

CROSS-LINKED SMECTITES. I. SYNTHESIS AND PROPERTIES OF HYDROXY-ALUMINUM-MONTMORILLONITE

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(Received 23 May 1977)

Abstract—A stable porous system consisting of montmorillonite cross-linked by Al-hydroxide oligomers was synthesized by reacting at room temperature an aqueous solution of such oligomers with a unit-layer dispersion of montmorillonite. The resulting cross-linked montmorillonite (Al-CLM) is a nonswelling material, showing basal spacings of 14.4 to 18.8 Å after air drying and between 14.2 to 18.0 Å after treatment at 110°C. The basal spacing is found to depend on the age and OH/Al ratio of the Al-hydroxide solution, as well as on the relative amounts of the two reactants. A specific surface area of 160 m²/g and a diffraction pattern with a dominant basal spacing of 17.5 Å is obtained by using Al-hydroxide with OH/Al = 1.85, aged for at least 5 days, and by applying an Al/montmorillonite ratio greater than 1.5 in the cross-linking process. The basal spacing of Al-CLM remains essentially unchanged after heating at 220°C, while the specific surface area is not affected by heat treatment up to 480°C.

Two possible configurations of Al-hydroxide oligomers, homogeneously distributed between parallel montmorillonite unit-layers, were considered in order to account for the basal spacing of 17.5–18.8 Å, viz. (a) stacking of two oligomeric ring units in parallel orientation relative to the clay lamellae and (b) perpendicular orientation of individual oligomeric units.

Key Words—Aluminum, Electrostatic, Hydroxide, Oligomer, Montmorillonite.

INTRODUCTION

Synthesis of molecular sieves by cross-linking of layer silicates with organic agents has been achieved recently by Shabtai et al. (1976). The process involves interaction of smectites with di- or polycations derived from rigid, preferably cage-like amines, which acquire a single stable orientation in the interlayer space due to steric requirements imposed by their particular configuration. A uniform "pillar" network is obtained by two- or multipoint attachment of such cations to opposite layer surfaces. The constant interlayer spacing in such structures is determined by the molecular dimensions of the cross-linking cation, while the lateral ("interpillar") distance can be regulated by the use of smectites possessing different charge densities. Ammonium ions derived from di- or higher amines, e.g., 1,4-diazabicyclo(2,2,2)octane, 1,4- or 2,6-diaminoadamantanes, tetrakis-(p-aminophenyl)methane, and some 2,2',6,6'-tetrasubstituted benzidines which are sterically hindered from a flatwise orientation, are found to serve as suitable cationic species for preparation of cross-linked smectites. A 1,4-diazabicyclo(2,2,2)octane-montmorillonite system prepared by this method was found to possess pronounced molecular sieve properties and markedly higher catalytic activity for esterifi-

cation of carboxylic acids compared to ordinary alkylammonium-exchanged montmorillonites. Cross-linked systems of the above-mentioned type have been described recently also by Mortland and Berkheiser (1976).

The main shortcoming of organo-clay molecular sieves is their insufficient thermal stability for application as catalysts in high-temperature processes. Accordingly, a systematic study was undertaken with the objective of developing thermostable molecular sieves by interaction of platy clay minerals with suitable inorganic cross-linking agents.

GENERAL CONSIDERATIONS

Description of relevant systems

The molecular sieve model consists of parallel unit-layers (platelets, lamellae) cross-linked by inorganic oligomeric species, as shown schematically in Figure 1. The basal spacing, stability, surface properties and structural regularity of the sieve depend on the type of clay mineral and cross-linking agent, as well as on the preparative method and conditions. The cross-linked framework shown in Figure 1 is similar to both natural and synthetic hydroxy-interlayered expandable silicates, and, therefore, it would be appropriate to con-

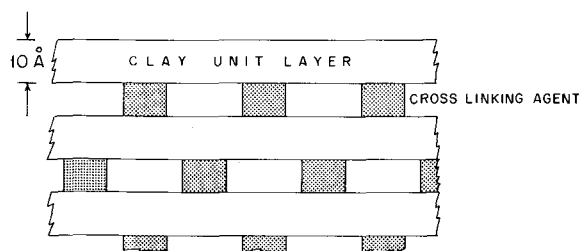


Fig. 1. Schematic view of an idealized molecular sieve obtained by cross-linking of montmorillonite.

sider first these types of minerals since their occurrence and properties have been extensively investigated during the past three decades.

The important factors which affect the formations and properties of hydroxy interlayers are pH, heterogeneity, and other surface properties of the clay mineral, type of interlayer ions, electrolyte concentration, wetting-drying cycles, and aging time (Jackson 1963a, b; Rich, 1968; Hsu, 1968; Carstea et al., 1970). Recently, Heller-Kallai et al. (1973) emphasized the promoting role of organic bases in the formation of Al-chlorites.

