

## SYNTHESIS AND PROPERTIES OF TITANIUM OXIDE CROSS-LINKED MONTMORILLONITE

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**Abstract**—Titanium was introduced into the montmorillonite structure by cation exchange with polymeric Ti cations, formed by partial hydrolysis of  $\text{TiCl}_4$  in HCl. On further hydrolysis and heating,  $\text{TiO}_2$  pillars in the form of anatase were formed between the montmorillonite layers. The resulting  $\text{TiO}_2$ -cross-linked montmorillonites possessed surface areas in the range 200–350  $\text{m}^2/\text{g}$  and pore volumes of about 0.2  $\text{cm}^3/\text{g}$  and were thermally and hydrothermally stable to 700°C. The basal spacing of products heated at temperatures > 200°C was about 28 Å, as determined by X-ray powder diffraction and by  $\text{N}_2$ -desorption pore-size analysis. The surface area increased and the pore volume decreased with increasing HCl-concentration in the Ti-solution. The uptake of  $\text{TiO}_2$  by the montmorillonite, the surface area, and the pore volume increased with increasing amount of Ti added in the preparation, to about 10 mmoles of Ti/g of montmorillonite. A further increase in the amount of Ti added resulted in a decrease in surface area, but the pore volume and the uptake of  $\text{TiO}_2$  remained almost constant. The high porosity and the interlayer spacing of the product are consistent with a structure similar to that previously proposed for smectites, cross-linked with hydroxy-Al oligocations.

**Key Words**—Cross-linked smectite, Montmorillonite, Pillared interlayer complex, Porosity, Thermal stability, Titanium oxide.

### INTRODUCTION

A new class of porous, high surface area materials of potential interest as catalysts and adsorbents was introduced by the synthesis of cross-linked (CLS) or pillared smectites (Brindley and Sempels, 1977; Vaughan *et al.*, 1979; Pinnavaia, 1983; Shabtai *et al.*, 1984b). Preparation of these CLSs usually involves an exchange of the cations in the interlayer region of the smectite by poly- or oligomeric hydroxy-metal cations. On heating, these inorganic polycations or oligomers form metal oxide pillars which permanently prop open the smectite layers. The cavities so formed are easily accessible for adsorption of gases and vapors.

Smectites cross-linked with oligomeric hydroxy-Al (Brindley and Sempels, 1977; Lahav *et al.*, 1978), hydroxy-Zr (Yamanaka and Brindley, 1979), and hydroxy-Cr cations (Brindley and Yamanaka, 1979) have been prepared and are characterized by surface areas of 200–500  $\text{m}^2/\text{g}$ , pore volumes of 0.15–0.20  $\text{cm}^3/\text{g}$ , and interlayer spacings of 7–10 Å.

Because the number of metals which form poly- or oligomeric cations upon hydrolysis is limited, an alternative method for preparing CLS materials that involves hydrolysis of complex cations between the smectite layers has also been used. For example, the preparation of  $\text{SiO}_2$ -cross-linked smectites through interlayer hydrolysis of  $\text{Si}(\text{acac})_3^+$  by Endo *et al.* (1980) demonstrated the usefulness of this synthetic approach. In their materials the layer separation was limited to one layer of silicon atoms. Using a related method, Yamanaka *et al.* (1984) prepared  $\text{Fe}_2\text{O}_3$ -cross-linked mont-

morillonite by the hydrolysis of  $(\text{Fe}_3(\text{OCOCH}_3)_7\text{OH})^+$  in the interlayer region of the clay. Recently, Lewis *et al.* (1985) developed techniques for preparing smectites cross-linked with three-dimensional  $\text{SiO}_2$ -oligomers. One metal cation, not previously investigated for the preparation of cross-linked smectites but reported to form polymeric cations upon hydrolysis, is  $\text{Ti}^{4+}$  (Einaga, 1979; Nabivanets and Kudritskaya, 1967). The present paper reports on the synthesis and characterization of  $\text{TiO}_2$ -cross-linked montmorillonite by cation exchange of montmorillonite with polymeric, partially hydrolyzed, Ti-bearing cations.

### EXPERIMENTAL

#### Montmorillonite

A Wyoming  $\text{Na}^+$ - $\text{Ca}^{2+}$ -montmorillonite (commercial designation, Volclay SPV 200) was obtained from the American Colloid Company. Impurity quartz was removed by fractionation using conventional sedimentation techniques. The <2- $\mu\text{m}$  fraction, which was practically free from impurities as determined by X-ray powder diffraction (XRD) analysis, was used as starting material in all preparations. The cation-exchange capacity of the montmorillonite was determined to be 89 meq/100 g; an elemental analysis of the clay is given in Table 2.

#### Cross-linking agent

The cross-linking agent, consisting of a solution of partially hydrolyzed Ti-polycations, was prepared by

first adding TiCl<sub>4</sub> into 6.0 M HCl. This mixture was then diluted by slow addition of distilled water with stirring to reach a final Ti-concentration of 0.82 M. HCl in amounts corresponding to final concentrations in the range 0.11–1.0 M were used in the preparations. The solutions were aged at room temperature for 3 hr to 20 days prior to their use.

