PREPARATION AND PROPERTIES OF LARGE-PORE La-Al-PILLARED MONTMORILLONITE

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Abstract—Large-pore La-Al-pillared montmorillonite was prepared by reacting montmorillonite with hydrothermally treated mixtures of aluminum chlorohydrate and lanthanum chloride. The large-pore La-Al-pillared montmorillonite is characterized by basal spacings of about 26 Å, surface areas of 300–500 m²/g, and pore volumes in the range 0.2–0.3 cm³/g. Large-pore pillared montmorillonite products were obtained from solutions refluxed for >72 hr or treated in autoclaves at 120°–160°C for 12–96 hr. The most favorable pillaring solution for the production of large-pore La-Al-pillared montmorillonite had an OH/Al ratio of 2.5, a La:Al ratio of 1:5, and was 2.5 M with respect to Al. The elemental composition of large pore La-Al-pillared montmorillonite is similar to that of a conventional Al-pillared montmorillonite that has a basal spacing of about 19 Å. The 26-Å spacing is believed to be associated with the formation of large polymeric La-bearing Al-cations upon hydrothermal treatment of the solutions.

Key Words—Aluminum, Cross-linked smectite, Lanthanum, Montmorillonite, Pillared interlayer complexes, X-ray powder diffraction.

INTRODUCTION

In terms of catalyst usage and product value, catalytic cracking is the most important unit operation of the petroleum refining industry. In most modern cracking catalysts, zeolite Y is the active component. Catalysts based on different types of zeolite Y are excellent for cracking of lighter feed oils, but not so for heavier ones. The inherent problem with zeolite catalysts in processing such oils is the relatively small pore opening of the zeolite, about 10 Å. These openings are too small to allow entrance and conversion of some of the molecules making up heavy oil fractions (Nilsson and Otterstedt, 1987).

One solution to this problem could be the use of a zeolite or a zeolite-like material having pores larger than those of zeolite Y. It was in the search for such a material that clays pillared with inorganic polycations were first prepared by Vaughan *et al.* (1979). These authors also demonstrated the potential of Al-pillared smectites as cracking catalysts. The commercial use of such pillared montmorillonite for this application is, however, limited by lack of hydrothermal stability. At the hydrothermal conditions in the regenerator of a catalytic cracker, it rapidly looses most of its surface area and catalytic activity (Sterte, 1989).

Recently, McCauley (1988) found that hydrothermally stable pillared smectites can be prepared by using hydrothermally treated pillaring solutions containing mixtures of aluminum chlorohydrate and a cerium salt. Pillared smectites prepared from such solutions differ from conventional Al-pillared smectites in that the basal spacing as measured by X-ray powder diffraction (XRD) is considerably larger, i.e., 25–28 Å compared with 18–20 Å. This larger spacing is believed to be due to formation of a large Ce-Al-polycation upon hydrothermal treatment of the solution. For use as catalysts for cracking of heavy oils, this larger spacing is another advantage over conventional Al-pillared smectites, in addition to the improved hydrothermal stability. When tested as catalyst for cracking of heavy oil, these large pore Ce-Al-pillared smectites showed a high cracking activity even after steam deactivation at 760°C for 5 hr. When they were used in combination with zeolite USY, the resulting activity was higher than that expected from the activities of the components. McCauley (1988) found that these large-pore Ce-Al-pillared smectites can be prepared from solutions having Ce:Al molar ratios as small as 1:52, hydrothermally treated either by refluxing for several days, or by treatment in autoclaves at higher temperatures for shorter times. No systematic investigation of the dependence of the properties of the resulting material on different synthesis parameters has, however, been reported. Although his work was primarily concerned with pillaring solutions prepared from Ce-Al-mixtures, McCauley claimed that, in addition to cerium(III), other rare earth cations in admixture with aluminum chlorohydrate can be used for the preparation of large-pore pillared smectites.

