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PREPARATION AND PROPERTIES OF PILLARED INTERSTRATIFIED ILLITE/SMECTITE

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Abstract—Pillared, regularly and randomly interstratified illite/smectite (I/S) was prepared by interacting aluminum chlorohydrate with I/S in aqueous dispersion. I/S samples from Kinnekulle, Sweden, ranging in composition from 30–60% smectite layers, were used as starting clays. The pillaring resulted in a separation of the smectite layers in the I/S of about 9 Å, as estimated by X-ray powder diffraction and by nitrogen adsorption studies. Only the smectite layers of the clay were modified by the pillaring procedure. The pillared products had surface areas of 200–260 m^2/g and pore volumes of about 0.18 cm^3/g. The uptake of Al by the clay and the micropore surface area of the pillared products were proportional to the fraction of smectite layers in the I/S. The thermal and hydrothermal stability of the pillared I/S was similar to that of pillared montmorillonite prepared using the same procedure.

Key Words—Cross-linking, Illite/smectite, Pillaring, Smectite, Thermal stability, X-ray powder diffraction.

INTRODUCTION

In recent years, great interest has been focused on the preparation and characterization of different types of pillared clays and on possible applications for this type of material. One of the most interesting potential applications for pillared clays is as active components in catalysts for cracking of heavy oil fractions. Although pillared smectite is simple to prepare, has the advantage of great versatility in adjusting pore sizes, and is highly active for catalytic cracking, its thermal and hydrothermal stabilities are not sufficient for their use as cracking catalysts (Vaughan *et al.*, 1979; Occelli, 1983; Vaughan, 1988). At the thermal and hydrothermal conditions in the regenerator of a fluid catalytic cracker, these materials rapidly break down and lose most of their surface area and catalytic activity (Occelli and Tindwa, 1983; Sterte, 1989). Several preparation methods for pillared smectites having improved thermal stability, all involving stabilization of the pillars, have been investigated. Vaughan *et al.* (1981) showed that the stability could be substantially improved by hydrothermal treatment (reflux conditions) of the basic aluminum chloride solution used as the pillaring precursor. A study on the effects of hydrothermal treatment, at temperatures of 100°–160°C, of Al-hydroxy cation precursor solutions on the stability of pillared smectite was reported by Sterte and Otterstedt (1987). Incorporation of Si into the oligomeric Al-cations acting as pillaring precursors by treatment with Na silicate (Vaughan *et al.*, 1979) or with tetraethyl orthosilicate (Sterte and Shabtai, 1987) also resulted in some improvement of the stability of the pillared products. These improvements have, however, not resulted in a stability sufficient for use of the materials in a commercial cracking unit.

Recently, Jie *et al.* (1986) showed that a hydrothermally stable pillared clay can be prepared by using rectorite as a starting material instead of a smectite. Their product retained most of its initial surface area and cracking activity even after deactivation under rather severe conditions, i.e., using 100% steam at 800°C for 20 hr. Rectorite is a regularly interstratified clay mineral and is an alteration of pyrophyllite-like and water-swelling, smectite-like layers. As the pillaring process only involves the water-swelling part of the rectorite, pillaring results in a material in which the distance between the pores in the *c*-direction corresponds to two 2:1 layers, compared with one layer in pillared smectite. This increase in distance between the pores was used by Jie *et al.* (1986) to explain the remarkable stability of their product.

In addition to rectorite, many regularly and randomly interstratified clay minerals containing water-swelling smectite-like layers have been reported. In some of these, such as allevardite and corrensite, ordering involving a perfectly alternating sequence of two different layer types can be recognized by an integral series of 00*l*-reflections based on a large unit cell (Grim, 1968). These minerals, however, have a relatively limited geologic distribution. The most interesting mixed-layer clays are illite/smectite (I/S) minerals, because they are ubiquitous, well characterized chemically, and can be obtained with different degrees of ordering and with a wide range of illite : smectite ratios. If pillaring of I/S minerals were to result in products having hydrothermal stabilities similar to that of the pillared rectorite of Jie *et al.* (1986), these materials may be of great interest as active components in catalysts for cracking of heavy oil fractions.

