CROSS-LINKED SMECTITES. III. SYNTHESIS AND PROPERTIES OF HYDROXY-ALUMINUM HECTORITES AND FLUORHECTORITES

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Abstract—Interaction of La³⁺ and Ce³⁺-exchanged hectorites with oligomeric hydroxy-Al cations results in the formation of cross-linked hectorites possessing moderately high surface areas (~220–280 m²/g) and high thermal stability. The basal spacings of these products were generally in the range 17.0–18.0 Å, the exact d(001) value depending on the age of the hydroxy-Al oligomeric solution and on the pH of the starting hectorite dispersion. Interaction of Li- or Ce-fluorhectorite with hydroxy-Al oligocations produced the corresponding cross-linked fluorhectorites, which showed markedly higher basal spacings (18.2–20.0 Å for air-dried samples), surface areas (~300–380 m²/g), and thermal stability, as compared with those of the cross-linked hectorites. The cross-linking agent applied in the synthesis of the hydroxy-Al hectorite and fluorhectorite products consisted of a solution of hydroxy-Al oligomers aged for periods of 7 to 27 days. A constant ratio of 2.0 mmole Al/g of smectite was used in all preparations. The high basal spacings and porosity of the newly synthesized products are consistent with a structure similar to that previously proposed for cross-linked hydroxy-Al montmorillonite.

Key Words—Cross-linking, Fluorhectorite, Hectorite, Hydroxyaluminum, Molecular sieve, Surface area, Synthesis, Thermal stability.

INTRODUCTION

The process of smectite cross-linking has recently attracted considerable attention (Pinnavaia, 1983). It provides a versatile method for preparing a new class of molecular sieves which are structurally different from natural and synthetic zeolites and which offer new possibilities for application as catalysts and adsorbents (Shabtai, 1979, 1980; Shabtai and Lahav, 1980; Vaughan and Lussier, 1980; Vaughan et al., 1979, 1981a, 1981b; Lussier et al., 1980).

Cross-linked smectites (CLS), referred to by some authors also as pillared interlayered clays (PILC), are characterized by fixed porosity and are fundamentally different from smectite systems obtained by conventional intercalation of neutral molecules in the interlamellar space. The cross-linking process involves interaction of the polyanionic smectite layers with di- or polycationic species derived from suitable organic or inorganic compounds. With inorganic cross-linking agents, thermally stable CLS products can be derived (Brindley and Sempels, 1977; Lahav et al., 1978; Yamanaka and Brindley, 1979; Vaughan and Lussier, 1980).

In 1971 Barrer and Jones prepared porous forms of montmorillonite, hectorite, and fluorhectorite by ion exchange with tetramethylammonium and ethylene-diammonium cations. The products, however, had very small interlamellar spacings (3–4 Å) and showed low resistance to swelling. Subsequently, cross-linked organo-smectite (CLOS) systems possessing larger interlayer spacings (Δd(001) > 5 Å) and higher resistance to swelling were prepared by using di- or polycations derived from rigid or cage-like amines as cross-linking agents. The first bona fide CLOS system of this type (Δd(001) = 5.1 Å; lateral pore size, ~6.0 Å) was prepared by ion exchange of Na-montmorillonite with the diammonium ion of 1,4-diazabicyclo[2,2,2]octane (Shabtai et al., 1976; Mortland and Berkheiser, 1976). This system showed typical molecular sieve properties and high catalytic activity for esterification of carboxylic acids with alkanols. Products with larger Δd(001) values were prepared by using bulkier cross-linking di- or tetracationic species derived from 1,4-diaminoadamantane, tetrakis(p-aminophenyl)methane, and 2,2',6,6'-substituted benzidines. A general feature of such CLOS systems is that simultaneous vertical attachment of cross-linking polycationic species to anionic sites of opposite aluminosilicate surfaces becomes requisite due to steric and electronic effects which exclude alternative orientation modes (Shabtai, 1979).

Derivatives showing some similarities to CLS systems were also prepared by interaction of Na-hectorite with Fe²⁺- and Cu²⁺-1,10-phenanthroline chelates, or

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1 On leave of absence from EKA AB, Surte, Sweden, 1982.
2 On leave of absence from the University of Mining and Metallurgy, Krakow, Poland, 1981–1983.