Preliminary experiments in our laboratory have indicated lanthanum to be the rare earth element that most readily forms complex cations with aluminum suitable for the preparation of this type of material. The present paper reports on the preparation and characterization of large-pore La-Al-pillared montmorillonite by cation exchange of the montmorillonite with polymeric La-Al-cations prepared by hydrothermal treatment of mixtures of lanthanum chloride and aluminum chlorohydrate.

EXPERIMENTAL

Montmorillonite

A Wyoming Na^+-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-μm fraction, which was essentially free from impurities as determined by XRD, 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 4.

Pillaring agents

The pillaring solutions were prepared by hydrothermal treatment of solutions containing aluminum chlorohydrate (Locron L, Hoechst; 23.4% (w/w) Al_2O_3, OH/Al = 2.5) and lanthanum chloride (lanthanum chloride solution, Rhone Poulenc; 29.5% (w/w) La_2O_3, pH = 3.2). The hydrothermal treatments were carried out either by refluxing of the solutions for 24–120 hr or by treating the solutions in PTFE-coated stainless steel autoclaves at 120°–160°C for 12–96 hr. In the reflux experiments, solutions were used that were 0.50–4.0 M with respect to Al, that had La:Al molar ratios ranging from 0 to 1:2.5, and that were prepared from aluminum chlorohydrate having OH/Al molar ratios of 1.5–2.5. Aluminum chlorohydrate solutions having OH/Al-ratios of 1.5 and 2.0 were prepared by addition of calculated amounts of 6.0 M HCl solution to the commercial aluminum chlorohydrate solution. The autoclave experiments were all performed using solutions having an Al concentration of 2.5 M and a La:Al molar ratio of 1:5 and that were prepared from an aluminum chlorohydrate solution having an OH/Al molar ratio of 2.5.

Preparation of pillared products

One gram of montmorillonite was dispersed in 200 ml of distilled water (25°C) by prolonged stirring (5 hr) with a magnetic stirrer. The amount of pillaring solution required to obtain an Al/montmorillonite ratio of 20 mmole Al/g montmorillonite was then added to the vigorously stirred dispersion. The resulting product was left in contact with the solution for 1 hr and then separated by centrifugation. The product was then washed by redispersing it in distilled water and separated by centrifugation. This procedure was repeated until the supernatant was free from chloride ions as determined by $AgNO_3$.

Characterization of pillared 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 0.995.

XRD analyses of the pillared products were made on oriented samples prepared by spreading about 0.5 cm^3 of a water suspension of the sample on a glass slide and drying the slide at room temperature. The XRD patterns of the air-dried samples were obtained on a Philips powder diffractometer using Ni-filtered, fine-focus $CuK\alpha$-radiation.

Elemental analysis of the pillared samples was carried out by atomic absorption spectroscopy (AAS) employing $LiBO_2$-fusion (Medlin *et al.*, 1969).