I/S occurs in the Kinnekulle region of southwest Swe-

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Table 1. Percentage of smectite layers and cation-exchange capacity (CEC) of starting illite/smectite (I/S).

Sample[1]	Smectite in I/S (%)		CEC[2] (meq/100 g)
	From XRD[2]	From $K_{6x}/K_{6x,max}$[3]	
A2	32	42	46
B33	41	56	78
B36	46	63	78
B39	54	68	91
VC	100	98	89

[1] Samples of I/S used for the preparation of pillared products; see Experimental.
[2] Data for I/S from Byström (1956) and Brusewitz (1986). X-ray powder diffraction.
[3] Data for I/S from Byström (1956) and Brusewitz (1986). For further descriptions of methods used, see Brusewitz (1986).

den, in which sedimentary rocks are interbedded with K-bentonites that contain a series of I/S materials showing a wide range of systematic changes in the proportion of smectite layers (Byström, 1956; Brusewitz, 1986). The most interesting bentonites are found in the 2-m-thick B-bed and, above this bed, the two A-beds, each about 15 cm thick. A sample of the A2-bed was investigated by Reynolds and Hower (1970). They determined the expandable fraction to be 32% and found that the clay was ordered with a maximum I/S ordering. The B-bed bentonites are mostly randomly interstratified with 40–70% smectite in the I/S (Brusewitz, 1986).

The objective of the present investigation was to prepare Al_2O_3-pillared interstratified I/S and to investigate its properties. K-bentonites from the Kinnekulle A and B beds were chosen as starting clays because they contain a wide range in the proportion of smectite layers in the I/S. The products were characterized using X-ray powder diffraction, nitrogen adsorption, thermal analysis, and elemental analysis. The thermal and hydrothermal stabilities of the products were compared with those of a reference sample of pillared smectite prepared from a Wyoming montmorillonite.

EXPERIMENTAL

Starting materials

Samples of K-bentonites from the Kinnekulle A and B layers were provided by A.-M. Brusewitz, Geological Survey of Sweden. The sample designations used for these clays (A2, B33, B36, and B39) are the same as those used by Brusewitz (1986). A Wyoming montmorillonite (commercial designation, Volclay SPV 200) was obtained from the American Colloid Company. The clay samples were fractionated by conventional sedimentation techniques, and the <2-μm fraction was collected. The major impurities of the Kinnekulle bentonites were biotite, pyrite, quartz, and sandine (Byström, 1956; Brusewitz, 1986), whereas the Wyoming montmorillonite contained small amounts of quartz. The <2-μm fraction of the Kinnekulle bentonite samples contained small amounts of quartz and kaolinite; the corresponding fraction of the Wyoming montmorillonite was essentially free from impurities as determined by XRD. Some important chemical and physicochemical properties of the clay samples used as starting materials in this investigation are given in Table 1. Elemental analyses are given in Table 2. XRD patterns of air-dried samples of the different clays are shown in Figure 2.

Pillaring solutions

An aluminum chlorohydrate solution having an Al-concentration of 0.25 M, an OH/Al ratio of 2.5, and a pH of 4.4 was prepared by dilution of a commercial aluminum clorohydrate solution (Locron L, Hoechst). The solution was aged for 20 hr after dilution, prior to use as pillaring solution.

Preparation of pillared products

Four grams of the <2-μm fraction of the clay sample was dispersed in 4 liters of distilled water by prolonged stirring (5 hr). The aluminum chlorohydrate solution (80 ml, 0.25 M) was added to the vortex of the vigorously stirred clay dispersion in order to obtain an

Table 2. Elemental analyses (wt. %) of starting illite/smectite and pillared products.