The term Δd(001), recently introduced by Pinnavaia et al. (1979), denotes the interlayer spacing in smectites; Δd(001) = d(001) – t, where t is the thickness of the smectite unit layer.
with Fe$^{2+}$-, Cu$^{2+}$-, and Rh$^{3+}$-tris bipyridyl complexes (Berkheiser and Mortland, 1977; Traynor et al., 1978). The preparation of such derivatives involved ion-exchange with the complex ion, accompanied and/or followed by intercalation of excess complex salt beyond the exchange capacity of the smectite. In another study (Loeppert et al., 1979), intercalated phases were prepared by interaction of Na-montmorillonite or n-butylammonium vermiculite with sulfate salts of Fe$^{2+}$-, Co$^{2+}$-, or Ni$^{2+}$-tris bipyridyl or tris 1,10-phenanthroline complexes. Products containing 1.0 cation-exchange capacity (CEC) equivalent of the complex ion collapsed upon firing at 550°C, whereas products containing an excess of intercalated complex salt remained expanded to 18 Å (for montmorillonite systems) and 29 Å (for vermiculite derivatives) after the same heat treatment, due to the presence of residual, inorganic decomposition products in the interlamellar space. There was no indication as to the possible catalytic activity of such systems, prior to or after firing.

In an interesting recent development, cationic hydrogenation catalyst precursors, e.g., Rh(PPh$_3$)$_n$, where $n = 2$ or 3, have been intercalated in hectorite (Pinnavaia et al., 1979; Quayle and Pinnavaia, 1979; Raythatha and Pinnavaia, 1981, 1983; Pinnavaia, 1983). Such systems showed good catalytic activity for hydrogenation of alkenes, alkadienes, and alkynes, and considerable difference in reaction specificity when compared to the same rhodium complex in solution. Hydroformylation catalysts, based on intercalated RhH(CO)$_x$(P-P$^+$)$_2$ complexes (where P-P$^+$ denotes a phosphonium-phosphine ligand), were also prepared (Pinnavaia, 1982; Farzaneh and Pinnavaia, 1983). The application of the above intercalated systems as catalysts necessitates the use of a solvent, e.g., methanol, which for Rh(PPh$_3$)$_n$- Hectorite causes limited swelling (Δd(001) = 7.7 Å), allowing the reactant to penetrate into the interlamellar space. Although such metal complex-smectite catalysts cannot be considered as CLS systems per se, their potential importance for functionalization of inorganic cross-linked frameworks (see below) is obvious.

A turning point in the synthesis of bona fide CLS molecular sieves was achieved by cross-linking of smectites with fully inorganic, positively charged species, e.g., hydroxy-Al oligocations (Brindley and Sempels, 1977; Lahav et al., 1978; Vaughan et al., 1979, 1981a, 1981b; Shabtai and Lahav, 1980; Vaughan and Lussier, 1980; Brindley and Kao, 1980) or tetrameric hydroxy-Zr cations (Yamanaka and Brindley, 1979). The cross-linked products showed high thermal stability, considerable surface areas, and intrinsic catalytic activity. When properly functionalized, such CLS molecular sieve catalysts showed increased activity and selectivity for certain types of reactions. For example, acidic (H$^+$, La$^{3+}$, and Ce$^{3+}$) forms of cross-linked montmorillonite showed high catalytic cracking activity (Shabtai, 1980; Shabtai et al., 1981).

In continuation of previous work on the preparation of CLS systems, a study of the cross-linking of hectorites and synthetic fluorhectorites with hydroxy-Al oligocations was undertaken. The present paper reports on the synthesis of cross-linked hectorites and fluorhectorites and their characterization by X-ray powder diffraction, surface area and thermal stability determinations, transmission electron microscopy, and elemental analysis.