It should be noted that although hydroxy interlayered clays per se have never been treated as molecular sieves, the properties of these systems as porous structures have been recognized long ago (see Rich, 1968). The extent of filling of the interlayer space has been estimated by various methods and was found to vary from incipient interlayering to complete "brucite" sheets. Since the interlayers are usually filled only in part, interlayered clays can be considered as natural molecular sieves, provided that there is a continuity in the porous system which they produce. The exact spatial arrangement of the hydroxy interlayers and the pore size distribution have not been determined experimentally. According to Grim and Johns (1954) the interlayers form randomly dispersed "islands" in the interlayer space. Dixon and Jackson (1959) and Frink (1965) interpreted their dissolution data as indicating an Al-interlayer resembling an atoll, where the interlayer material is more concentrated near the edges. According to Rich (1968) a significant distribution of material throughout the entire interlayer space does take place.

Numerous investigators have been successful in synthesizing interlayered minerals in the laboratory (see Rich, 1968, for literature up to 1968; Ahlrichs, 1968; Carstea, 1968; Greenland and Oades, 1968; Sawhney, 1968; Davey and Low, 1968, 1972; Gupta and Malik, 1969; Herrera and Peech, 1970; Herrera et al., 1972; Hsu, 1968; Kidder and Reed, 1972; El-Rayah and Rowell, 1973; Heller-Kallai et al., 1973; Nagasawa et al., 1974; Tullock and Roth, 1975). Of special interest is the work by Kodama and Webber (1975), who prepared hydroxy-aluminum-phosphate-montmorillonite complexes and estimated the pore space of the inter-

layered structures formed. Following Rich (1968), the different methods employed in these studies are subdivided as follows.

- 1) Reacting a clay sample with a solution containing the metal hydroxide.
- 2) Acidifying a clay sample with an H-resin to induce Al release from the silicate crystal structure, with subsequent incorporation in the interlayer space.
- 3) Boiling of Al-saturated clays to increase hydrolysis.
- 4) Reacting Al-montmorillonite with organic bases.

In almost all of these methods, the formation time was at least several days and, in many cases, several weeks or months. In many of the preparations, porous derivatives were formed, but no application of these materials as porous adsorbents or catalysts was sought. However, a close analysis of the above methods shows that they can be divided into two main categories as follows.

a. *The in situ formation method.* The relevant metal cation is introduced into the clay exchange complex followed by in situ transformation into the hydroxide by raising the pH (Caillere and Henin, 1949; Slaughter and Milne, 1960; Turner and Brydon, 1965, 1967; Barnhisel and Rich, 1963, 1965, 1966; Brydon and Kodama, 1966; Ahlrichs, 1968; Davey and Low, 1968, 1971; Greenland and Oades, 1968; Gupta and Malik, 1969; Meyers and Aldrich, 1972; Tullock and Roth, 1974; Kodama and Webber, 1975).

b. *The cross-linking method.* The metal hydroxide oligomer (polymorph) is prepared separately and then interacted with the clay particles, leading to the formation of a cross-linked framework (Hsu and Bates, 1964b; Barnhisel and Rich, 1965; Carstea et al., 1968; Sawhney, 1968; Herrera and Peech, 1970; Somasiri and Huang, 1972; El-Rayah and Rowell, 1973; Brown and Newman, 1973).

Application of method (a) which can be considered as a simulated natural process, leads to slow, gradual formation of the interlayered structure, whereas in method (b), the metal hydroxide oligomers cross-link the clay platelets in a fast reaction and the product is obtained almost instantaneously. However, it should be noted that in the latter case some subsequent crystallographic changes in the product may occur, and consequently it is not always possible to make a clear-cut distinction between the two methods (Barnhisel and Rich, 1965; Carstea et al., 1970; Herrera et al., 1972). As mentioned later, if a freshly prepared metal hydroxide solution is used in method (b), both the in situ sequence and cross-linking probably take place, since the formation of stable oligomeric species is a slow process.