#### Preparation of cross-linked smectites

Two grams of montmorillonite was dispersed in 0.5 liters of distilled water by prolonged stirring (5 hr) with a magnetic stirrer. The amount of cross-linking agent required to obtain a Ti/montmorillonite ratio of 4–40 mmole Ti/g montmorillonite was then added to the vortex of the vigorously stirred dispersion. The resulting product was left in contact with the solution for 16 hr and then separated by centrifugation. pH values were recorded directly after mixing and after the samples had stood for 16 hr; some values are given in Table 3. The product was then washed by redispersing it in distilled water, followed by separation by centrifugation. This procedure was repeated until the supernatant was free of chloride ions as determined by AgNO<sub>3</sub>. The conditions used for the preparations discussed in this presentation are specified in Table 1.

Because an acidic environment during the cross-linking procedure may affect the properties of the montmorillonite, a reference sample was prepared using the same procedure and adding 100 ml of 1.0 M HCl to the montmorillonite dispersion. This amount corresponds to the highest amount of HCl used in the TiO<sub>2</sub>-cross-linked montmorillonite preparations and resulted in a final pH of 0.8 in the dispersion.

#### Characterization of TiO<sub>2</sub>-cross-linked montmorillonite (TiO<sub>2</sub>-CLM)

N<sub>2</sub>-adsorption-desorption isotherms were determined using a Digisorb 2600 surface-area, pore-volume analyzer (Micromeretics Instrument Corporation). The samples were first outgassed at 200°C for 3 hr, and the isotherms were recorded at liquid nitrogen temperature. Surface areas were calculated using the BET equation, and pore volumes were estimated to be the liquid volume adsorbed at a relative pressure of 0.995. Pore-size distributions were calculated from the desorption branches of the isotherms using parallel plates as a geometrical model (Thomas and Thomas, 1967). The Halsey equation (Halsey, 1948) was used to calculate the nitrogen monolayer thickness at a particular relative pressure.

XRD analyses of CLMs were performed on samples prepared by spreading about 0.5 ml of a water suspension of the sample on a glass slide and drying the slide at room temperature. By using this method of preparation, the platelike particles presumably oriented themselves so that the 001 reflection was amplified

Table 1. Conditions used for preparation of TiO<sub>2</sub>-cross-linked montmorillonites.

Sample designation	Aging time (hr)	C <sub>HCl</sub> <sup>1</sup> (M)	mmole Ti/g clay <sup>2</sup>
TiA1	3	1.0	40
TiA2	24	1.0	40
TiA3	96	1.0	40
TiA4	240	1.0	40
TiA5	480	1.0	40
TiB1	3	1.0	40
TiB2	3	1.0	30
TiB3	3	1.0	20
TiB4	3	1.0	10
TiB5	3	1.0	4
TiC1	3	1.0	10
TiC2	3	0.62	10
TiC3	3	0.34	10
TiC4	3	0.16	10
TiC5	3	0.11	10

<sup>1</sup> Concentration of HCl in cross-linking solution. Ti-concentration = 0.82 M in all preparations.

<sup>2</sup> Amount of Ti added per gram of montmorillonite in the cross-linking procedure.

compared with a powder sample. The XRD patterns were obtained on a Philips powder diffractometer using Ni-filtered, fine-focus CuK $\alpha$  radiation.

Elemental analysis of TiO<sub>2</sub>-CLMs was carried out by atomic absorption spectroscopy (AAS) employing LiBO<sub>2</sub> fusion (Medlin *et al.*, 1969). SiO<sub>2</sub> was separately determined colorimetrically using the beta silicomolybdate method (Iler, 1979). Analysis of calcium in magnesium chloride extracts of calcium-saturated samples by AAS was used to determine cation-exchange capacities (CEC).

Thermal stability was investigated by exposing separate samples to temperatures in the range 100°–800°C for 3 hr in air. Hydrothermal stability was also investigated by subjecting separate samples to temperatures in the range 400°–800°C in the presence of steam. Thermogravimetric analyses were made with a Mettler Thermoanalyzer. The weight loss was recorded in the range 25°–1000°C at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Dependence of properties on amount of Ti added in the cross-linking procedure

The elemental compositions of TiO<sub>2</sub>-montmorillonite samples prepared using 4, 10, 20, and 40 mmole Ti/g montmorillonite are given in Table 2, together with the data for the Na<sup>+</sup>-Ca<sup>2+</sup>-montmorillonite and the HCl-treated montmorillonite. In Table 3, the pHs of the product solutions, measured directly after preparation (<10 min) and after 16 hr are given. The HCl concentration of the cross-linking solution used in these preparations was 1.0 M; the solution was aged for 3 hr prior to its use (see preparations TiB1, TiB3, TiB4, and

Table 2. Elemental analysis of Na<sup>+</sup>-Ca<sup>2+</sup>-montmorillonite, HCl-treated montmorillonite, and TiO<sub>2</sub>-cross-linked montmorillonites.

