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# PREPARATION AND CHARACTERIZATION OF BIDIMENSIONAL ZEOLITIC STRUCTURES OBTAINED FROM SYNTHETIC BEIDELLITE AND HYDROXY-ALUMINUM SOLUTIONS

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**Abstract**—Beidellite was synthesized hydrothermally from a noncrystalline gel at 320°C and 130 bar pressure. The beidellitic character of the product was verified by infrared spectroscopy on the $NH_4^+$-exchanged form. Intercalation was achieved with hydroxy-aluminum solutions having different OH/Al molar ratios. The solutions were investigated by several methods, including $^{27}Al$ nuclear magnetic resonance. Essentially, two Al species were detected: monomeric Al and a polymerized form containing Al in four-fold coordination. This latter species was found to be selectively fixed in the interlamellar region, which resulted in a stable spacing of 18 Å at 110°C and 16.2 Å at 700°C. The pillared beidellites had specific surface areas of >300 $m^2/g$, mainly due to micropores. Both Brönsted and Lewis acid sites were evidenced by infrared spectroscopy using pyridine as a probe molecule.

**Key Words**—Acid sites, Beidellite, Hydroxy-Al, Infrared spectroscopy, Nuclear magnetic resonance, Pillaring, Synthesis.

**Résumé**—Une beidellite obtenue par synthèse hydrothermale (320°C, 130 bar) à partir d'un gel précurseur et identifiée comme telle sur base des spectres infrarouges de la forme échangée à l'ammonium, a été pontée par des solutions hydroxy-aluminiques de rapports OH/Al différents. Les solutions de pontage ont été étudiées par différentes méthodes, dont la résonance magnétique nucléaire. Deux espèces d'aluminium, l'une monomérique, l'autre polymérique contenant de l'aluminium en coordination tétraédrique coexistent dans ces solutions. On a observé que l'espèce polymérique s'adsorbe préférentiellement dans l'espace interlamellaire, conférant à l'édifice un espacement de 18 Å à 120°C et de 16,2 Å après calcination à 700°C. La surface spécifique de ces beidellites pontées est de l'ordre de 300 $m^2/g$. La spectrométrie infrarouge de la pyridine adsorbée décèle la présence des acidités Brönsted et Lewis.

## INTRODUCTION

The preparation and properties of smectites (mostly montmorillonites) pillared with Al-hydroxy polymers have recently been reported in the literature (Brindley and Sempels, 1977; Lahav *et al.*, 1978; Vaughan and Lussier, 1980; Pinnavaia *et al.*, 1984; Occelli and Tindwa, 1983). Several authors (Vaughan and Lussier, 1980; Vaughan *et al.*, 1981; Pinnavaia *et al.*, 1984) postulated that the pillaring species was similar to the $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ polymer described by Johansson *et al.* (1960). The following indirect arguments were invoked to support this view: (1) this polymer was the only one known to contain Al in four-fold coordination; (2) its size is consistent with the d values observed for smectites pillared using hydroxy-aluminum solutions; and (3) the presence in Al-OH solutions of an Al species containing $Al^{IV}$ was evidenced by $^{27}Al$ nuclear magnetic resonance (NMR) spectroscopy and ascribed by Bottero *et al.* (1980) to the $Al_{13}$ polymer, supporting the previous suggestion of Rausch and Bale (1964), based on small-angle X-ray diffraction scattering data.

In a recent study, Plee *et al.* (1985b) showed by high-resolution solid-state $^{27}Al$ NMR that the $Al^{IV}$-containing species found in solution and the species intercalated in pillared hectorite gave a similar NMR signal at 62.5 ppm.

Pillared clays exhibit interesting physico-chemical properties. Specific surface areas between 250 and 350 $m^2/g$, mean pore diameters of 7–9 Å, and the ability to adsorb hydrocarbons (Vaughan and Lussier, 1980; Occelli *et al.*, 1984) define a bidimensional porous system accessible to relatively voluminous molecules. Both Brönsted- and Lewis-type acidities have been reported in pillared montmorillonites (Occelli and Tindwa, 1983; Pinnavaia, 1983). According to Vaughan and Lussier (1980), the protonic acidity in pillared montmorillonite should be generated during the dehydroxylation of the pillars, as follows:

$$Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+} \rightarrow 6.5Al_2O_3 + 8.5H_2O + 7H^+$$

The Brönsted acid sites, however, are not very stable and are of lower acid strength than those in H-Y zeolite (Plee *et al.*, 1984; Schutz *et al.*, 1987; Poncelet and Schutz, 1986).