Sample[1]	A2[2]	Pi-A2	B33[3]	Pi-B33	B36[3]	Pi-B36	B39[3]	Pi-B39	VC	Pi-VC
SiO_2	52.9	47.2	54.0	47.9	53.6	46.8	52.9	46.2	56.7	44.2
Al_2O_3	23.0	25.2	20.0	23.2	20.6	24.4	19.7	23.6	19.6	24.7
Fe_2O_3	2.25	1.81	2.59	2.40	3.13	2.68	3.03	2.50	3.84	3.28
MgO	3.11	2.37	4.20	3.60	4.45	3.77	4.49	3.88	3.02	2.41
CaO	1.4	0.0	1.7	0.0	1.9	0.0	1.9	0.0	0.8	0.0
K_2O	4.83	4.30	3.30	2.73	2.81	2.44	2.39	2.10	0.39	0.17
Na_2O	0.00	0.04	0.04	0.05	0.04	0.06	0.03	0.03	1.94	0.12
H_2O	12.6	17.4	12.5	18.7	13.6	19.4	14.2	19.9	13.1	23.3
Total	100.1	98.3	98.3	98.6	100.1	99.6	98.6	98.2	99.4	98.2

[1] Sample of illite/smectite (A2, B33, B36, B39, and VC) and the corresponding pillared product (Pi-).
[2] From Byström (1956).
[3] From Brusewitz (1986).

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Al/clay ratio of 5 mmole of Al/g of clay. The pillared product was washed by redispersion in distilled water and then separated by centrifugation. This procedure was repeated until the supernatant was free from chloride ions as determined by $AgNO_3$.

Analysis and characterization of products

N_2-adsorption-desorption isotherms were determined using a Digisorb 2600 surface-area, pore-volume analyzer (Micromeritics 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 0.990. Surface areas calculated using the Langmuir equation are also reported if the adsorption data correlated better with this equation than with the BET equation. External surface areas and micropore volumes were estimated using α_s-plots (Gregg and Sing, 1982), using adsorption of N_2 on hydroxylated silica as a standard isotherm. The surface area in micropores was calculated by subtracting the external surface area from the BET surface area.

XRD were performed either on un-oriented or oriented mounts. The XRD patterns were obtained on a Philips powder diffractometer using Ni-filtered, fine-focus CuKα radiation. Elemental analysis was carried out by atomic absorption spectroscopy (AAS) employing $LiBO_2$ fusion (Medlin *et al.*, 1969). SiO_2 was separately determined colorimetrically using the beta-silicomolybdate method (Iler, 1979).

Thermogravimetric analyses were made with a Mettler Thermoanalyzer. The weight loss was recorded in the range 25°–950°C at a heating rate of 10°C per min. Thermal stability was investigated by subjecting separate samples to temperatures in the range 200–800°C in air. Hydrothermal stability was investigated by exposing separate samples to 100% steam for 18 hr at 750°C.

RESULTS AND DISCUSSION

Elemental analysis

The elemental compositions of the Al_2O_3-pillared products prepared from the different I/S samples and from the montmorillonite are given in Table 2, together with the analyses for the corresponding starting clays. For a more accurate evaluation of the amount of Al taken up by the clays, structural formulae (Table 3) were calculated for the pillared products using the structural composition of the respective starting clay and assuming a constant tetrahedral and octahedral occupancy of Si and Al, respectively. The calculated charge per Al in the interlayer region of the products is also listed in Table 3. The amount of Al taken up by the clay increased with increasing fraction of smectite in the I/S. This was expected, because the cation-exchange capacity (CEC) of the clays increased with increasing smectite content (see Table 1). If the preparation of the pillared products had been a simple cation-exchange process, the charge per Al atom in the interlayer of the different pillared products should have been similar. As seen in Table 3, this charge varied over a relatively wide range, indicating that properties other than the CEC may have affected the amount of Al taken up by the clay in the pillaring process.

Table 3. Calculated structural formulae for pillared illite/smectite products and for pillared reference montmorillonite.