### EXPERIMENTAL

#### Starting materials

**Hectorites.** A natural Na- Hectorite sample from Hector, California, was obtained from The Clay Minerals Society. Some quartz and calcite present as impurities was removed by fractionation, using conventional sedimentation techniques. The < 1-μm fraction used in the study contained only traces of the above impurities as determined by X-ray powder diffraction analysis. Homolonic Ce$^{3+}$- and La$^{3+}$-exchanged hectorites were prepared by subjecting the purified Na- Hectorite to repetitive (4 times) ion exchange at 90°C with 0.4 N aqueous CeCl$_3$ and LaCl$_3$ solutions, respectively. The Ce$^{3+}$- and La$^{3+}$-exchanged hectorites were washed with deionized water until chloride-free and air dried. Basal spacings of the air-dried Na-, Ce-, and La- Hectorite samples were 12.7, 14.7, and 14.6 Å, respectively; the surface areas of all samples were less than 100 m$^2$/g. Elemental analysis of the Ce- and La- Hectorite showed a Ce content of 10.6% and a La content of 9.40%, respectively (see also Table 3).

**Fluorhectorites.** Li-fluorhectorites were prepared according to a method described by Barrer and Jones (1970). The solid state synthesis was performed using reagent grade LiF, MgO, MgF$_2$, and SiO$_2$ gel as reactants. Prior to the reaction, SiO$_2$ and MgO were ignited at 800°C for 3 hr, and LiF and MgF$_2$ were dried at 15°C for 3 hr. The four reactants were then intimately mixed by grinding in an appropriate molar ratio (LiF:MgO:MgF$_2$:SiO$_2$ = 1:2:1:4). This reactant mixture was heated in a closed platinum crucible at 800°C for 24 hr. The product was cooled to 500°C at a controlled rate of 30°C/hr and then transferred to a dessicator and allowed to cool to room temperature. The Li-fluorhectorite product was washed with hot deionized water and thoroughly purified by sedimentation. X-ray powder diffraction analysis of the < 1-μm fraction of the product showed the presence of only minor amounts (<5%) of impurities, mainly quartz, amphiboles, and, in some samples, Li$_2$SiO$_3$. Some samples of Li-fluorhectorite were prepared by an alternative procedure in which mixtures of the above reactants were heated at 850°C for 2 hr to form melts (Barrer and...
Jones, 1970). Otherwise, the same procedure as described above was used. The final purity of the <1-μm Li-fluorhectorite product obtained by the two procedures was essentially the same (≥95%). Changes in the composition of the starting reactant mixture, e.g., increases in the molar amounts of LiF and MgF₂, gave products which, after washing out of the excess soluble fluorides, were similar to those obtained by using the above indicated molar ratios. Purified Li-fluorhectorite fractions showed d(001) values in the range of 12.4–12.8 Å and very low N₂ (BET) surface areas (<10 m²/g).

Hydroxy-Al oligomeric solution

The method of preparation of the cross-linking agent, consisting of a solution of hydroxy-Al oligomers, was the same as previously described (Lahav et al., 1978; Shabtai and Lahav, 1980). It involved gradual addition of aqueous 0.2 M NaOH to a 0.2 M AlCl₃ solution until a final pH of 4.35 was attained, corresponding to an OH/Al ratio of 1.85. This solution was aged at room temperature for 1–4 weeks prior to its use.

Preparation of cross-linked smectites

The cross-linking experiments were carried out in a recently designed apparatus (to be described elsewhere) equipped with reactant containers, two tubing pumps, a mixing chamber, and a receiver for the CLS product (Figure 1). A dilute aqueous dispersion of the starting smectite was prepared by prolonged mixing (15 hr) with magnetic stirrer (in some cases dispersion for a period of 5–15 min in an ultrasonic bath was used). The pH of separate batches of the smectite dispersion was adjusted prior to the cross-linking step to different values in the range 4.5–7.8 using aqueous 0.1 M potassium hydrogen phthalate, in conjunction with either aqueous 0.1 N NaOH or 0.05 N HCl. The two reagents, i.e., the buffered smectite dispersion (A) and the aged cross-linking solution (B), were pumped at appropriate relative flow rates to the mixing chamber where fast cross-linking and flocculation took place. A ratio of 2 mmole Al per gram of smectite was applied in all of the preparations. The cross-linked smectite formed in the mixing chamber was continuously removed from the reaction zone and collected in the product receiver. After completion of the reaction (usually 3–5 min), the product mixture was allowed to stand for 15 hr, the supernatant was syphoned off, and the solid precipitate was washed with deionized water until chloride-free and freeze-dried.