Theoretical and experimental aspects of the interaction between two types of colloidal particles possessing opposite electrical charge have been examined previously. Kruyt (1952) has cited several early theo-

ries and Weise and Healy (1975) have reviewed modern approaches for such an interaction in dispersed systems. Evidence for the interaction between positively charged oxides and negatively charged clay flakes, and its effect on soil structure and swelling, have been reviewed and discussed by Sumner, 1963; Deshpande et al., 1964; Davidtz and Sumner, 1965; Follett, 1965; Rowell, 1965; Rich, 1968; Kidder and Reed, 1972; El-Rayah and Rowell, 1973; El-Swaify and Emerson, 1975; and El-Swaify, 1976. Further, electron micrograph studies have been carried out on kaolinite-negative gold sol (Thiessen, 1942), kaolinite-positively charged AgI particles (Weiss and Russow, 1963), and kaolinite-positive ferric hydroxide particles (Follett, 1965). Flocculation of kaolinite particles by adsorption of montmorillonite platelets to the positively charged edges of the former has been studied by Schofield and Samson, 1954. Matijevic et al. (1961) used negatively charged, colloidal silver halide to coagulate positively charged aluminum hydroxide species. Bundy and Murray (1973) studied the flocculation of kaolinite induced by Al-hydroxide oligomers. El-Swaify (1976) studied the colloidal interaction between Al and Fe hydroxides and clays. In all of these studies, no effort has been made to prepare and use cross-linked systems as molecular sieves.

It should be noted that whereas the cross-linking process is based on electrical coulombic attraction between two types of oppositely charged colloidal particles, other forces are undoubtedly involved in later stages of the reaction, once close contact between the particles has been established.

APPLICATION OF CROSS-LINKING FOR SYNTHESIS OF MOLECULAR SIEVES

General method

Although it seems that both the *in situ* and the cross-linking methods can be used to produce molecular sieves, the latter method has been selected since it has the advantage of greater versatility and allows preparation of the cross-linking agent as a pure system under controlled conditions. The present work deals with the synthesis of a cross-linked montmorillonite molecular sieve by interaction of negatively charged clay unit layers with positively charged metal hydroxide oligomers, using both the reactants in the form of aqueous dispersions.

Clay mineral

As noted by Rich (1968), a large number of ions can form interlayers in expansible layer silicates, but because of their solubility and natural abundance, Al^{8+} , Fe^{2+} , Fe^{3+} , and Mg^{2+} could be considered suitable cations. Further, Cr, Ni, Mn, or Li can substitute Mg or Al in trioctahedral chlorites (Bailey and Brown, 1962). Other potential cross-linking agents include Ni-hydrox-

ide (see Brindley and Maksimovic, 1974; Brindley and De Souza, 1975; Wiewiora and Szpila, 1975), and Cu-hydroxide (see Rich, 1968).

Synthetic interlayers of Al, Mg, Fe, Ni, and Co hydroxides have been prepared by several investigators (see above). Because of its abundance in nature and the multitude of available literature data, Al-hydroxide was selected for the initial work on the production of molecular sieves. Other metal hydroxides were likewise tested as cross-linking agents in this laboratory, and results obtained will be reported later.

The solubility of aluminum hydroxide in water, and the form and stability of solute species containing aluminum hydroxide, have been the subject of numerous studies since the beginning of this century (see Hsu and Bates, 1964a, b; Hem and Roberson, 1967; Schoen and Roberson, 1970; Smith and Hem, 1972; Patterson and Tyree, 1973). According to Hem and Roberson (1967) and Smith and Hem (1972), aluminum is found in three distinct forms in acid aqueous solutions, i.e.,

- 1) Al_a , which includes all of the ionic forms, e.g., $Al(H_2O)_6^{3+}$, $AlOH(H_2O)_5^{2+}$, and $Al(OH)_2(H_2O)_4^+$;
- 2) Al_b , which includes polynuclear solute species with $OH/Al < 2.0$;
- 3) Al_c , the submicroscopic crystalline particles of $Al(OH)_3$, displaying the characteristic behavior of a solid.

Form Al_b is a polynuclear material (oligomeric species) probably containing 6–400 aluminum atoms per structural unit, depending on the OH/Al ratio and the aging period. The exact form of the oligomeric species of Al_b is not known, probably because of the marked effect of experimental conditions such as electrolyte concentration and temperature upon the rate of aluminum hydrolysis (see Patterson and Tyree, 1974). Form Al_c is composed of relatively large, microcrystalline particles.

The present work describes the preparation and structure determination of a cross-linked aluminum hydroxide-montmorillonite system (indicated below as Al-CLM).

EXPERIMENTAL

Montmorillonites

Three different types of montmorillonite were used in the study.

a. Fisher bentonite B-235. The homoionic Na form (particle size $< 2 \mu m$) was prepared by washing the commercial bentonite 5 times with 1 N NaCl solution, followed by removal of excess chloride by dialysis, and separating the $< 2 \mu m$ fraction by gravity sedimentation. The clay suspension was stored at the laboratory for 3 years. The C.E.C. of the $< 2 \mu m$ fraction was 0.9 meq/g.