RESULTS AND DISCUSSION

Reflux experiments

A series of samples was prepared from solutions 2.5 M with respect to Al and that had La:Al molar ratios of from 0 to 1:2–5 and that were refluxed for 0–120 hr. Figure 1 shows the XRD patterns of samples prepared from solutions having different La:Al-ratios and that had been refluxed for 120 hr. The sample prepared from the solution containing no La (La:Al = 0) showed a strong 001 reflection corresponding to a basal spacing of 19.6 Å. Although the crystallinity of the product, as reflected by the intensity of the 001 peak, increased to some extent with time of reflux, a sample prepared from the unrefluxed solution showed the same basal spacing (i.e., 19.6 Å). The XRD pattern of the sample prepared from the solution having a La:Al ratio of 1:25 was similar to, but less intense than that recorded for the sample containing no La. In the XRD pattern recorded for the sample prepared from the La:Al = 1:10 solution, a shoulder was present at an angle corresponding to a basal spacing of about 24 Å. The major basal spacing of this sample was, however, 19.2 Å, which is close to that of the samples described above. In the pattern of the sample prepared from the solution containing La:Al in a ratio of 1:5, the major basal spacing was at about 26 Å. This basal spacing is similar to those observed by McCauley (1988) for Ce-Al-pillared montmorillonite and fluorhectorite, i.e., 27.4 and 25.6 Å, respectively. In this XRD pattern two other peaks were present at angles corresponding to about 16.7 and 13.8 Å, respectively. The 16.7-Å peak may have been the result of incomplete exchange of the montmorillonite with the large La-Al-oligomer, which is believed to be responsible for the pillaring. The 13.8-Å peak is probably a second order of the 26-Å peak. The fact that the 13.8-Å peak is at a lower angle than that corresponding to a regular structure having a basal spacing of 26 Å is a further indication of some irregularity in the structure. The XRD pattern of the sample prepared from the solution having a La:Al ratio of 1:2.5
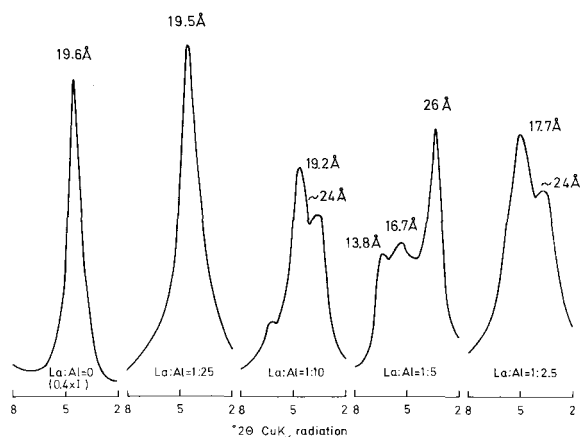
Figure 1. X-ray powder diffraction patterns of La-Al-pillared montmorillonites prepared from solutions 2.5 M with respect to Al, refluxed for 120 hr, and having La:Al molar ratios of 0–1:2.5.
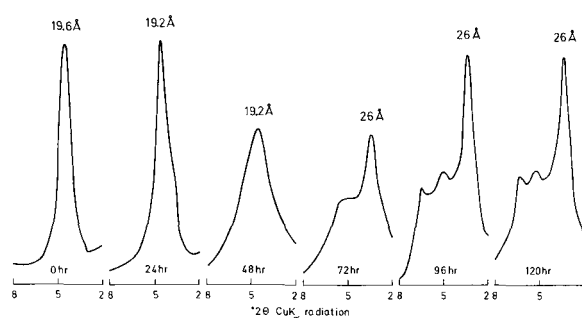

Figure 2. X-ray powder diffraction patterns of La-Al-pillared montmorillonites prepared from solutions 2.5 M with respect to Al, having a La:Al molar ratio of 1:5, and refluxed for 0, 24, 48, 72, 96, and 120 hr.

was similar to that of the La:Al = 1:10 sample. According to McCauley (1988), large pore Ce-Al-pillared smectites can be prepared from solutions with Ce:Al molar ratios as small as 1:52; however, the solution having a La:Al ratio of 1:25, used in this study, did not result in a large-pore product after 120 hr of reflux.

Figure 2 shows the XRD patterns of samples prepared using solutions 2.5 M with respect to Al, having a La:Al molar ratio of 1:5, and refluxed for 0–120 hr. The solution refluxed for 24 hr resulted in a product similar to that obtained from the untreated solution and also to a conventional pillared montmorillonite prepared using aluminum chlorohydrate containing no La. In the XRD pattern of the sample prepared from the solution refluxed for two days, the 001 reflection is broad, but it is still at about 19 Å. Refluxing of the solution for 72 hr yielded a product having a major basal spacing of about 26 Å, indicating the formation of large cationic species in the pillaring solution. For the sample refluxed for 96 hr, the 26 Å basal reflection is more intense; however, the XRD pattern of the sample prepared from the solution refluxed for 120 hr is very similar to that of the sample refluxed for 96 hr, indicating that no further reaction took place in the solution upon further refluxing.