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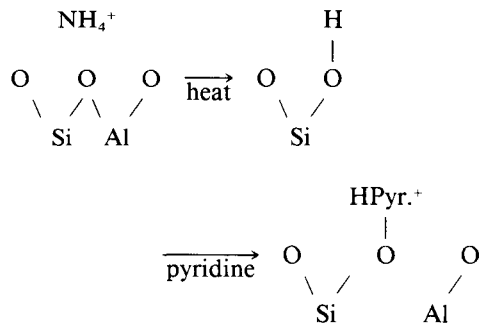
From dehydration tests of alcohols on dioctahedral smectites having various degrees of cationic substitution in the tetrahedral layers, Davitz (1976) showed that the activities were directly related to the degree of substitution. Plee *et al.* (1985a), Schutz *et al.* (1987), and Poncelet and Schutz (1986), on the other hand, reported that the acidity of pillared beidellite was much stronger, compared with that of pillared montmorillonites prepared under similar conditions. Schutz *et al.* (1987) observed that upon calcining pillared beidellite, an additional IR band appeared at 3440 $cm^{-1}$. This band disappeared upon adsorption of pyridine, whereas, at the same time, the typical band of pyridinium ions developed at 1540 $cm^{-1}$. This behavior is similar to that reported by Ward (1967) for $NH_4$-Y zeolite and is represented by the following transformation:




Magic angle spinning NMR spectra of $^{27}Al$ and $^{29}Si$ indicate that the shifts in the frequencies observed upon calcining pillared beidellite may be due to a change of tetrahedral sites into a more tridimensional-like structure (Plee *et al.*, 1985b). The main weakness of pillared montmorillonite is the poor thermal stability of their acid sites. Pillared beidellites, in contrast, exhibit acid properties that are almost unaffected after calcining at 500°C. They transform hydrocarbons at rates that are similar to those achieved with H-Y zeolites (Schutz *et al.*, 1987; Poncelet and Schutz, 1986; Plee *et al.*, 1984).

The present paper is concerned with the preparation and characterization of hydroxy-Al pillared synthetic beidellites. It also reports $^{27}Al$ NMR data on the pillaring solutions.

## EXPERIMENTAL

### *Synthesis of beidellite*

Beidellite was synthesized in hydrothermal conditions from a gel having a chemical composition (after calcination at 500°C) of $Na_{0.7}Al_{4.7}Si_{7.3}O_{22}$. Two hundred grams of gel and 640 ml of 0.1 M NaOH were introduced in a 1-liter autoclave which was heated to 320°C (130 bar) in less than 24 hr and held at that temperature for 5 days. The reacted slurry was suspended in 2 liters of distilled water to separate the clay fraction from the coarse, unreacted gel particles. With respect to the weight of gel introduced, yields of >90% beidellite were easily achieved.

Samples of the suspension were examined by X-ray powder diffraction (XRD) and infrared (IR) and MAS-NMR spectroscopy. The cation-exchange capacity (CEC) of the product was measured by the micro-Kjeldahl method on $NH_4^+$-exchanged samples.

### *Preparation of the pillared beidellites*

Adequate volumes of 0.5 M NaOH were added to 0.2 M $AlCl_3 \cdot 6H_2O$ solutions with vigorous stirring to prepare hydroxy-Al solutions having OH/Al molar ratios between 0.8 and 2.4. Required volumes of distilled water were then supplied to make the final solutions 0.1 M in Al. The solutions were heated at 60°C for 2 hr and allowed to cool to room temperature. They were added to clay suspensions in volumes such as to introduce 5, 7.5, 10, 15, 20, and 30 meq Al/g of clay. The final concentration of Al was 0.05 M.

After standing for 0.5 hr, the clay samples were washed by centrifugation until the conductivity of the supernatant was that of distilled water. The solids were finally freeze-dried.

### *Characterization of pillaring solutions and pillared beidellite*

The hydroxy-aluminum solutions before and after pillaring were characterized by pH measurements; chemical analyses of the Al content by atomic absorption; $^{27}Al$ NMR spectroscopy (250 MHz Brücker instrument); Al monomer determination by 8-hydroxyquinoline, according to the procedure of Bersillon *et al.* (1980); and back-titration of hydroxy-Al polymer solutions with HCl, using a pH-stat (pH = 2.88).

The crystallinity of the synthetic beidellite and the d-values of the pillared samples were investigated using a Philips X-ray powder diffractometer (Ni-filtered, CuK$\alpha$ radiation). The IR spectra were recorded on self-supporting wafers (10–20 mg) using a 180 Perkin-Elmer grating instrument. The samples were outgassed and heated in an IR cell. Nitrogen adsorption-desorption isotherms (specific surface areas and porosities) were established at liquid $N_2$ temperature in a conventional glass volumetric apparatus equipped with Bell & Howell pressure gauges.