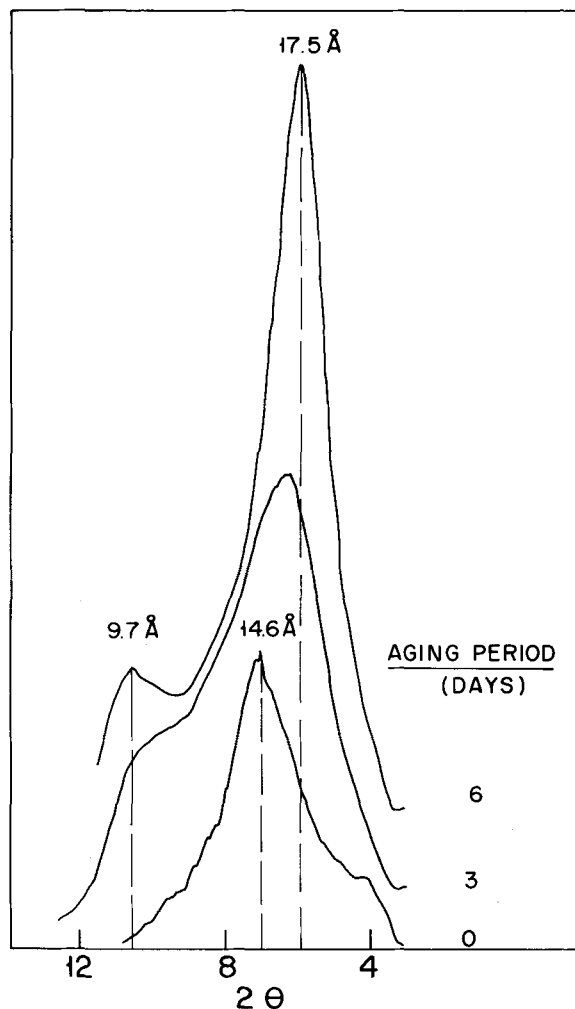


Fig. 2. X-ray powder diffraction patterns of oven-dry (110°C, 4 hr) films of Al-CLM as a function of the Al-hydroxide aging period (Fisher bentonite; OH/Al = 1.85; Al/bentonite = 1.96 mM/g).

b. Umiat bentonite* (Anderson and Reynolds, 1966). About 20 g of the raw material was suspended in water and the $<2 \mu\text{m}$ size fraction was separated by decantation and used without any additional treatment. This clay has been reported to have C.E.C. = 1.08 meq/g (Anderson and Reynolds, 1966).

c. Upton, Wyoming montmorillonite (No. 28, John C. Lane tract). The size fraction with equivalent diameter of 150 to 300 Å was used† (Paecht-Horowitz, 1973). The C.E.C. of the original clay was 0.9 meq/g.

Al-hydroxide solutions

AlCl_3 and NaOH solutions were prepared by dissolving the A.R. grade chemicals in redistilled water.

* Kindly supplied by D. M. Anderson, CRREL, Hanover, N.H. 03755, U.S.A.

† Kindly supplied by M. Paecht-Horowitz, Polymer Dept., Weizmann Institute of Science, Rehovot, Israel.

Al-hydroxide solutions with OH/Al molar ratios from nearly zero (no NaOH added) to 2.33 were prepared by dropwise addition of aqueous 0.2 M NaOH to a 0.2 M AlCl_3 solution. The resulting Al-hydroxide solutions were aged at 25°C. It was observed that they turned turbid at first, but within several hours became again transparent (see also Patterson and Tyree, 1973).

Cross-linking process

In most cases a clay suspension of 50 to 200 mg per liter was used. The Al-hydroxide solution was added dropwise with vigorous stirring, causing flocculation at a certain stage. The resulting system was usually left for several hours, the supernatant was then removed, and the sediment, i.e., the cross-linked clay product was centrifuged, collected and freeze-dried. For simplicity all cross-linked bentonites will be referred to as CLM (cross-linked montmorillonite).

Analytical determinations

Clay films for X-ray analysis were prepared by spreading about 0.5 ml of the clay suspension on a glass slide, and drying at room temperature. In several cases, clay powders were also analyzed. The X-ray determinations also included examination of clay films wetted by solvents, e.g., water or xylene.‡

RESULTS AND DISCUSSION

The dependence of the basal spacing and thermal stability of cross-linked aluminum hydroxide-montmorillonite (Al-CLM) systems upon experimental conditions, i.e., age of the Al-hydroxide oligomeric solution, OH/Al molar ratio in the oligomeric reactant prior to the cross-linking process, the ratio of Al to montmorillonite, and the type of montmorillonite, were systematically investigated. Results obtained are summarized below.

Basal spacing of Al-CLM as a function of the age of Al-hydroxide solution

Portions of a Fisher Na-montmorillonite dispersion were reacted with Al-hydroxide oligomeric solutions (OH/Al = 1.85), aged for different periods of time from 1 to 30 days. For comparison, a freshly prepared Al-hydroxide solution (no aging allowed) was also applied. X-ray examination of the Al-CLM products, after drying at 110°C, shows (Figure 2) that a minimal aging period of ca. 6 days is needed in order to obtain a product with dominant basal spacing of 17.5 Å. Further aging of the Al-hydroxide reactant for a period of up to 30 days does not cause any significant change in the basal spacing. Aging of the Al-CLM product, before drying, also does not affect the basal spacing.