Sample[1]	Calculated structural formula	Charge/interlayer Al
Pi-A2	$Al_{0.43}K_{0.43}(Mg_{0.27}Fe_{0.11}Al_{1.54})(Si_{3.68}Al_{0.32})O_{10}(OH)_2$	0.49
Pi-B33	$Al_{0.49}K_{0.27}(Mg_{0.42}Fe_{0.14}Al_{1.40})(Si_{3.76}Al_{0.24})O_{10}(OH)_2$	0.54
Pi-B36	$Al_{0.60}K_{0.25}(Mg_{0.45}Fe_{0.16}Al_{1.44})(Si_{3.75}Al_{0.25})O_{10}(OH)_2$	0.50
Pi-B39	$Al_{0.62}K_{0.22}(Mg_{0.47}Fe_{0.15}Al_{1.43})(Si_{3.78}Al_{0.22})O_{10}(OH)_2$	0.48
Pi-VC	$Al_{0.97}Na_{0.02}K_{0.02}(Mg_{0.32}Fe_{0.22}Al_{1.48})(Si_{3.89}Al_{0.11})O_{10}(OH)_2$	0.37

[1] Sample of pillared interstratified illite/smectite; see Experimental.

Pinnavaia *et al.* (1984) investigated the pillaring of different smectite samples using aluminum chlorohydrate and base-hydrolyzed aluminum chloride as pillaring precursor solutions. They found that the amount of Al taken up per unit cell varied only slightly and that the variation was not correlated with the layer charge of the smectite. They suggested that a more-or-less uniform monolayer of hydrated polyoxo cations formed between the expandable layers and that electrical neutrality was achieved by hydrolysis of the pillaring cations. A consequence of this reaction mechanism is that the amount of Al taken up by I/S samples should have been proportional to the internal surface area of the expandable part of the clay and, thus, to the smectite content of the clay.

In Figure 1, the amount of Al taken up by the clay is plotted against the fraction of smectite in the I/S, as estimated by XRD and by the content of non-exchangeable K^+ in the clays (Brusewitz, 1986). In the latter method, the smectite fraction of the I/S is estimated as $(1 - K_{fix}/K_{fix,max})$, where K_{fix} is the number of non-exchangeable K^+ per $O_{10}(OH)_2$ in the I/S and $K_{fix,max}$, the corresponding number in a sample containing only illite layers. A good correlation can be seen between the amount of Al taken up and the smectite content of the clay, supporting the mechanism suggested by Pinnavaia *et al.* (1984). To determine which of the two estimates of the smectite content of the I/S gives the best correlation, the uptake of Al by pure illite should be investigated.

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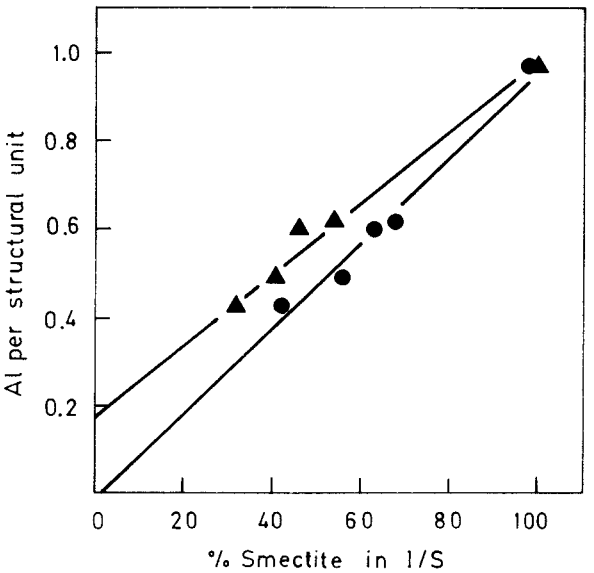


Figure 1. Uptake of Al by the clay vs. percentage of smectite layers as estimated by X-ray powder diffraction (●) and from $K_{fix}/K_{fix,max}$ (▲).

X-ray powder diffraction analysis

Figure 2 shows the XRD patterns of air-dried, oriented samples of the starting clays and the corresponding pillared products. For all the clays, pillaring resulted in a considerable increase in the d-values of basal reflections, as evidenced by the shift of the 001 peaks to lower angles. For the reference montmorillonite (VC), this increase in basal spacing was about 6.8 Å, whereas the increase for sample A2 was about 6.2 Å. The 001 peaks for the other three clay samples (B33, B36, and B39) and the corresponding pillared products were too broad for an accurate measurement of the layer separation caused by the pillaring process.