The BET surface areas of these samples are given in Table 1. As seen, the surface areas are all in the range 300–370 m²/g, and no major dependence of the surface area on the time of reflux of the pillaring solution is evident. The C parameters of the BET equation calculated for the different samples are also given in Table 1. The change from negative to positive reflect the change from microporous to, presumably, supermicroporous materials with increasing time of reflux of the pillaring solution. This change is also reflected by the fact that the former, i.e., microporous, materials gave a better correlation with the Langmuir equation

than with the BET equation, whereas the opposite was true for the latter, supermicroporous, materials.

A series of samples was prepared from solutions having a La:Al molar ratio of 1:5 and Al-concentrations of 0.50–4.0 M; reflux time = 0–120 hr. A sol started to form in the 0.50 M solution after about 2 days and continued to form during the 120 hr of the experiment. In the 4.0 M solution a white precipitate formed after the solution had been cooled after refluxing for >48 hr. The solutions 1.25 and 2.5 M with respect to Al remained clear during the five days of the experiment. XRD patterns for samples prepared from these solutions, refluxed for 120 hr, are shown in Figure 3. The samples prepared from the 0.50 and the 1.25 M solutions gave XRD patterns characteristic of conventional Al-pillared montmorillonite, i.e., basal spacings = 18.5–19.5 Å. The sample prepared from the 2.5 M solution was discussed above. The XRD pattern of the sample prepared from the 4.0 M solution showed two rather broad peaks, one corresponding to a basal spacing of about 24.5 Å, indicating a partial formation of a large-pore pillared structure.

A series of samples was prepared from solutions having a La:Al molar ratio of 1:5, 2.5 M with respect to Al, prepared from aluminum chlorohydrate having OH/Al molar ratios of 1.5 and 2.0 and refluxed for 0–120 hr. All these preparations resulted in products having basal spacings in the range 18.0–19.5 Å. Apparently, a high basicity of the pillaring solution favored the

Table 1. Effect of time of reflux of pillaring solution on the BET surface area and the BET parameter C of derived La-Al-pillared montmorillonite.

Time of reflux[1] (hr)	0	24	48	72	96	120
Surface area (m²/g)	308	369	324	306	338	334
C parameter	−127	−241	−1997	277	116	166

[1] Samples were prepared from solutions 2.5 M with respect to Al and with La:Al = 1:5, refluxed for given times; see Experimental.
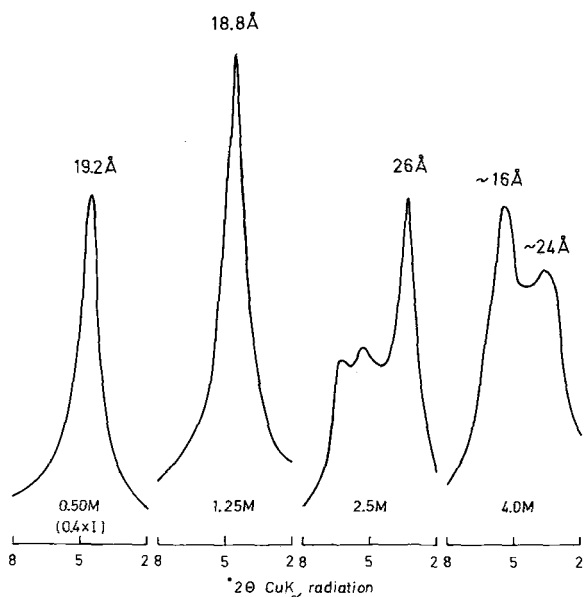
Figure 3. X-ray powder diffraction patterns of La-Al-pillared montmorillonites prepared from solutions having a La:Al molar ratio of 1:5, refluxed for 120 hr, and being 0.50, 1.25, 2.5, and 4.0 M with respect to Al.
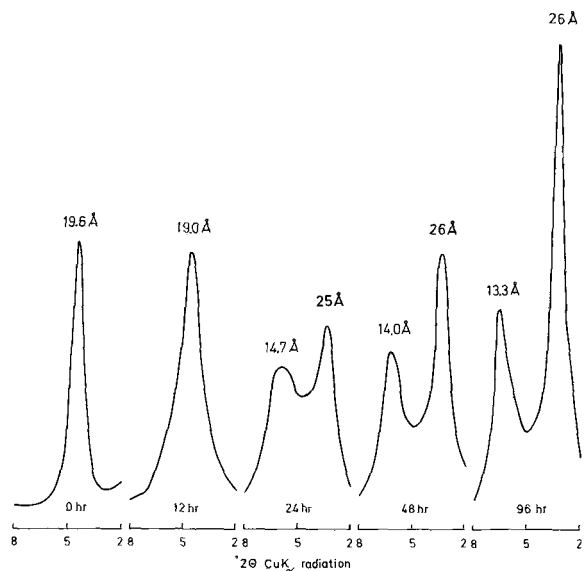