‡ Some of these X-ray measurements were kindly carried out by Dr. R. Fahn and Dr. K. Fenderl, Süd-Chemie A.G., Moosburg, W. Germany.

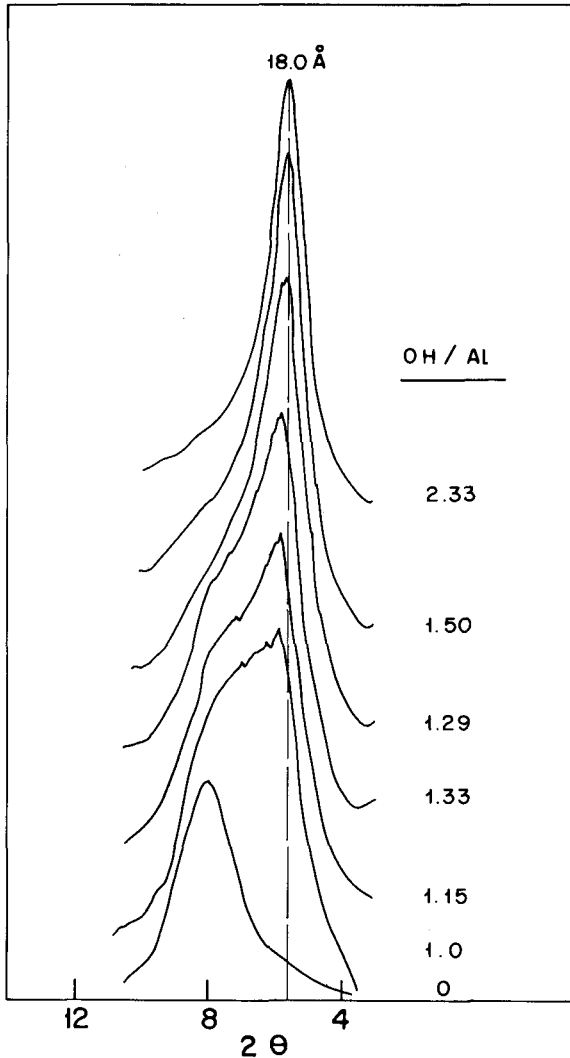


Fig. 3. X-ray powder diffraction pattern of oven-dry (110°C, 4 hr) films of Al-CLM as a function of the OH/Al ratio in the Al-hydroxide solution (Fisher bentonite; 30-day-aged Al-hydroxide solutions with different OH/Al ratios; the solution with OH/Al = 0 was a six-day-old 0.2 M AlCl_3 solution).

Basal spacing of Al-CLM as a function of the OH/Al ratio in the Al-hydroxide solution

A series of Al-hydroxide solutions was prepared by titrating aqueous 0.2 M AlCl_3 with different amounts of aqueous 0.2 M NaOH. After aging for 30 days, the resulting solutions were reacted with proper amounts of a Fisher montmorillonite suspension, keeping a constant Al/montmorillonite ratio of 1.96 mM/g in all cases. X-ray examination of the Al-CLM products shows (Figure 3) that the proportion of basal spacing of ca. 18.0 Å increases with increase in the OH/Al ratio from nearly zero to 2.33. The most marked changes in the X-ray powder diffraction patterns are observed, however, in the low range of OH/Al ratios (up to 1.22 mM/g).