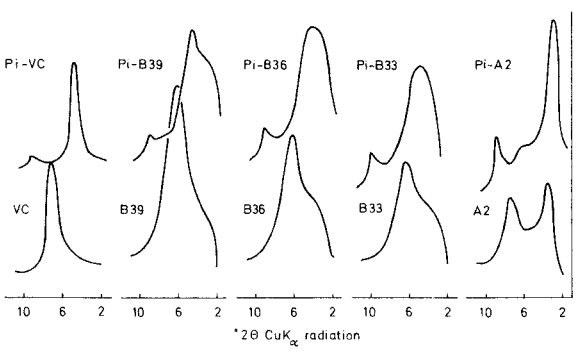


Figure 2. X-ray powder diffraction patterns of air-dried, oriented samples of pillared interstratified illite/smectite and the corresponding starting clays.

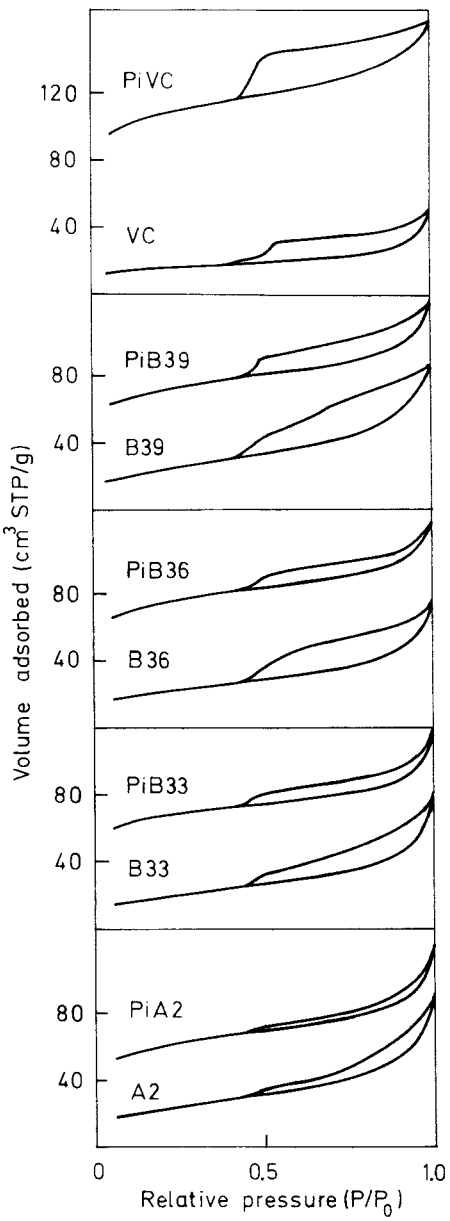


Figure 3. Nitrogen adsorption-desorption isotherms for pillared interstratified illite/smectite and the corresponding starting clays.

Nitrogen adsorption-desorption measurements

Complete adsorption-desorption isotherms were recorded for all starting clays and pillared products (Figure 3). The isotherms of the untreated clays were all type-II isotherms in the classification of Brunauer, Deming, and Teller, characteristic of non-porous solids. The isotherms recorded for the pillared products differed from those of the starting clays primarily in that a considerably larger volume was adsorbed at low

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Table 4. Surface areas (SA) and pore volumes (P_v) of illite/smectite clays and of derived pillared products.

	SA (BET) (m^2/g)	SA (Langmuir) (m^2/g)	P_v (cm^3/g)	External SA[1] (m^2/g)	Micropore SA[1] (m^2/g)	Micropore P_v[1] (cm^3/g)	Layer distance[2] (Å)
Starting clays[3]							
A2	80.9	—	0.133	89.4	—	—	—
B33	68.5	—	0.118	76.7	—	—	—
B36	75.4	—	0.110	76.1	—	—	—
B39	85.6	—	0.130	87.2	—	—	—
VC	51.2	—	0.072	40.8	—	—	—
Pillared products[4]							
Pi-A2	202	270	0.183	91.8	110	0.0545	9.9
Pi-B33	229	307	0.172	73.5	156	0.0729	9.4
Pi-B36	254	340	0.184	93.2	161	0.0748	9.3
Pi-B39	243	325	0.188	85.6	157	0.0739	9.4
Pi-VC	362	483	0.248	126	236	0.1098	9.3