## RESULTS AND DISCUSSION

### *Investigation of the hydroxy-Al solutions*

The hydroxy-Al solutions prepared with different OH/Al molar ratios were analyzed by $^{27}Al$ NMR spectroscopy. The peak width and the chemical shift of a quadrupolar nucleus (Al, spin = +5/2) may be affected by four factors: the nature of the ligand, the coordination number, the symmetry around the nucleus, and the exchange phenomena between the various species in equilibrium (Karlik *et al.*, 1983). The NMR spec-

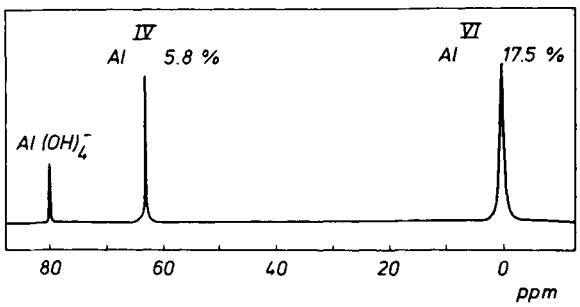



Figure 1. $^{27}$Al nuclear magnetic resonance spectrum of solution having OH/Al = 2.0, using sodium aluminate solution as internal reference (80 ppm).

trum of the solution having OH/Al = 2.0 is shown, as an example, in Figure 1. The chemical shift was previously calibrated at 0 ppm with a solution of $AlCl_3 \cdot 6H_2O$ using, as an internal standard, the signal at 80 ppm of sodium aluminate contained in a capillary concentric to the NMR tubing. Two signals were observed for the hydroxy-Al solutions: one at 0 ppm, corresponding to monomeric species $Al(H_2O)_6^{3+}$ and $[Al(OH)(H_2O)_5]^{2+}$, and a second at 62.5 ppm, attributed to Al atoms in four-fold coordination ($Al^{IV}$) within a polymeric structure (Akitt *et al.*, 1972).

The low symmetry of octahedral Al in some of the monomers broadened the band due to the interactions between the electrical field gradients near the nucleus and the quadrupolar moment. The low half-height width value of the signal at 62.5 ppm, smaller than that of the monomers, implied that the electrical field gradient near $Al^{IV}$ atoms was negligible. Therefore, the $Al^{IV}$ was assumed to be in a symmetric environment at the center of a highly symmetrical polymer.

The integrated values of the NMR signals of the different solutions (Table 1, column 1) showed that the monomer content progressively diminished as the OH/Al molar ratio increased. Monomers were practically absent in the solution with OH/Al = 2.4. The percentage of tetrahedral Al increased slowly and reached a maximum value of 6.6 in the solutions having the highest OH/Al molar ratios. These $^{27}$Al NMR results are qualitatively similar to those reported earlier by Pinnavaia *et al.* (1984).

At OH/Al = 2.0, 77% of the total Al in solution was not detected on the high-resolution NMR spectrum because of interactions which markedly broadened the signals. This amount is much larger than that (~20%) not observed by Akitt *et al.* (1972). These Al atoms constituted probably condensed species having a low net positive charge per Al atom. The percentages of monomers determined by the complexation method with ferron (Bersillon *et al.*, 1980) (Table 1, column 2) were similar to those established by NMR and corresponded to the two types of monomers mentioned above.

Back-titration of the hydroxy-Al solutions with HCl, at pH 2.88 (Hem and Roberson, 1967), allowed the amount of Al involved in $[Al(OH)(H_2O)_5]^{2+}$ species that reacted very rapidly with protons (Table 1, column 3) to be quantified. Subtracting these values from the percentage of monomeric Al determined by NMR yielded the proportion of Al present as $Al(H_2O)_6^{3+}$ and $[Al(OH)(H_2O)_5]^{2+}$ and, by difference, the proportion of Al in polymeric species (Table 1, column 4).

The average degree of hydrolysis, as defined by the OH/Al ratio (Table 1, column 5), was calculated from the balance of the OHs in the solution (the weak variations of pH between the solutions were neglected). This balance was established from the difference between the total OH content of the solution and the extrapolated values to time t = 0 of the first-order kinetic functions $\log[OH_r]_t = \log[OH_r]_{t=0} - kt$. Divid-

Table 1. Percentages of monomeric and polymeric species for aluminum solutions having different OH/Al molar ratios.