Metal oxide <sup>1</sup> (%)	Na <sup>+</sup> -Ca <sup>2+</sup> -montmorillonite <sup>2</sup>	H <sup>+</sup> -montmorillonite <sup>3</sup>	TiB5 (4 mmole/g) <sup>4</sup>	TiB4 (10 mmole/g) <sup>4</sup>	TiB3 (20 mmole/g) <sup>4</sup>	TiB1 (40 mmole/g) <sup>4</sup>
SiO <sub>2</sub>	60.9	59.8	45.2	33.3	31.3	33.8
TiO <sub>2</sub>	—	—	25.0	39.8	44.5	39.8
Al <sub>2</sub> O <sub>3</sub>	21.1	20.3	14.5	10.8	10.3	11.4
Fe <sub>2</sub> O <sub>3</sub>	4.13	4.11	3.19	2.61	2.15	2.60
MgO	3.25	2.70	1.96	1.48	1.27	1.52
CaO	0.84	0.14	0.15	0.08	0.08	0.06
K <sub>2</sub> O	0.42	0.34	0.26	0.14	0.14	0.14
Na <sub>2</sub> O	2.08	0.23	0.19	0.17	0.11	0.18
H <sub>2</sub> O <sup>5</sup>	6.6	11.0	9.2	9.7	9.3	9.6
Total	99.9	98.6	99.6	98.1	99.1	99.1

<sup>1</sup> All samples were dried at 110°C overnight, prior to analysis.

<sup>2</sup> Na<sup>+</sup>-Ca<sup>2+</sup>-montmorillonite, Volclay SPV 200, used as starting material in all preparations.

<sup>3</sup> Na<sup>+</sup>-Ca<sup>2+</sup>-montmorillonite treated with 0.17 M HCl for 16 hr.

<sup>4</sup> Amount of Ti/g of montmorillonite used in the cross-linking procedure. Conditions used for preparations TiB1–TiB5 are given in Table 1.

<sup>5</sup> Ignition loss between 110° and 1000°C.

TiB5 in Table 1). The uptake of Ti in the montmorillonite first increased with increasing amount added but then reached a constant value, corresponding to about 40% TiO<sub>2</sub> in the products, indicating saturation of the montmorillonite with respect to polymeric Ti-cations. The pH of each product solution was constant during the 16 hr the product was left in contact with the solution. Inasmuch as further hydrolysis of the excessive Ti-polycations probably involved the release of protons, this reaction did not appear to proceed at a significant rate in the product solution. A minor leaching of Al from the montmorillonite, due to the acidity of the product solutions, was detected by the elemental analyses of the TiO<sub>2</sub>-cross-linked samples and the HCl-treated montmorillonite.

N<sub>2</sub>-adsorption/desorption isotherms were measured on all samples. A typical isotherm is shown in Figure 1. The adsorption isotherm is type II in the classification of Brunauer, Deming, and Teller, whereas the hysteresis loop is of type B in the classification of de Boer (Thomas and Thomas, 1967). Among the materials showing this type of hysteresis are those in which the pore structure is built up of parallel plates. The difference between the type II isotherm shown in Figure 1 for the TiO<sub>2</sub>-cross-linked montmorillonite and the type I isotherms observed for Al<sub>2</sub>O<sub>3</sub>-cross-linked samples (Shabtai *et al.*, 1984a) reflects the larger interlayer

spacing in the former materials. In the Al<sub>2</sub>O<sub>3</sub>-cross-linked smectites, the interlayer spacing (~10 Å) approaches the size of two layers of nitrogen molecules (~7 Å). Multilayer adsorption of nitrogen is thus sterically hindered, and a type I, or Langmuir-type, isotherm, characteristic of monolayer adsorption, is obtained. In Figure 2, pore-volume and pore-area distributions are shown, as calculated from the desorption branch of the isotherm recorded for the sample treated with 40 mmole Ti/g montmorillonite. Most of the pore volume and pore area appears to be in pores of about 20 Å. Here, the pore size is defined by the distance between the montmorillonite layers in the product.

In Figure 3, the surface areas and pore volumes of the samples described above are plotted as a function of mmoles of Ti added in the cross-linking procedure. The surface area at first increased with increasing amount of Ti added in the preparation. After reaching a maximum at about 10 mmole Ti/g montmorillonite, an amount slightly greater than that required for saturation of the clay, the surface area gradually decreased with further increase in amount of Ti added. The pore volume first increased with increasing amount of Ti added, but then reached a constant value of about 0.2 cm<sup>3</sup>/g. The fact that the surface area decreased with increasing amounts of Ti added in the cross-linking procedure while the pore volume and the actual uptake of Ti remained constant is reflected in an increase in average pore size, with increasing amounts of Ti added.