Analysis of CLS products

X-ray powder diffraction (XRD) analyses of cross-linked smectites were performed with oriented samples prepared by spreading about 0.5 ml of a water suspension of the smectite on a glass slide and drying the slide at room temperature. Homionic smectites, used as starting materials for preparing the CLS systems, were analyzed for purity using powdered samples. The XRD patterns were obtained with a Norelco diffractometer using CuKα radiation and a graphite monochromator.

Surface areas of CLS samples were determined using an Orr Surface Area Pore Volume Analyzer, Model 2100 (Micrometrics Instrument Company). The samples were first degassed at 230°–250°C (0.001 torr) and their surface areas determined at liquid nitrogen temperature, using N₂ as the sorbate. Inasmuch as multilayer adsorption of N₂ (kinetic diameter = 3.64 Å) in CLS systems is probably prevented due to steric restrictions, the Langmuir equation, which is more appropriate for monolayer adsorption, was used in the surface area calculations.

The thermal stability of the CLS products was examined by subjecting them to heat treatment at 250°
and 400°C, and then determining their basal spacings and surface areas. The samples were pretreated by heating in a Pyrex glass-tube reactor under a flow of dry N₂ for 3 hr.

Some CLS samples were also examined by transmission electron microscopy (TEM), using the thin section technique. The powder samples were first embedded in Spurr resin (Spurr, 1969) and then sectioned with a diamond knife on a Porter-Blum MT-2 microtome. Micrographs were taken with a Philips, Model EM400HTG electron microscope.

Elemental analysis of the starting smectites and of the CLS products were performed by inductively coupled plasma spectrometry (ICPS). Samples were dissolved in a mixture of HF, HCl, HNO₃, and HClO₄ and analyzed with a Bausch & Lomb ICPS apparatus using as an excitation source an argon plasma (flame temperature, ~10,000°C). Duplicate analyses of several samples showed very good reproducibility. The fluoride content was separately determined with a specific ion electrode (Orion & Orion Meter, Model 407A), using the method of standard additions. SiO₂ was separately determined by the molybdenum blue colorimetric method (Kolthoff and Elving, 1962).

RESULTS AND DISCUSSION
La³⁺- and Ce³⁺- Hectorites cross-linked with hydroxy-Al oligomers (La-Al-CLH and Ce-Al-CLH)

The basal spacings and surface areas of La³⁺- and Ce³⁺-exchanged hectorites, cross-linked with hydroxy-Al oligomers, were investigated as a function of the pH (4.5 to 7.8) of the starting hectorite dispersion. The d(001) and surface areas of the cross-linked products (La-Al-CLH and Ce-Al-CLH) obtained from hectorite dispersions having different pH are summarized in Table 1 and in Figures 2 and 3. As seen, the pH of the starting RE³⁺-exchanged hectorite dispersion had a marked effect on the d(001) value as well as on the shape and intensity of the XRD peaks. Likewise, the pH influenced the surface areas of the RE-Al-CLH products. For La-Al-CLH, d(001) values of 17.0 to 17.4 Å were found for the pH range of 4.8–5.5 Å, using a 22-day aged hydroxy-Al oligomeric solution in the cross-linking step. The highest value (17.4 Å) was observed using a starting dispersion with pH = 5.0, whereas an increase in the pH to 7.8 caused sharp decrease in d(001). Furthermore, the XRD peaks of products formed at pH 4.8–5.5 were much sharper and more intense than those of products formed at pH 7.8 (Figure 2). The surface areas showed a similar trend, with values of 220–276 m²/g for products formed at pH 4.8–5.5 and a considerably lower value (168 m²/g) for those formed at pH 7.8.

For Ce-Al-CLH (Figure 3), d(001) gradually increased (from 16.0 to 17.5 Å) with increase in the pH of the starting hectorite dispersion, and then remained only slightly lower (17.2 Å) for pH = 7.5. The surface areas were in the range of 227–253 m²/g for products formed at pH 5.4–6.5, but were considerably lower for those formed at higher or lower pH. Ultrasonic dis-

![Figure 2](image-url)
Figure 3. X-ray powder diffraction patterns of Ce-Al-CLH samples as a function of the pH of the starting hectorite dispersion (CuKα radiation).