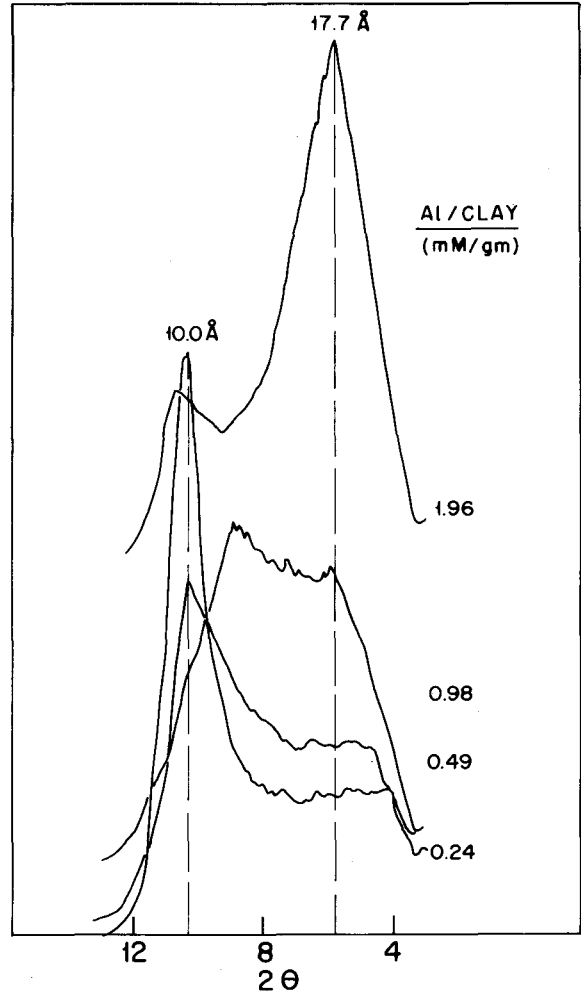


Fig. 4. X-ray powder diffraction patterns of Al-CLM films as a function of the Al-hydroxide/clay ratio (Fisher bentonite; aged Al-hydroxide solution with OH/Al = 1.85 mM/g; all Al-CLM samples heat-treated at 220°C for 2.5 hr).

In another experiment, Fisher bentonite was treated by AlCl_3 solution to give several Al/clay ratios. Part of the suspension was dried and X-ray examined immediately, whereas the other part was kept without drying out for three more days before examination. Both treatments had sharp peaks but the basal spacings of the oven-dry films shifted from 12.8 Å for the non-aged to 14.4 Å–14.8 Å for the aged samples (Table 1). Apparently the aluminum ion has been transformed into aluminum hydroxide (in situ formation) as a result of the aging. However, a separating distance of only one Al-hydroxide layer was formed in this case.

Stability of the basal spacing in Al-CLM as a function of the Al/montmorillonite ratio

After establishing that an OH/Al ratio > 1.8 produces a predominant basal spacing of ca. 17.5 Å, the effect of the relative amounts of Al-hydroxide and clay, used in

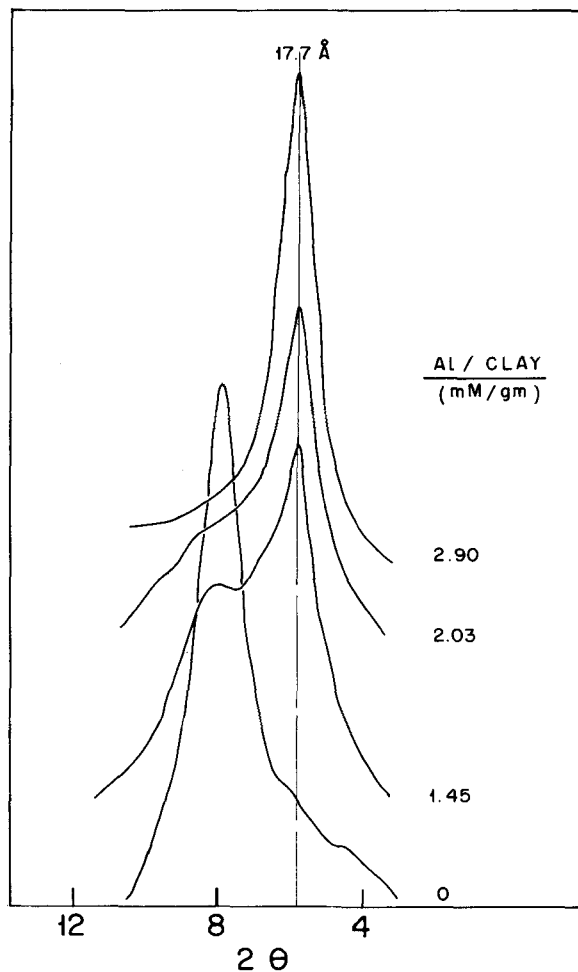


Fig. 5. X-ray powder diffraction patterns of Al-CLM films dried at 110°C prepared from Umiat bentonite and an aged Al-hydroxide solution (OH/Al = 1.85 mM/g).

the cross-linking process, upon the thermal stability of the Al-CLM product was investigated. For this purpose the ratios of the Al-hydroxide solution (OH/Al = 1.85) and the clay dispersion were varied in order to obtain a series of products with an Al/montmorillonite ratio in the range of 0.24 to 1.96 mM/g. The Al-CLM samples were subjected to heat treatment at 220° for 2.5 hr, and then X-ray analyzed. As seen from Figure 4, the basal spacing shows remarkable stability at an Al/clay ratio = 1.96 mM/g, in spite of the fact that at this point the Al-CLM possesses considerable porosity (vide infra).

It should be noted that in the synthesis of an Al-CLM molecular sieve a compromise should be made between the need to decrease the Al/montmorillonite ratio§ for the purpose of increasing the pore size, and the necessity to keep this ratio sufficiently high in order to secure good thermal stability of the porous system.