The CEC of the TiO<sub>2</sub>-CLM sample prepared using 40 mmole Ti/g montmorillonite (TiB1) was determined to be 52 meq/100 g of TiO<sub>2</sub>-CLM, compared to 89 meq/100 g of starting montmorillonite. Because about 7 mmole Ti was taken up per gram of montmorillonite, 1 g TiO<sub>2</sub>-CLM contained about 0.65 g of montmorillonite and 0.35 g of TiO<sub>2</sub>, indicating that

Table 3. pH of product solutions, directly after mixing and after 16 hr.

Amount of Ti added (mmole/g)	pH directly after mixing	pH after 16 hr
4	1.5	1.5
10	1.1	1.1
20	0.8	0.9
40	0.6	0.7

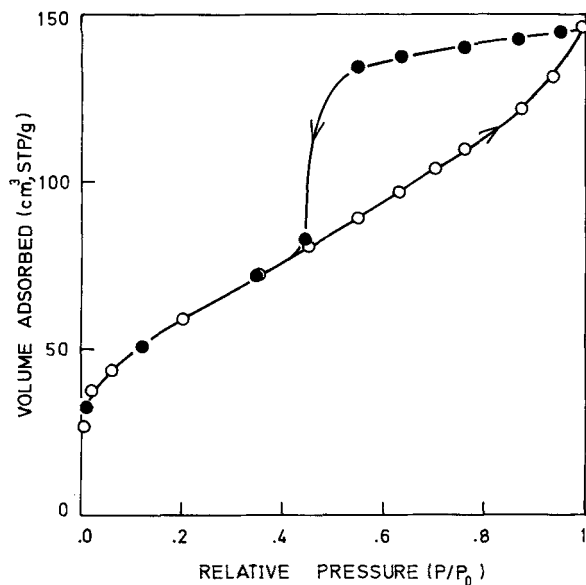


Figure 1. Nitrogen adsorption-desorption isotherm for TiA1 (see Table 1). Sample prepared using 40 mmole Ti/g montmorillonite.

the montmorillonite retained most of its original CEC in the TiO<sub>2</sub>-CLM structure.

#### Dependence of surface area upon HCl concentration

A series of samples were prepared from solutions 0.82 M with respect to TiCl<sub>4</sub> and 0.11–1.0 M with respect to HCl. Amounts corresponding to 10 mmole Ti/g montmorillonite were used in all preparations, and all

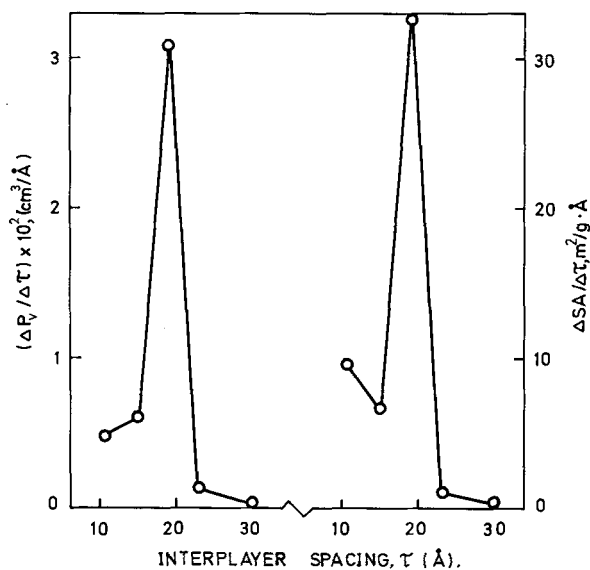


Figure 2. Pore-volume (left) and pore-area (right) distributions for TiA1 (see Table 1), calculated from the N<sub>2</sub>-desorption isotherm shown in Figure 1.

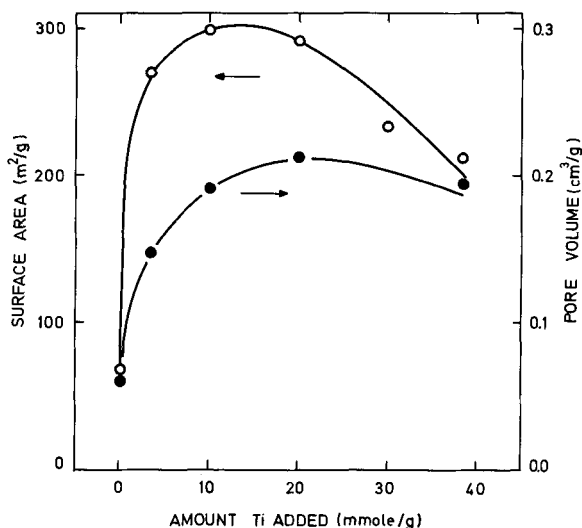


Figure 3. Dependence of surface area (open circles) and pore volume (solid circles) on amount of Ti added in the cross-linking procedure.

solutions were used after standing for 3 hr at room temperature (see preparations TiC1–TiC4 in Table 1). Surface areas of these samples as a function of HCl concentration of the cross-linking solution are shown in Figure 4. The surface areas at first increased with a decrease in HCl concentration of the solution, but then reached a constant value of about 335 m<sup>2</sup>/g. Pore-size distributions were calculated for some of the preparations in this investigation. A general decrease in average pore size with increasing surface area and decreasing HCl concentration was noted.