The effect of the age of the hydroxy-Al oligomeric solution upon the basal spacings and surface areas of the CLH products was also examined by cross-linking of La-hectorite dispersions with hydroxy-Al solutions aged for different lengths of time, i.e., 7, 15, 22, and 27 days, under otherwise identical conditions. As seen in Table 2, aging for a period of 15 days produced La-Al-CLH/42 having both a relatively large d(001) value (17.8 Å) and a high surface area (260 m²/g). Longer aging periods, e.g., 22–27 days, resulted in a decrease in the surface area.

It should be noted that the data in Table 1 relate to La-Al-CLH and Ce-Al-CLH samples prepared by cross-linking with a hydroxy-Al oligomeric solution aged for 22 days. Somewhat higher surface areas and basal spacings, i.e., 17.8–18.0 Å, were found for products formed at pH 5–6.5 of the starting hectorite when the cross-linking agent was aged for 14–15 days (see, e.g., La-Al-CLH/40, Table 2). Heat treatment of La-Al-CLH samples up to 400°C under a flow of dry nitrogen, or under vacuum, caused only minor changes in basal spacings and surface areas.

Table 2. Basal spacings and surface areas of La-Al-CLH as a function of the age of the hydroxy-Al oligomeric solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Age of solution (days)</th>
<th>d(001) (Å)</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La-Al-CLH/42</td>
<td>7</td>
<td>16.8</td>
<td>251</td>
</tr>
<tr>
<td>La-Al-CLH/40</td>
<td>15</td>
<td>17.8</td>
<td>260</td>
</tr>
<tr>
<td>La-Al-CLH/30</td>
<td>22</td>
<td>17.0</td>
<td>220</td>
</tr>
<tr>
<td>La-Al-CLH/41</td>
<td>27</td>
<td>18.0</td>
<td>218</td>
</tr>
</tbody>
</table>

1 The pH of the starting La-hectorite dispersion was 5.5 in all the preparations.
2 Measured after preheating the sample at 250°C (0.001 torr).

Table 3 summarizes the elemental composition of the starting La- and Ce-hectorites and of some typical La-Al-CLH and Ce-Al-CLH products derived by cross-linking with hydroxy-Al oligomers. The La- and Ce-hectorites contained a high concentration of RE³⁺ ion, i.e., 9.40% La and 10.64% Ce, respectively. Cross-linking resulted in a major decrease in La and Ce and a sharp increase in Al. Mg decreased slightly, indicating that it was not significantly extracted from the hectorite layers under the moderately acidic conditions (pH of aqueous 0.4 N LaCl₃ = 4.5; pH of aqueous 0.4 N CeCl₃ = 3.8) of the ion exchange. The presence of significant residual La³⁺ and Ce³⁺ in the Al-CLH products indicates that these ions were not completely displaced during the cross-linking process when using 2.0 mmole Al/g RE³⁺-exchanged hectorite. As anticipated, in some experiments with lower Al/hectorite ratios the concentration of residual La³⁺ or Ce³⁺ ion in the cross-linked products was higher than that found for the RE-Al-CLH samples in Table 3.

Table 3. Elemental composition of RE³⁺-hectorites and of some derived RE-Al-CLH products.

<table>
<thead>
<tr>
<th>Component (wt. %)</th>
<th>La-hectorite</th>
<th>La-Al-CLH/32</th>
<th>Ce-hectorite</th>
<th>Ce-Al-CLH/19</th>
<th>Ce-Al-CLH/23</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>0.62</td>
<td>0.30</td>
<td>0.41</td>
<td>0.95</td>
<td>8.61</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.24</td>
<td>0.26</td>
<td>0.22</td>
<td>0.24</td>
<td>0.21</td>
</tr>
<tr>
<td>MgO</td>
<td>27.92</td>
<td>26.13</td>
<td>26.92</td>
<td>24.20</td>
<td>24.27</td>
</tr>
<tr>
<td>CaO</td>
<td>0.68</td>
<td>0.10</td>
<td>0.08</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.18</td>
<td>0.14</td>
<td>0.19</td>
<td>0.20</td>
<td>0.15</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.10</td>
<td>0.10</td>
<td>0.11</td>
<td>0.12</td>
<td>0.09</td>
</tr>
<tr>
<td>Li₂O</td>
<td>0.54</td>
<td>0.49</td>
<td>0.49</td>
<td>0.39</td>
<td>0.47</td>
</tr>
<tr>
<td>La</td>
<td>9.40</td>
<td>2.50</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ce</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

