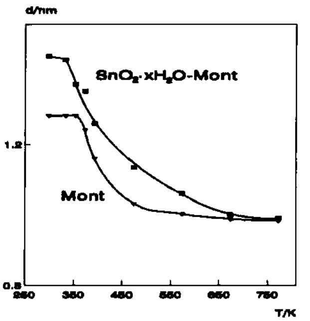

FIGURE 4 Interlayer distance v. temparature for Mont and $SnO_2.xH_2O$-Mont

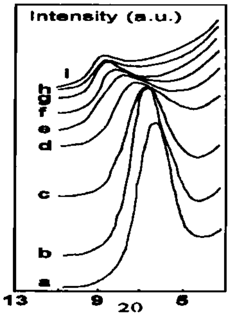

FIGURE 5 (001) reflection in $SnO_2.xH_2O$-Mont, treated at (a) 333 K, (b) 353 K, (c) 373 K, (d) 393 K, (e) 473 K, (f) 573 K, (g) 673 K, (h) 773 K, (i) 873 K

It is clearly seen that even moderately high temperature has a detrimental effect on the structure. It collapses gradually upon increasing temperature and from 673 K the $d_{(001)}$ value becomes the same as that of the parent montmorillonite. On heat treatment the intensities decrease drastically as well, revealing the gradual loss of crystallinity and finally the collapse of the sheet silicate structure.

DISCUSSION

Upon adding an $(NH_4)_2SnCl_6$ solution to a well-stirred aqueous slurry of Na-montmorillonite, the compound enters the interlayer spacing of the swollen clay. At the same time spontaneous hydrolysis of the Sn compound starts which is accelerated by refluxing the slurry. The hydrolysis results in various partially hydrated SnO_2 species (XRD) which are held by the silicate layer via presumably hydrogen bonds. Upon heat treatment the precipitated Sn derivatives gradually dehydrate and/or dehydroxylates (TG). Consequently, the strength of hydrogen bonding decreases and the dehydrated/dehydroxylated species migrate to the outer surface of the clay (BET, XRD). Probably they agglomerate to a certain extent, but the lack of well-developed bands typical for SnO_2 in the IR spectra of the heat treated samples show that finely dispersed clay-supported SnO_2 starts to form from 393 K. Above 673 K SnO_2 is practically completely on the outer surface of the clay. Similar observations, deduced from Mössbauer measurements, have been reported when organotin compounds were introduced to montmorillonite[4] or laponite[5].

ACKNOWLEDGEMENT

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