[1] Estimated using α_s-plots (Gregg and Sing, 1982).
[2] Calculated from micropore surface areas and micropore volumes using parallel plates as a geometrical model.
[3] Sample of illite/smectite; see Experimental.
[4] Sample of pillared illite/smectite; see Experimental.

relative pressures. The isotherms of the pillared products appear to be composite isotherms of the type-II isotherm of the respective starting clay and a type-I isotherm due to adsorption in the micropores introduced by the pillaring procedure.

In Table 4, properties calculated from the adsorption measurements are given. Note that the BET surface areas of the pillared products increased with increasing fraction of smectite in the I/S. To analyze the adsorption measurements of the pillared products further, external surface areas, surface areas, and pore volumes in micropores were estimated using α_s-plots (Gregg and Sing, 1982). The external surface areas of the starting clays were found to be close to the surface areas calculated using the BET equation. With the exception of sample Pi-VC, the external surface area of all the pillared clays was similar to the external surface areas of the starting clays. For sample Pi-VC, the external surface area was considerably larger than that of the starting montmorillonite. The large external surface area of sample Pi-VC may have been caused by delamination of the smectite layers in the pillaring process.

As expected, the surface area and the pore volume of the micropores of the pillared products increased with increasing fraction of expandable layers in the I/S. In terms of the pillaring mechanism discussed above, the micropore surface area (and the micropore volume) should be proportional to the fraction of montmorillonite in the I/S. Furthermore, a plot of the micropore surface area vs. the fraction of smectite in the I/S should intercept at a point close to the origin, because pure illite does not form pillared products. In Figure 4, the micropore surface area is plotted against the fraction of smectite in the I/S, as estimated by XRD and by the content of non-exchangeable K^+ in the clays. Although a relatively good correlation (correlation coefficients: 0.920 and 0.960, respectively) was found between the micropore surface area and the smectite fraction as estimated by either of the two methods, only if this fraction was estimated from the amount of non-exchangeable K^+ did the line intercept at a point close to the origin. Assuming that the pillaring mechanism is valid, these results indicate that, at least for these particular clays, the method of calculating the fraction of smectite layers from the amount of non-exchangeable K^+ resulted in a better estimate compared with the XRD method.

Average distances between the layers in the pillared structures were calculated using the micropore surface areas and the micropore volumes, using parallel plates as a geometrical model (Table 4). The average interlayer distances were in the range 9.3–9.9 Å, indicating that the porous structure of the pillared I/S did not differ from that of the reference montmorillonite. Moreover, these average interlayer distances were very close to the value (9.3 Å) obtained from the XRD pattern of the pillared montmorillonite used as reference in this study by subtracting the thickness of one montmorillonite layer, 9.6 Å (Grim, 1968), from the recorded d(001)-value, 18.9 Å.

Table 5. Effects of thermal and hydrothermal treatment on the surface areas of pillared illite/smectite.

Sample[1]	Thermally treated[2] 400°C	600°C	700°C	800°C	Steamed[3] 750°C
Pi-A2	181	168	165	62	32
Pi-B33	199	175	173	75	27
Pi-B36	201	200	189	77	28
Pi-B39	201	169	158	80	36
Pi-VC	267	174	172	91	44

[1] Sample of pillared interstratified illite/smectite; see Experimental.
[2] Samples exposed to given temperatures in air for 3 hr.
[3] Samples exposed to 100% steam for 18 hr.