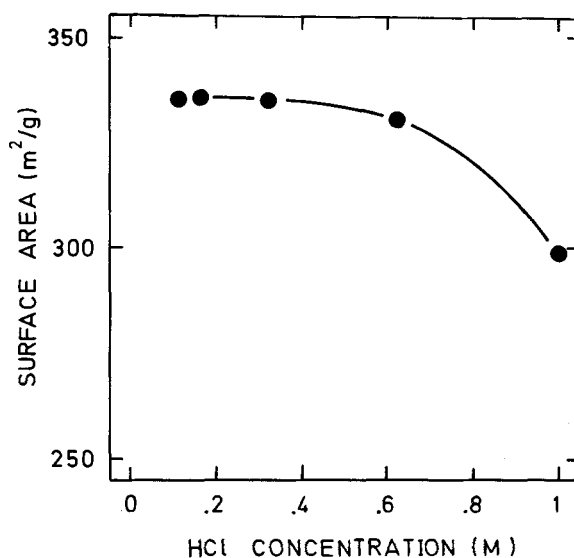


Figure 4. Surface area of TiO<sub>2</sub>-cross-linked montmorillonites vs. HCl concentration in cross-linking solution (see preparations TiC1–TiC5 in Table 1).

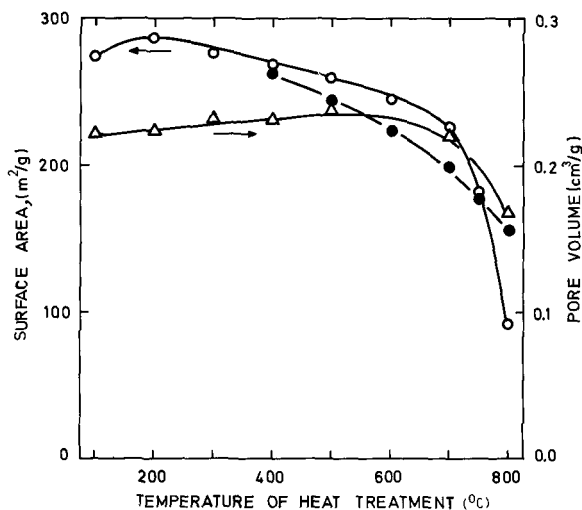


Figure 5. Dependence of surface area upon temperature of heat treatment (open circles) and of steam treatment (solid circles) and dependence of pore volume upon temperature of heat treatment (open triangles) for preparation TiB3.

#### Dependence of surface area upon aging time of solution

Surface areas were measured on samples prepared from solutions aged 3, 24, 96, 240, and 480 hr at room temperature. The Ti and HCl concentrations of the solutions were 0.82 and 1.0 M, respectively, and amounts of solution corresponding to 40 mmole Ti/g montmorillonite were used in all preparations (see preparations TiA1–TiA5 in Table 1). A minor increase in surface area from about 220 to 250 m<sup>2</sup>/g was observed with an increase in aging time from 3 to 480 hr. All solutions used in this study were oversaturated with respect to TiO<sub>2</sub>. Attempts to age less acidic solutions resulted in the precipitation of TiO<sub>2</sub> in 24 to 360 hr depending on acidity of solution.

#### Thermal and hydrothermal stability of TiO<sub>2</sub>-CLM

The thermal stability of TiO<sub>2</sub>-CLM was investigated for a sample prepared using Ti and HCl concentrations of 0.82 and 1.0 M, respectively, in the cross-linking solutions. Ten millimoles of Ti per gram of montmorillonite was used in the preparation, and the solution was aged for 3 hr before use (see preparation TiB3 in Table 1). Surface areas and pore volumes of heat- and steam-treated samples as a function of temperature are shown in Figure 1. The material was stable after being heat treated to 700°C, at which temperature the surface area started to decrease. The steam-treated samples, however, showed a more gradual decrease in surface area with increasing temperature, and retained a surface area of about 170 m<sup>2</sup>/g at 800°C. The pore volume of the heat-treated sample remained constant to about 700°C, but then decreased in the same manner as the surface area. The TiO<sub>2</sub>-CLM showed a higher