Figure 4. X-ray powder diffraction patterns of La-Al-pillared montmorillonites prepared from solutions 2.5 M with respect to Al, having a La:Al molar ratio of 1:5, and autoclaved at 120°C for 0, 12, 24, 48, and 96 hr.

formation of the large La-Al-cations believed to be responsible for the formation of large pore La-Al-pillared montmorillonite.

Autoclave experiments

A series of samples was prepared from solutions 2.5 M with respect to Al, having a La:Al molar ratio of 1:5, and hydrothermally treated in autoclaves at 120°–160°C for 12–96 hr. Figure 4 shows the XRD patterns of samples prepared from solutions treated at 120°C for 0, 12, 24, 48, and 96 hr. The samples prepared from solutions treated at this temperature for 0 and 12 hr gave basal spacings characteristic of conventional Al-pillared smectites (i.e., 18.5–19.5 Å). For the sample prepared from the solution treated for 24 hr, the basal reflection was at an angle corresponding to a spacing of about 26 Å, which is apparently characteristic of large pore La-Al-pillared smectites. The 001 peak of this sample is rather broad and has a relatively low intensity, indicating a poor crystallinity of the product. With increasing time of hydrothermal treatment of the pillaring solution at 120°C for as long as 96 hr, the 001 reflections of the resulting products became sharper and more intense. The sample treated for 96 hr gave a very sharp 001 reflection corresponding to a basal spacing of 26.0 Å. Heating this solution at 140° or 160°C yielded pillared products having 26-Å spacings after 12 hr. For the 140°C samples, the 001 peak became sharper and more intense with increasing time of treatment of the pillaring solution to 48 hr. A further increase in time of treatment resulted in a decline in

crystallinity of the pillared products. For the 160°C samples, the crystallinity of the products started to decline after only 24 hr of hydrothermal treatment of the solution.

In Table 2, BET surface areas of samples prepared from autoclaved solutions are given. For the samples prepared from the solutions treated at 120°C, a continous increase in surface area with increasing time of hydrothermal treatment can be seen. For the samples prepared from solutions treated at 140° and 160°C, the surface area increased upon treatment for 12 hr and then decreased with increasing time of hydrothermal treatment. The surface areas measured for the samples prepared from the solution treated at 140° were somewhat lower than of those prepared from solutions treated at 120° and 160°C. The observed trends in surface areas corresponds well with those observed by XRD. From XRD and surface area measurements, the rate of formation of the cationic species responsible for the formation of large-pore products appears to have in-

Table 2. BET surface areas of La-Al-pillared montmorillonites prepared from autoclaved solutions.