1 A ratio of 2.0 mmole Al/g of RE³⁺-hectorite was used in the preparation of all RE-Al-CLH products.
2 Cross-linking was performed using a La³⁺-hectorite dispersion having pH 5.0.
3 Cross-linking was performed using a Ce³⁺-hectorite dispersion having pH 5.4.
4 As in footnote 3, but pH 6.5.
Li⁺- and Ce³⁺-fluorhectorites cross-linked with hydroxy-Al oligomers (Li-Al-CLFH and Ce-Al-CLFH)

A number of synthetic Li-fluorhectorite samples (see Experimental) and a Ce³⁺-exchanged fluorhectorite sample were cross-linked with the previously described hydroxy-Al oligomeric solution, using a 2.0 mmole Al/g fluorhectorite ratio. The basal spacings and surface areas of some typical Li-Al-CLFH and Ce-Al-CLFH products are summarized in Table 4. The d(001) values for air-dried (at 25°C) samples of these products are in the range of 18.2 to 20.0 Å, higher than those found for the cross-linked hectorites (see Tables 1 and 2). Heat treatment at 250°C and 400°C generally resulted in relatively small decreases in d(001) values, e.g., 0.5–1.5 Å. Typical XRD patterns and their change with pretreatment temperatures for Li-Al-CLFH and Ce-Al-CLFH products are given in Figures 4 and 5, respectively. As seen, the XRD peaks of the d(001) reflection are very sharp and intense, possibly indicating that synthetic fluorhectorites underwent more effective cross-linking than natural hectorites. The surface areas of the Li-Al-CLFH and Ce-Al-CLFH samples (Table 4) after pretreatment at 250°C were ~300–380 m²/g, considerably higher than those of cross-linked natural hectorites (Tables 1 and 2).

Table 5 summarizes the elemental compositions of the synthetic Li-fluorhectorite and of the Ce³⁺-exchanged fluorhectorite. Also included are data on the composition of two cross-linked products, Li-Al-CLFH and Ce-Al-CLFH, derived from these starting smectites. The composition of Li-fluorhectorite corresponds closely to that anticipated for Li(Mg, Li)Si₄O₁₀F₄ which in turn is very close to the formula previously proposed for this synthetic smectite (Barrer and Jones, 1970). As expected, the cross-linked derivative (Li-Al-CLFH) contains a large amount of alumina and the lithium is considerably reduced due to displacement during the cross-linking process. The change in composition resulting from cross-linking of Ce-fluorhectorite follows the same pattern, i.e., the cross-linked product (Ce-Al-CLFH) contains a significant amount of incorporated alumina, and the exchangeable ion (Ce³⁺) is markedly reduced. The presence of some residual lithium in Ce-Al-CLFH indicates that some of this element is present in the layer structure of the fluorhectorite.

Some of the Al-CLH and Al-CLFH products were examined by transmission electron microscopy (TEM). A typical micrograph of a Li-Al-CLFH sample (Li-Al-CLFH/39, Table 4) is shown in Figure 6. In agreement with the XRD results (Table 4), basal spacings of approximately 19–20 Å were discerned. No satisfactory micrographs were obtained for the Li-fluorhectorite, prior to cross-linking.
Table 4. Basal spacings and surface areas of typical Li-Al-CLFH and Ce-Al-CLFH products as a function of pretreatment temperature.

<table>
<thead>
<tr>
<th>Pretreatment temp. (°C)</th>
<th>Cross-linked fluorohectorite</th>
<th>d(001) (Å)</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li-Al-CLFH/38</td>
<td>20.0</td>
<td>18.4</td>
</tr>
<tr>
<td></td>
<td>Li-Al-CLFH/39</td>
<td>18.8</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>Li-Al-CLFH/48</td>
<td>18.9</td>
<td>18.5</td>
</tr>
<tr>
<td></td>
<td>Li-Al-CLFH/51</td>
<td>19.6</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td>Li-Al-CLFH/52</td>
<td>18.2</td>
<td>18.5</td>
</tr>
<tr>
<td></td>
<td>Ce-Al-CLFH/45</td>
<td>19.1</td>
<td>18.3</td>
</tr>
</tbody>
</table>