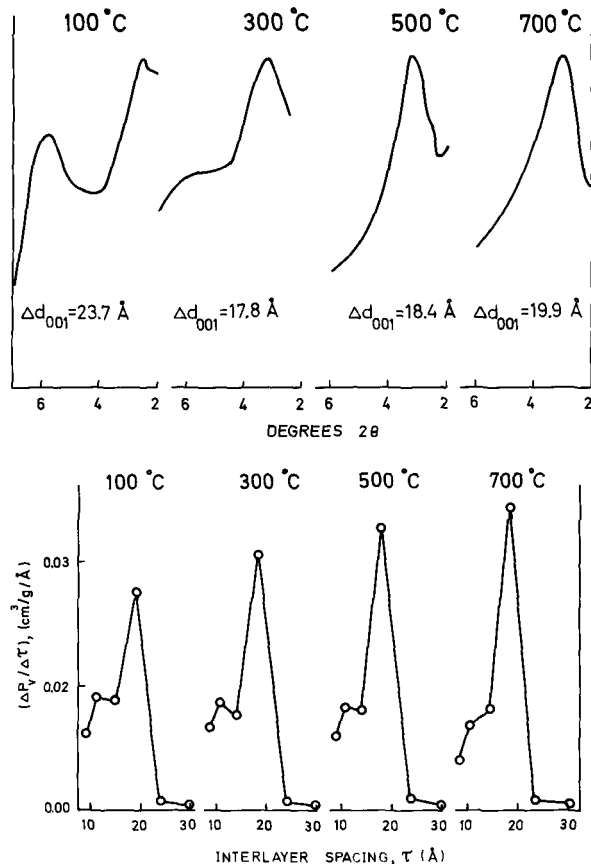


Figure 6. X-ray powder diffractograms (upper) and pore-volume distribution (lower) for TiB3 (see Table 1) vs. temperature of heat treatment (CuK $\alpha$  radiation).

hydrothermal than thermal stability at high temperatures. In Figure 6, XRD patterns of samples treated in air at 100°, 300°, 500°, and 700°C are shown together with desorption pore-volume distributions for the same samples. The d(001) peaks shown in these diffractograms represent the distance between two montmorillonite layers, including the thickness of one of the layers. By subtracting this thickness, 9.6 Å (Grim, 1953), from the recorded d(001) value, the pore size (or interlayer distance) of the product can be estimated (given as  $\Delta d_{001}$  in Figure 6). The pore sizes determined as  $\Delta d_{001}$  values from the XRD patterns correspond well with the maxima in the pore-size distributions calculated from the desorption branch of the N<sub>2</sub>-isotherms. In the XRD pattern of the sample treated at 100°C, a second peak is present at about 5.8°2 $\theta$ , corresponding to an interlayer distance of 5.7 Å. With increasing temperature, this peak turned into a shoulder and finally disappeared in the diffractogram recorded for the sample treated at 500°C. This peak may have been due to the presence of thermally less stable, microporous material in the product. The collapse of the micropores was also reflected in the pore volume distributions.

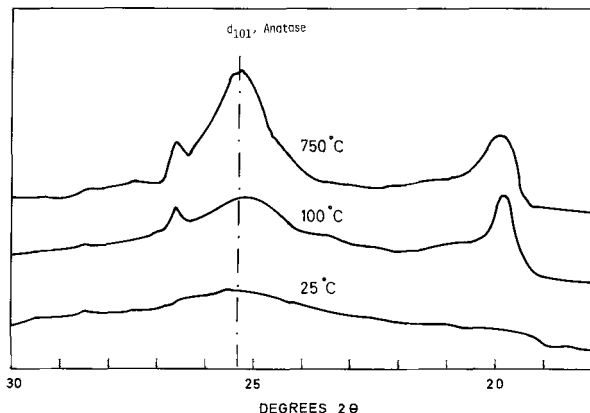


Figure 7. X-ray powder diffraction patterns of TiO<sub>2</sub>-CLM treated at 25°, 100°, and at 750°C, showing the development of the 25.3°2θ anatase peak (CuKα radiation).

In the XRD patterns of samples treated at 100°C and above, weak reflections of anatase were noted that became more intense with increasing temperature. The particle size of the TiO<sub>2</sub> was estimated from the broadening of the 25.3°2θ peak of anatase to be about 50 Å, using the full width of the peak at half maximum. XRD patterns, showing this peak for the air-dried sample and for samples treated at 100° and 750°C are shown in Figure 7. Because the thickness of the TiO<sub>2</sub> particles between the montmorillonite layers was limited to about 20 Å, according to the XRD patterns, the presence of flat TiO<sub>2</sub> particles with a side length considerably larger than the thickness is indicated.

A thermogravimetric analysis of the TiO<sub>2</sub>-CLM sample and the starting montmorillonite is shown in Figure 8. For both materials, the weight loss occurred in two steps. After losing the physically adsorbed water at a temperature of less than about 100°C, the weight of the montmorillonite remained nearly constant to about 500°C, where weight loss due to dehydroxylation of the structure began. The TiO<sub>2</sub>-CLM sample, however, showed a more continuous loss of weight to about 500°C, probably due to dehydroxylation of OH groups associated with interlayer titania. Between this temperature and 700°C, a small step loss occurred, after which the weight remained constant.