Treatment[1] temp. (°C)	Time of treatment (hr)				
	0	12	24	48	96
120	323	422	436	463	493
140	323	428	410	389	374
160	323	487	428	412	408

[1] Samples were prepared from solutions 2.5 M with respect to Al and with La:Al = 1:5, treated at given temperatures for given times; see Experimental.
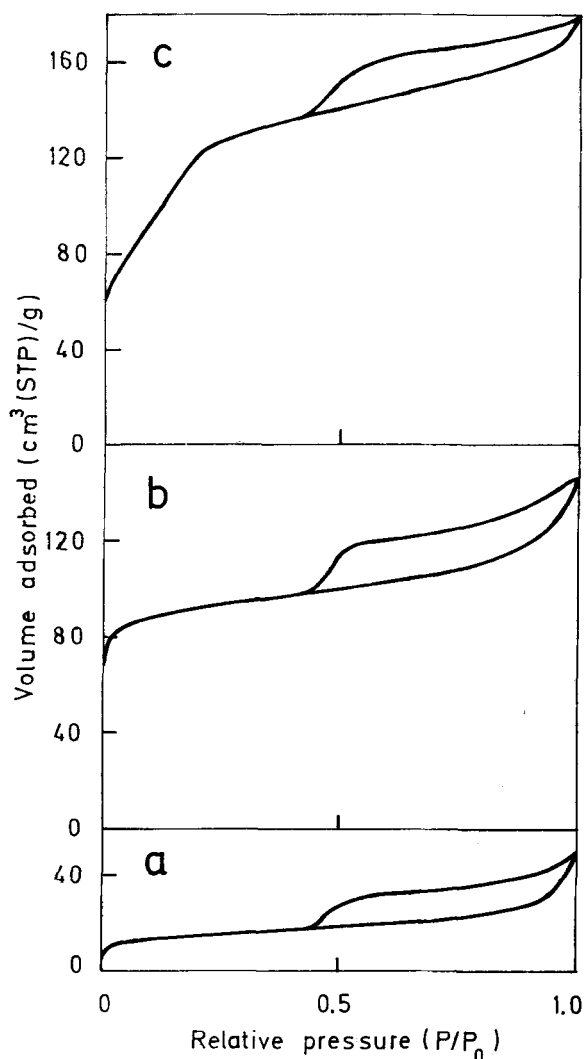
Figure 5. Nitrogen adsorption-desorption isotherms for (a) Na$^+$-Ca^{2+}-montmorillonite, (b) for La-Al-pillared montmorillonites prepared from a solution, 2.5 M with respect to Al, and having a La:Al molar ratio of 1:5, untreated, and (c) autoclaved at 120°C for 96 hr, respectively.

creased with increasing temperature of hydrothermal treatment. The surface area as well as the XRD pattern and the N$_2$ adsorption-desorption isotherm of the sample prepared from the solution treated at 160°C for 12 hr were almost identical with those of the sample prepared from the same solution treated at 120°C for 96 hr.

Figure 5 shows N$_2$-adsorption-desorption isotherms of the Na$^+$-Ca^{2+}-montmorillonite and for samples prepared from an untreated solution, 2.5 M with respect to Al and having a La:Al molar ratio of 1:5 and from the same solution treated at 120°C for 96 hr. The isotherm recorded for the starting montmorillonite was type II in the classification of Brunauer, Deming, Deming and Teller (Gregg and Sing, 1982), characteristic

of nonporous solids. The isotherms recorded for both pillared products can be described as composite isotherms of type II for the starting montmorillonite and type I due to adsorption in pores introduced by the pillaring procedure. The isotherm of the sample prepared from the untreated solution was similar to those peviously reported for conventional Al-pillared smectites, see e.g., Shabtai et al. (1984). A type-I isotherm is characteristic of microporous or supermicroporous materials.