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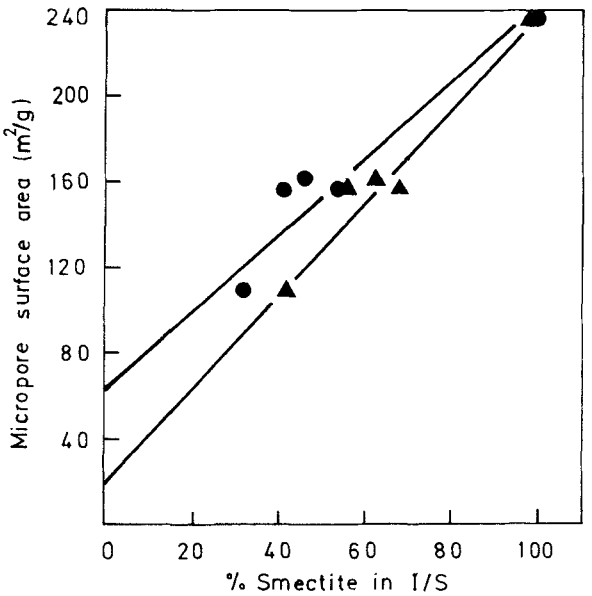


Figure 4. Micropore surface area of pillared illite/smectite as a function of smectite fraction in the starting clay, estimated by X-ray powder diffraction (●) and from $K_{fix}/K_{fix,max}$ (▲).

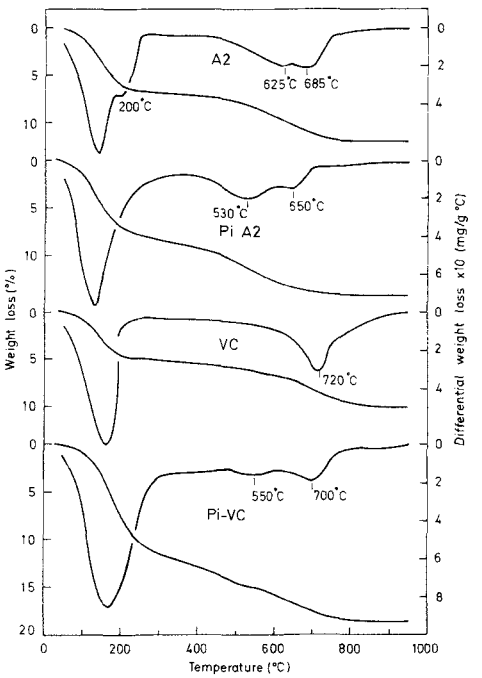


Figure 6. Thermogravimetric (TGA) and differential thermogravimetric (DTG) analyses of pillared montmorillonite, Pi-VC, pillared illite/smectite, Pi-A2, and the corresponding starting clays.

Thermal and hydrothermal stability of pillared products

Table 5 gives BET surface areas of samples of pillared I/S and pillared montmorillonite, heat-treated at given temperatures for 3 hr and treated at 750°C for 18 hr in 100% steam. The surface areas of the pillared I/S and that of the pillared montmorillonite decreased gradually with increasing temperature of heat treatment up to 700°C. Between 700° and 800°C, the surface area decreased significantly and the surface areas after treatment at 800°C were close to those of the starting clays. The pillared clays, however, differed from the starting clays in that, even after treatment at this temperature, part of the surface area was found in micropores, as indicated by α_s-plots. After steam treatment at 750°C, the surface areas decreased to values in the range 25–50 m^2/g, indicating a total collapse of the pillared structure.

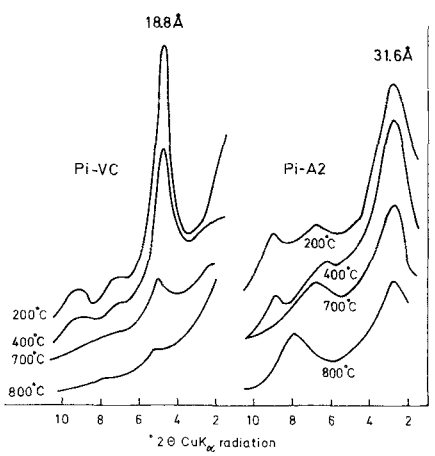


Figure 5. X-ray powder diffraction patterns of thermally treated samples of pillared montmorillonite, Pi-VC, and pillared illite/smectite, Pi-A2.