1 d(001) and surface areas were determined after heat pretreatment of the Al-CLFH products at 250° or 400°C for 3 hr under a stream of dry nitrogen.
2 Air-dried samples (at 25°C).
3 Surface areas could be slightly higher if the small amounts (<5%) of nonporous impurities present in the samples are taken into account.
4 Derived by cross-linking of different Li-fluorohectorite dispersions (generally pH = 5.0-6.0) with hydroxy-Al oligomers (2.0 mmole Al/g smectite). Numbers following the slash = batch number.
5 Prepared by cross-linking of a Ce³⁺-fluorohectorite dispersion (pH = 5.0) with hydroxy-Al oligomers (2.0 mmole Al/g smectite).

Structural features of cross-linked hectorites and fluorhectorites

A structural model for cross-linked hydroxy-Al montmorillonite (Al-CLM) which is also applicable to the above Al-CLH and Al-CLFH was proposed by Lahav et al. (1978) and in more detail by Shabtai (1979). It consists of montmorillonite unit layers cross-linked by means of polycationic, hydroxy-Al oligomeric species of essentially uniform size. To account for the Δd(001) value of 9.0-9.5 Å for Al-CLM, it was proposed that the cross-linking species consists of two stacked [Al₆(OH)₂(H₂O)₆]⁶⁺ ions with a combined height of ~9.4 Å. Recently, Pinnavaia (1983) suggested that the cross-linking species is an Al₁₃O₄(OH)₂₈³⁺ or Al₁₄O₄(OH)₂₉⁴⁺ cation, on the basis of Al²⁷ neutron magnetic resonance and potentiometric titration data, which indicated the presence of such species in hydroxy-Al oligomeric solutions having OH⁻/Al³⁺ ratios similar to those applied in the preparation of cross-linked smectites (Johansson, 1960; Bottero et al., 1980). Immobilized Al₁₃ oligocations should have a vertical dimension (~9.5 Å) similar to that of the previously proposed two-stacked oligocations.

As did Shabtai (1980) and Shabtai and Lahav (1980), we found that Na- or Li-smectite forms can be cross-linked to a stoichiometric extent by using an equivalent amount or excess of hydroxy-Al oligocations, whereas other forms, in particular Ce³⁺-exchanged smectites, undergo only partial cross-linking, i.e., incomplete replacement of the exchangeable cations. Assuming the maximal extent of cross-linking found for La³⁺-montmorillonite (~95%) and assuming an equivalent area of 70 Å²/charge for montmorillonite and a diameter of 11.7 Å (Brindley and Sempels, 1977) for the hydroxy-Al oligocation (stacked Al₆ ions or Al₁₃ oligocation), the average lateral (interpillar) distance in the La-Al-CLM should be about 12 Å. Recent adsorption data (Tsai, 1983) using polycyclic compounds of various critical diameters, i.e., coronene (11.1 Å), octaethylporphyrin (15.3 Å), and tetraphenylporphyrin (19.0 Å), are in good agreement with this calculation, showing that for maximally cross-linked La-Al-CLM the...
Predominant lateral pore sizes are in the range 11–15 Å.

For La-Al-CLH, based on an equivalent area of 98 Å²/charge for hectorite (Lagaly and Weiss, 1969) and a 75% extent of cross-linking with hydroxy-Al oligocations, the average lateral pore size should be ~19.5 Å; whereas for Li-Al-CLFH, on the basis of an equivalent area of ~70 Å²/charge and an extent of cross-linking of 95%, the calculated average lateral distance is ~16.4 Å. These lateral pore sizes are considerably larger than typical critical pore sizes found in Y- and X-type zeolites. Accordingly, recent catalytic cracking studies with Al-CLH, Al-CLFH, and Al-CLM (McCaughey, 1983) showed that these catalysts are 1 to 2 orders of magnitude more active than CeY-type zeolite for the cracking of large poly cyclic naphthenoaromatics, e.g., dodecahydrotriphenylene (kinetic diameter, 11.2 Å).

ACKNOWLEDGMENTS

We thank EKA AB, Surte, Sweden, for financial support of this project and Dr. W. M. Hess, Electron Optics Laboratory, Brigham Young University, for the TEM examination of the smectite samples.

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