If a solid contains micropores, the potential fields from the neighboring walls will overlap, and the interaction energy of the solid with a nitrogen molecule will be correspondingly enhanced. These reactions will result in a distortion of the isotherm, especially at low relative pressures (Gregg and Sing, 1982). This effect was clearly seen in the isotherm recorded for the sample prepared from the untreated solution, but less so for the sample prepared from the hydrothermally treated solution, indicating the existence of some larger pores in the latter material. On the other hand, all the isotherms were similar at relative pressures >0.4 and showed similar hysteresis loops, which all closed at a relative pressure of about 0.40. Hysteresis is a distinguishing feature of capillary condensation, which, in turn, is characteristic for mesopores (equivalent radii in the approximate range 20–2000 Å). As a relative pressure of 0.40 corresponds to a pore wall separation of about 23 Å (Innes, 1957), the similarity of the isotherms at relative pressures >0.40 implies that no pores >23 Å were created by the pillaring procedure in any of the preparations. Thus, at least some of the pores of the sample prepared from the hydrotheramally treated solution were larger than those of a conventional Al-pillared smectite but smaller than about 23 Å. These results are also compatible with the XRD analyses of the samples prepared from hydrothermally treated solutions that indicated a pore-wall separation of about 16 Å.

Table 3 shows some properties calculated from the isotherms shown in Figure 5. Surface areas and pore volumes in micropores (and supermicropores) were estimated using α_s-plots (Gregg and Sing, 1982). The use of a hydrothermally treated La-Al solution for pillaring of montmorillonite resulted in a product having larger total surface area and pore volume compared with that prepared from an untreated solution. A remarkable difference in micropore surface area between the two products was also observed. The sample prepared from the autoclaved solution had a micropore surface area of 430 m^2/g, which is about twice that of the sample prepared from the untreated solution. The micropore volume of the sample prepared from the autoclaved solution also exceeded that of the sample prepared from the untreated solution, but only by about 50%. The average layer distance calculated from the micropore surface area and pore volume using parallel plates as

Table 3. Properties of Na^+-Ca^{2+}-montmorillonite and La-Al-pillared montmorillonites calculated from N_2 adsorption-desorption isotherms.

Sample	Surface area (m²/g)	P_v[1] (cm³/g)	External SA[2] (m²/g)	Micropore SA[3] (m²/g)	Micropore P_v[2] (cm³/g)	Layer dist.[3] (Å)
Na^+-Ca^{2+}-mont.	51.2	0.07	40.8	—	—	—
La-Al-mont.[4] untreated	308	0.23	76.6	231	0.11	9.5
La-Al-mont.[5] autoclaved	493	0.28	62.5	430	0.15	7.0

[1] Total pore volume (P_v) estimated as liquid volume adsorbed at $P/P_0 = 0.995$.

[2] External surface area (SA), micropore SA and micropore pore volume were estimated using α_s-plots (Gregg and Sing, 1982).

[3] Calculated using parallel plates as a geometrical model.

[4] Sample prepared from an untreated solution, 2.5 M with respect to Al; La:Al = 1:5.

[5] Sample prepared from a solution, 2.5 M with respect to Al; La:Al = 1:5, autoclaved at 120°C for 96 hr.

a geometrical model is 9.5 Å for the sample prepared from the untreated solution. This value is close to the 9.6 Å obtained from the XRD analysis of this sample by subtracting the thickness of one montmorillonite layer, 9.6 Å (Grim, 1968), from the basal spacing. For the sample prepared from the autoclaved solution, the average layer distance calculated in the same manner was 7.0 Å, i.e., considerably less than would be expected from the XRD pattern of this sample (about 16 Å). This difference can be explained in part by a contribution from the pillars to the surface area in the latter material, which would result in an overestimation of the layer surface area and consequently an underestimation of the average interlayer distance. In the sample prepared from the untreated solution a contribution from the pillars to the surface area is unlikely inasmuch as the interlayer can only accomodate about two layers of nitrogen molecules (thickness = about 3.5 Å). Most likely, however, part of the surface area of the large pore La-Al-pillared montmorillonite is found in pores smaller than the 16 Å indicated by XRD.