#### Structure of TiO<sub>2</sub>-CLM

The data presented here indicate that the TiO<sub>2</sub>-CLM phase has a structure consisting of montmorillonite sheets separated by very small particles of TiO<sub>2</sub>, leaving part of the interlayer spacing open for adsorption of gases and vapors. The material was obtained by ion exchange of the montmorillonite with polymeric Ti-cations, produced by partial hydrolysis of TiCl<sub>4</sub> in HCl. The literature on Ti<sup>4+</sup>-hydrolysis was reviewed by Baes and Mesmer (1976). The degree of polymerization of Ti-cations by partial hydrolysis of TiCl<sub>4</sub> in HCl solu-

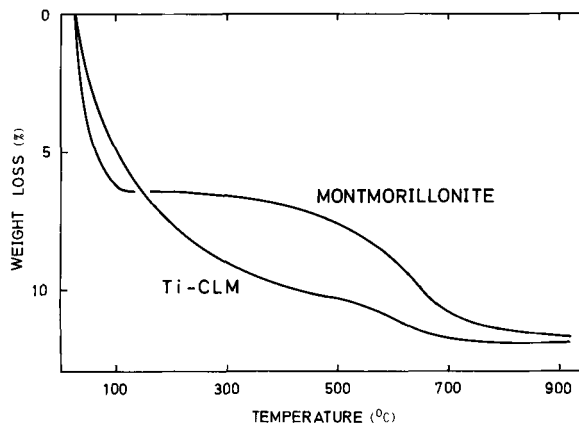


Figure 8. Thermogravimetric analysis of TiB3 (see Table 1) and of starting montmorillonite.

tions was found by Nabivanets and Kudritskaya (1967) to depend on both the Cl and Ti concentrations. They concluded that the polymeric species most likely are linked together by Cl-bridges, i.e. (TiO-Cl...TiO-Cl...)<sub>n</sub>. Einaga (1979) suggested from potentiometric measurements of Ti<sup>4+</sup> in aqueous hydrochloric acid solution the existence of the polynuclear cationic species ((TiO)<sub>8</sub>(OH)<sub>12</sub>)<sup>4+</sup>, but gave no structure of the complex.

After being introduced into the montmorillonite structure, the polymeric Ti-cations most likely underwent further hydrolysis to TiO<sub>2</sub>. The formation of TiO<sub>2</sub>-CLM can be described by the reaction sequence shown in Figure 9. The Ti is fixed in the final product as TiO<sub>2</sub>. In the idealized representation of TiO<sub>2</sub>-CLM in Figure 9, the pores have a rectangular shape. Although the distance between the montmorillonite layers in the structure can be measured by both XRD and desorption pore-size analysis, the distance between the pillars is more difficult to obtain, and no direct measurement of this distance has been found. A lower limit to this "interpillar" distance is set by the N<sub>2</sub>-desorption analysis, because the pore size measured by this technique represents the shortest distance between two walls in the pores. Thus, the lateral pore size is larger than the distance between the montmorillonite layers in the structure of TiO<sub>2</sub>-CLM.

Assuming a surface area of 800 m<sup>2</sup>/g for the montmorillonite sheets (Iler, 1955) and using parallel plates as a geometrical model, a value of the pore volume can be calculated from the measured interlayer distance and the elemental analysis of the product. Using preparation TiB4 as an example, the average interlayer distance, calculated from the N<sub>2</sub>-desorption isotherm, is 13 Å. From the elemental analysis, 1 g of TiB4 consists of about 0.58 g of montmorillonite and 0.42 g of TiO<sub>2</sub>. The pore volume is thus (800·0.5·10<sup>4</sup>)·(13·10<sup>-8</sup>)·0.58(0.42/3.84) = 0.19 cm<sup>3</sup>/g, where 3.84 g/cm<sup>3</sup> is the density of TiO<sub>2</sub> in the form of anatase. The good correspondence between this value of the pore volume

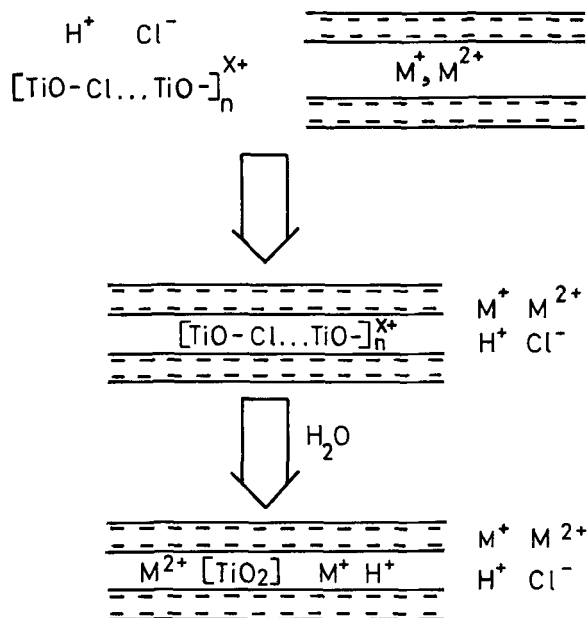


Figure 9. Suggested reaction sequence describing the formation of TiO<sub>2</sub>-cross-linked montmorillonite.

and that measured by N<sub>2</sub>-adsorption (0.19 cm<sup>3</sup>/g) supports the choice of geometrical model. Similar calculations for other samples give values of pore volumes that deviated by less than 50% from the measured ones.