§ For complete coverage of the montmorillonite surface area by Al-hydroxide a limit Al/montmorillonite value of 5.3 mM/g is indicated (Turner and Brydon, 1965).

Table 1. Basal spacing of oven dry (105°C, two hours) films of Fisher bentonite treated by AlCl₃ solution. Films were prepared either immediately or 3 days after mixing the AlCl₃ with the bentonite.

mM Al g Clay	Basal Spacing (Å)	
	Aging Period of Al-Treated Clay (days)	
	0	3
1.12	12.8	14.8
1.68	12.8	14.4
2.24	12.8	14.7
2.80	12.8	14.7

Type of montmorillonite

Samples of Umiat bentonite cross-linked with Al-hydroxide show X-ray powder diffraction patterns (Figure 5) similar to those observed with corresponding Fisher bentonite system. Similar patterns are obtained also with cross-linked Upton montmorillonite samples.

Swelling behavior and other properties of Al-CLM

All Al-CLM samples showing a dominant basal spacing of 17.5 Å were oven-dried at 110° before examination. Air-dried samples showed a dominant basal spacing of 18.5–18.8 Å. Rewetting of air-dried samples resulted in a limited swelling of up to ca. 20 Å. On the other hand, wetting of air-dried samples with xylene (a mixture of isomeric xylenes) resulted in a negligible (<0.3 Å) increase in basal spacing.

Preliminary surface area measurements by N₂ adsorption with Al-CLM samples possessing a dominant basal spacing of 17.5 Å, gave values in the range of 160–200 m²/g. These values do not change in the temperature range of 110–480°, indicating a marked stability of the porous Al-CLM system.

Mechanism of formation and structural features of Al-CLM

There are only a few reports on Al-hydroxide-montmorillonite systems with basal spacings >16 Å. Hsu and Bates (1964b) have mentioned a 19.4 Å peak in the case of such a system, but no additional details were given. Turner and Brydon (1965) reported basal spacings between 16.4–19.5 Å for Al-bentonite-Ca(Al) hydroxide complexes, and indicated that the thermal stability of such materials increases with increase in the Al/clay ratio. Further, Hsu and Bates (1964a) and Hem and Roberson (1967) have obtained evidence that a stable configuration, in the form of six-membered ring units, is attained in Al-hydroxide oligomers having an OH/Al ratio of ca. 1.85 (the same ratio used in the present study in synthesizing most of the Al-CLM samples). Formation of larger oligomeric species, however, is also possible.

It is proposed that the first stage in the interaction between the positively charged Al-hydroxide oligomers and the negatively charged montmorillonite platelets is mainly electrostatic. The observed fast flocculation can

be ascribed to the cross-linking of neighboring clay lamellae by means of the oligomeric species. Presumably, some rearrangement of the latter on the clay surface can take place after the cross-linking because of electrostatic repulsion between neighboring oligomers, or as a result of chemical changes induced by the sudden increase in pH, accompanying the interaction. During the freeze-drying and subsequent heat treatment of the Al-CLM product some additional structural changes in the clay surface (see for instance Lahav and Bresler, 1973) and in the configuration of the oligomers could occur. More important, heat treatment at temperatures of 250°C probably results in gradual transition from ionic to near-covalent bonding between the oligomeric species and the montmorillonite layers, and in consequent stabilization of the porous network.

The orientation of the Al-hydroxide oligomers relative to the surface of the montmorillonite layer could be parallel, perpendicular or tilted. Turner and Brydon (1965) have proposed parallel orientation of Al-hydroxide layers in interlayered structures. The thickness of such layers was found to depend on the Al/montmorillonite ratio and on the temperature applied during heat treatment of the material. The thickness of a $[\text{Al}_6(\text{OH})_{12}(\text{H}_2\text{O})_{12}]^{6+}$ six-membered ring unit or larger oligomers should be approximately equal to that of a single sheet of gibbsite, i.e., ca. 4.7 Å. Assuming a thickness of 9.6 Å for the montmorillonite unit layer (van Olphen, 1963), the basal spacing of montmorillonite cross-linked with oligomeric units consisting of two stacked Al-hydroxide rings should be ca. 19.0 Å. However, if partial overlapping between the montmorillonite oxygens and hydroxyl groups in the oligomeric species or between the oligomeric species occurs, the basal spacing could be less than 19 Å, as found in the case of dry Al-CLM.

An alternative but more remote possibility, in line with the observed basal spacing of Al-CLM, could involve a nonparallel orientation of oligomeric six-membered ring units relative to the clay lamellae. The maximal interlayer distance in such a case would be attained in an exactly perpendicular orientation of the ring units, corresponding to a basal spacing of 18.7 Å or less, depending on the extent of overlapping.