Elemental analysis

In Table 4 elemental analyses of the starting Na^+-Ca^{2+}-montmorillonite and of a sample prepared from an untreated aluminum chlorohydrate solution, 2.5 M with respect to Al and containing no La, are given. Table 4 also shows the elemental compositions of samples prepared from a solution 2.5 M with respect to Al and having a La:Al molar ratio of 1:5, refluxed for five days and autoclaved for 96 hr at 120°C, respectively. The elemental analysis of the samples prepared from treated, La-containing solutions are very similar to that of the sample prepared from the untreated, La-free solution, indicating a similar uptake of Al by the montmorillonite from the different solutions. This similarity in uptake is somewhat surprising in view of the great structural differences between the samples found by XRD and by N_2 adsorption-desorption analysis. The La-contents of the La-Al-pillared products were rather low. Assuming that all the La was bound in polymeric La-Al-polycations, the elemental analyses of the La-

Al-pillared samples indicate a La:Al molar ratio of 0.06–0.07, corresponding to 0.75–0.9 La ions per Al_{13}-unit. All the La found by the elemental analysis was, however, not necessarily bound in polymeric La-Al cations. Part of the lanthanum may have been exchanged into the montmorillonite as La^{3+} ions.

Structure of large-pore La-Al-pillared montmorillonite

The oligomer responsible for the layer separation of conventional Al-pillared smectites is generally accepted to be $Al_{13}O_4(OH)^{7+}_{24}$ (Plee *et al.*, 1985). The structure of this cation is a central four-coordinated Al atom surrounded by 12 AlO_6 octahedra joined by common edges to form a Keggin-type structure. McCauley (1988) found that large-pore Ce-Al-pillared montmorillonites can be prepared from hydrothermally treated solutions having Ce:Al-ratios as small as 1:52. This, combined with the fact that the interlayer spacing of these materials was about twice that of conventional Al-pillared smectites, led him to suggest that the polymeric cation

Table 4. Elemental analysis of Na^+-Ca^{2+}-montmorillonite, Al-pillared montmorillonite and La-Al-pillared montmorillonite.

Metal oxide (wt. %)	Na^+-Ca^{2+}-mont.[1]	Al-mont.[2]	La-Al-mont. (reflux)[3]	La-Al-mont. (autoclave)[4]
SiO_2	56.7	45.6	45.8	44.3
Al_2O_3	19.6	24.4	23.6	25.4
Fe_2O_3	3.84	3.27	3.27	3.20
MgO	3.02	1.99	1.95	2.24
CaO	0.80	0.21	0.23	0.12
K_2O	0.39	0.40	0.39	0.30
Na_2O	1.94	0.24	0.26	0.25
La_2O_3	—	—	1.7	1.9
H_2O	13.1	22.4	21.9	22.2
Total	99.4	98.5	99.1	99.9

[1] Na^+-Ca^{2+}-montmorillonite, Volclay SPV 200, used as starting material in all preparations.

[2] Al-pillared montmorillonite prepared using La-free aluminum chlorohydrate.

[3] La-Al-pillared montmorillonite prepared using a solution with a La:Al molar ratio of 1:5, refluxed for 120 hr.

[4] La-Al-pillared montmorillonite prepared using a solution with a La:Al molar ratio of 1:5, autoclaved at 120°C for 96 hr.

responsible for the pillaring in large-pore pillared smectites consists of four Al_{13}-units, linked together by a tetrahedrally bound cerium atom. McCauleys work, however, does little to substantiate this suggestion and, no such polymeric ion has so far been reported in the literature. Further investigations of hydrothermally treated mixtures of aluminum chlorohydrate and rare earth salts are required to establish the structure of this polycation.

SUMMARY AND CONCLUSIONS

Large-pore La-Al-pillared montmorillonites were prepared from hydrothermally treated mixtures of aluminum chlorohydrate and lanthanum chloride. The hydrothermal treatment was carried out either at reflux conditions for several days or at high temperatures and for shorter durations in an autoclave. These large-pore La-Al-pillared montmorillonite products were characterized by basal spacings of about 26 Å and surface areas in the range 300–500 m²/g. At least part of this surface area was found in pores >9 Å, which is the pore-size characteristic for conventional Al-pillared smectites. Such large-pore La-Al-pillared montmorillonites may be of great interest as active components in catalysts for cracking of heavy oil fractions.

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