### CONCLUSIONS

The most important difference between TiO<sub>2</sub>-cross-linked montmorillonite and other cross-linked smectites is the considerably larger interlayer spacing of this material. The interlayer spacing of TiO<sub>2</sub>-CLM is approximately 18 Å compared with about 10 Å for smectites cross-linked with hydroxy-Al (Lahav *et al.*, 1978) or hydroxy-Zr (Yamanaka and Brindley, 1979) oligomeric cations. The larger interlayer distance is accompanied by a thermal and hydrothermal stability comparable with that of hydroxy-Al and hydroxy-Zr cross-linked smectites in various forms (Vaughan *et al.*, 1981). Due to the larger pore size of TiO<sub>2</sub>-CLM, cracking of heavy oil fractions and biomass oils are two of the most interesting catalytic applications of this material. Catalytic activity for cracking of heavy oil fractions, using a micro-activity test (ASTM method D 3907-80) is now being investigated.

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### REFERENCES

- Baes, F. B. and Mesmer, R. E. (1976) *The Hydrolysis of Cations*: Wiley, New York, 147-151.
- Brindley, G. W. and Sempels, R. E. (1977) Preparation and properties of some hydroxy-aluminum beidellites: *Clay Miner.* **12**, 229-236.
- Brindley, G. W. and Yamanaka, S. (1979) A study of hydroxy chromium montmorillonites and the form of the hydroxy-chromium polymers: *Amer. Mineral.* **64**, 830-835.
- Einaga, H. (1979) Hydrolysis of titanium(IV) in aqueous (Na,H)Cl solution: *J. Chem. Soc. Dalton Trans.*, 1917-1919.
- Endo, T., Mortland, M. M., and Pinnavaia, T. J. (1980) Intercalation of silica in smectites: *Clays & Clay Minerals* **28**, 105-110.
- Grim, R. E. (1953) *Clay Mineralogy*: McGraw-Hill, London, p. 56.
- Halsey, G. (1948) Physical adsorption on non-uniform surfaces: *J. Chem. Phys.* **16**, 931-937.
- Iler, R. K. (1955) *The Colloid Chemistry of Silica and Silicates*: Cornell University Press, Ithaca, New York, 194-195.
- Iler, R. K. (1979) *The Chemistry of Silica*: Wiley, New York, 95-98.
- Lahav, N., Shani, U., and Shabtai, J. (1978) Cross-linked smectites. I. Synthesis and properties of hydroxy-aluminum montmorillonite: *Clays & Clay Minerals* **26**, 107-115.
- Lewis, R. M., Ott, K. C., and Van Santen, R. A. (1985) Silica-clay complexes: *U.S. Patent 4,510,257*, Apr. 9, 1985, 10 pp.
- Medlin, J. H., Suhr, N. H., and Bodkin, J. B. (1969) Atomic absorption analysis of silicates employing LiBO<sub>2</sub> fusion: *At. Absorpt. Newsl.* **8**, 25-29.
- Nabivanets, B. I. and Kudritskaya, L. N. (1967) A study on the polymerization of titanium (IV) in hydrochloric acid solutions: *Russ. J. Inovg. Chem.* **12**, 616-620.
- Pinnavaia, T. J. (1983) Intercalated clay catalysts: *Science* **220**, 365-371.
- Shabtai, J., Massoth, F. E., Tokarz, M., Tsai, G. M., and McCauley, J. (1984a) Characterization and molecular shape selectivity of cross-linked montmorillonite (CLM) catalysts: in *Proc. 8th Internat. Congress Catal., Berlin, 1984, Vol. 4*, G. Ertl, ed., Verlag Chemie, Berlin, 735-745.
- Shabtai, J., Rosell, M., and Tokarz, M. (1984b) Cross-linked smectites. III. Synthesis and properties of hydroxy-aluminum hectorites and fluorhectorites: *Clays & Clay Minerals* **32**, 99-107.
- Thomas, J. M. and Thomas, W. J. (1967) *Introduction to the Principles of Heterogeneous Catalysis*: Academic Press, London, 197-204.
- Vaughan, D. E. W., Lussier, R. J., and Magee, J. S. (1979) Pillared interlayered clay materials useful as catalysts and sorbents: *U.S. Patent 4,176,090*, Nov. 27, 1979, 7 pp.
- Vaughan, D. E. W., Lussier, R. J., and Magee, J. S. (1981) Pillared intercalated clay products: *U.S. Patent 4,271,043*, June 6, 1981, 6 pp.
- Yamanaka, S. and Brindley, G. W. (1979) High surface area solids obtained by reaction of montmorillonite with zirconyl chloride: *Clays & Clay Minerals* **27**, 119-124.
- Yamanaka, S., Doi, T., Sako, S., and Hattori, M. (1984) High surface area solids obtained by intercalation of iron oxide pillars in montmorillonite: *Mat. Res. Bull.* **19**, 161-168.
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