It should be noted that the distribution and orientation of the oligomeric species in the interspace is important in determining the lateral distance between the immobilized "pillars" of the network, and the geometry of its pore structure. The lateral distance can be regulated by the use of smectites possessing different charge densities or by changing the Al/montmorillonite ratio of the system.

Since the total amount of Al-hydroxide oligomeric species in Al-CLM is considerably less than that needed for complete coverage of the clay surface, the indicated stacked Al-hydroxide oligomeric units in the interspace is unexpected. The strongest interaction of the

oligomeric units and the layer surface, at least in the first stage of the process, should be electrostatic. However, after partial neutralization of the electric charges on both the clay and Al-hydroxide oligomers, any further introduction of the latter in the interspace, which involves overcoming the hydration energy of the layer surface, would become increasingly difficult. Thus, although a major part of adsorbed water molecules are probably removed in an early stage of the reaction, further removal of water molecules becomes gradually less efficient. Consequently the formation of the stacked Al-hydroxide units is preferred over a uniform single unit distribution on the clay surface.

ACKNOWLEDGMENTS

The technical help of Mr. D. Zaretsky is appreciated. The discussions with Prof. L. Heller-Kalai and Dr. S. Yariv are gratefully acknowledged.

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Резюме- Устойчивая пористая система, состоящая из монтмориллонита, поперечно-связанного олигомером гидроокиси Al, была синтезирована в результате реакции, протекавшей при комнатной температуре, между водным раствором этих олигомеров и диспергированным однородно-слоистым монтмориллонитом. Образованный поперечно-связанный монтмориллонит (Al-ПСМ) представляет собой неразбухающий материал с основными промежутками от 14,4 до 18,8 Å после воздушной просушки и от 14,2 до 18,0 Å после обработки при 110°C. Было обнаружено, что величина основных промежутков зависит от возраста и отношения OH/Al раствора гидроокиси а также от относительных количеств двух реагентов. Специфическая площадь поверхности в 160 м²/г и дифракционная картина с доминирующим основным промежутком в 17,5 Å были достигнуты с использованием гидроокиси Al с OH/Al=1,85, имеющим возраст не менее 5 дней и использованием отношения Al/монтмориллонит больше 1,5 при процессе поперечного связывания. Основной промежуток Al-ПСМ остается существенно неизменным после прогревания при 220°C, в то время как специфическая площадь поверхности не изменяется при тепловой обработке до 480°C.

Были рассмотрены две возможные конфигурации олигомеров гидроокиси Al, гомогенно распределенных между параллельными однородными слоями монтмориллонита, чтобы объяснить основной промежуток в 17,5-18,8 Å, а/а/ пакет двух олигомерных колец, параллельно ориентированных по отношению к слоям глины и б/б/ перпендикулярно ориентированные отдельные олигомеры.

Kurzreferat- Ein stabiles, poröses System, welches aus mit Al-Hydroxyd oligomeren querverbundenen Montmorillonit besteht, wurde synthetisiert indem bei Zimmertemperatur eine wässrige Lösung dieser Oligomere mit einer Einheitsschichtdispersion von Montmorillonit reagiert wurde. Der resultierende querverbundene Montmorillonit (Al-CLM) ist ein quellfestes Material, das einen Basisabstand von 14,4 bis 18,8 Å nach Lufttrocknen und zwischen 14,2 und 18,0 Å nach Behandlung bei 110°C besitzt. Es wurde herausgefunden daß der Basisabstand sowohl vom Alter und OH/Al Verhältnis der Al-Hydroxydlösung wie auch von den relativen Mengen der beiden reagierenden Substanzen abhängt. Eine spezifische Oberfläche von 160 m²/g und ein Diffraktionsmuster mit einem dominanten Basisabstand von 17,5 Å wird erhalten indem Al-Hydroxyd mit OH/AL = 1,85, mindestens 5 Tage lang gealtert, benutzt wird und indem ein Al/Montmorillonit Quotient für die Querverbindung benutzt wird, der größer als 1,5 ist. Der Basisabstand des Al-CLM bleibt im wesentlichen unverändert nach Erhitzen bei 220°C, während die spezifische Oberfläche nicht von Hitzebehandlung bis 480°C beeinflusst ist. Zwei denkbare Konfigurationen der Al-Hydroxydligomere, homogen verteilt zwischen parallelen Montmorilloniteinschichten, wurden erwogen, um den Basisabstand von 17,5-18,8 Å zu begründen, nämlich (a) aufstapeln von zwei oligomeren Ringeinheiten in parallel zu den Tonlamellen- Orientierung und (b) senkrechte Orientierung von individuellen oligomeren Einheiten.