Figure 5 shows the XRD patterns of samples of the pillared reference montmorillonite (Pi-VC) and one of the pillared I/S (Pi-A2) heated in air at 200°–800°C for 3 hr. The basal spacing of the pillared montmorillonite treated at 200° and 400°C was about 18.6 Å. After the sample had been heated at 700°C, the 001 peak was less intense and shifted to a 2θ value corresponding to a basal spacing of about 17.7 Å. Heating at 800°C resulted in an almost complete disappearance of the 001 reflection, indicating a collapse of the pillared structure. The basal spacing of sample Pi-A2 was about 31.5 Å after heating at 200°C. Upon heat treatment at higher temperatures, the 001 reflection of sample Pi-A2 was less intense, but remained at an angle corresponding to a basal spacing of about 32 Å, indicating that a fraction of the pillared structure persisted, even after treatment at 800°C.

Figure 6 shows the results of the thermogravimetric (TGA) and differential thermogravimetric analyses (DTG) of I/S sample A2, the reference montmorillon-

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ite VC, and the respective pillared products (Pi-A2 and Pi-VC). The montmorillonite lost physically adsorbed water <200°C and structural water primarily in the range 500°–850°C, with a peak in the DTG at about 720°C. The pillared montmorillonite showed a more gradual loss of both physically adsorbed water and water formed by dehydroxylation of the pillars. In the DTG of this sample, two peaks were detected in the high-temperature region, centered at about 550° and 700°C. The absence of a peak in the vicinity of 550°C in the DTG of the starting montmorillonite suggests that this peak was associated with the dehydroxylation of the pillars, whereas the peak at about 700°C was probably connected with the dehydroxylation of the montmorillonite layers.

The I/S lost physically adsorbed water <250°C and structural water primarily in the range 500°–800°C. DTG revealed two peaks in the low- as well as in the high-temperature region. The TGA and DTG patterns of the pillared I/S were very similar to those recorded for the pillared montmorillonite. The pillared I/S showed a more gradual loss of water over the whole temperature range compared with the untreated I/S. The DTG for the pillared I/S showed two peaks in the high-temperature range, one at about 530°C and the other at about 650°C. Although two peaks were noted in the high-temperature region in the DTG of the starting clay as well, the peak at 530°C was probably primarily connected with the dehydroxylation of the pillars, whereas the peak at about 650°C was probably due to dehydroxylation of the clay sheets.

As mentioned in the Introduction, Jie *et al.* (1986) showed that thermally and hydrothermally stable pillared clays can be prepared from a Ba-Tou rectorite. Their pillared rectorite was essentially stable to 750°C on heating in air for 2 hr, as shown by XRD. On heating in 100% steam at 800°C for 17 hr, the surface area of their pillared rectorite showed a small decrease from an initial value of 174 to 129 m^2/g.

The pillared I/S investigated in this study does not show the enhanced stability of the pillared rectorite of Jie *et al.* (1986); the stability was similar to that of the pillared montmorillonite. Although the pillared I/S of this study is structurally similar to rectorite, both structural and compositional differences, which may explain differences in stability of the pillared products, exist between the two types of starting clays. In the rectorite of Jie *et al.* (1986), essentially all the layer charge was due to substitutions of Al for Si in the tetrahedral layers of the clay. In the Kinnekulle I/S, on the other hand, only 30–50% of the layer charge was due to tetrahedral substitutions, whereas 50–70% of the layer charge was due to substitutions in the octahedral layers. Using high-resolution solid-state ^{27}Al and ^{29}Si nuclear magnetic resonance, Plee *et al.* (1985) found that, on calcining, a reaction occurred between the pillars and the clay surface in pillared beidellite. This structural transformation was interpreted as the growth of a three-dimensional network grafted on the two-dimensional network of the clay. Calcining pillared smectites without tetrahedral substitutions did not modify the tetrahedral layers of the clay. This difference between tetrahedrally and octahedrally substituted clays in the binding of the pillars to the clay layers may explain the difference in stability between the pillared I/S of this study and the pillared rectorite of Jie *et al.* (1986). Another difference that may be important is that the non-smectite layers in the I/S are illitic and, thus, contain a considerable amount of potassium. In rectorite, these layers are pyrophyllite-like and contain no potassium.

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