| | (1) | | (2) | (3) | (4) | | | (5) |
|---|---|---|---|---|---|---|---|---|
| OH/Al ratio in solution | Monomers (%) (NMR) | $Al^{IV}$ (%) (NMR) | Monomers (%) (ferron) | Monomers (%) (pH stat) | $Al(H_2O)_6^{3+}$ (%) | $Al(OH)(H_2O)_5^{2+}$ (%) | Polymers (%) | OH/Al ratio of polymers |
| 0.0 | 100 | 0 | 100 | 0 | 100 | 0 | 0 | 0 |
| 0.8 | 68 | 1.7 | 74 | 16.2 | 51.8 | 16.2 | 32 | 2.0 |
| 1.0 | 56 | 2.3 | — | 15.3 | 41.7 | 15.3 | 43 | 2.0 |
| 1.2 | 53 | 3.0 | 52 | 13.3 | 36.7 | 13.3 | 50 | 2.1 |
| 1.4 | 40 | 3.6 | — | 13.8 | 27.2 | 13.8 | 59 | 2.1 |
| 1.6 | 33 | 4.5 | 32 | 9.4 | 22.6 | 9.4 | 68 | 2.2 |
| 1.8 | 26 | 4.8 | — | 7.8 | 17.2 | 7.8 | 75 | 2.3 |
| 2.0 | 17 | 5.8 | 17.5 | 6.4 | 11.6 | 6.4 | 82 | 2.4 |
| 2.2 | 11 | 6.6 | — | 4.7 | 5.3 | 4.7 | 90 | 2.4 |
| 2.4 | 4 | 6.6 | 5.5 | 4.0 | 0.0 | 4.0 | 96 | 2.4 |

(1) From nuclear magnetic resonance spectra.
(2) From ferron procedure.
(3) From back-titration method.
(4) Distribution of the different OH species.
(5) Calculated OH/Al ratio of polymers.

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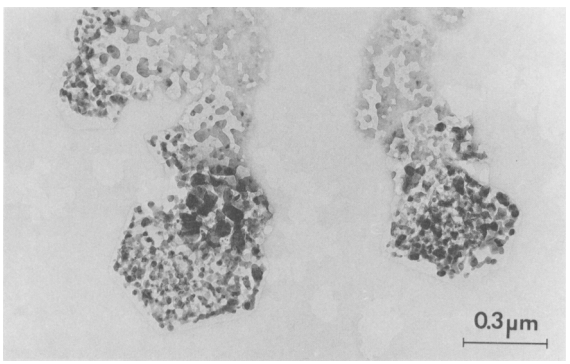


Figure 2. Transmission electron micrograph obtained after drying solution having OH/Al = 2.0.

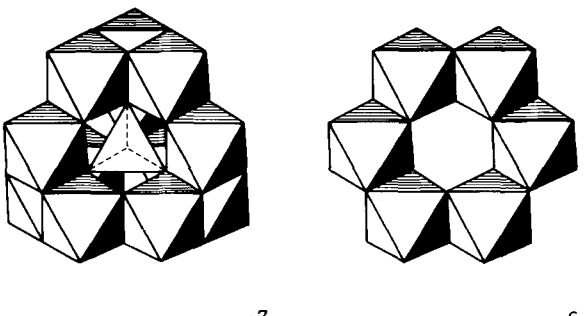


Figure 3. Structural model of the hydroxy-Al polymers after (a) Johansson *et al.* (1960) and (b) Hsu (1977).

ing the $[OH_t]_{t=0}$ values by the percentage of Al in the polymer yielded the mean OH/Al values as given in Table 1, column 5. This ratio ranged between 2 and 2.4, indicating that the charge and size of the polymers varied with the OH/Al ratio of the solutions.

An aliquot of the solution having OH/Al = 2.0 was dried in a desiccator and examined by transmission electron microscopy (TEM) and XRD. Whereas no crystalline phase was evident from the XRD pattern, a TEM (Figure 2) showed a bidimensional hexagonal array, similar to the morphology of gibbsite-like microcrystals. The $^{27}Al$ MAS-NMR spectrum of the solid obtained after precipitation with NaOH at pH 6.6–7.0 and drying of the same solution (OH/Al = 2.0) showed that it still contained an appreciable amount of tetrahedral aluminum.

Hem and Roberson (1967), Stol *et al.* (1976), and Hsu (1977) proposed a structure based on a six-membered ring $[Al_6(OH)_{12})(H_2O)_{12}]^{6+}$ unit (Figure 3b) which condensed into larger bidimensional assemblies corresponding to a gibbsite-like or bayerite monolayer. From the potentiometric curves and the formulae of Sillèn (1954), Van Cauwelaert and Bosmans (1969) defined an average condensation unit having the formula $[Al_7(OH)_{16}]^{5+}$ for the solutions having OH/Al molar ratios of 0.5–1.6. They interpreted the neutralization curves obtained for different Al concentrations in terms of the "core and links" hypothesis (Sillèn, 1954), in which the complexes consist of a nucleus "B" and ligands "$BA_t$". In that way they obtained the following series:

$[AlAl_3(OH)_8]^{4+}$, $[AlAl_6(OH)_{16}]^{5+}$, $[AlAl_9(OH)_{24}]^{6+}$, $[AlAl_{12}(OH)_{32}]^{7+}$, etc.,

where B = Al and $BA_t = Al(OH)_{8/3}$.

The tetrahedral aluminum observed by $^{27}Al$ NMR in solution adds a new element to these early literature data. To take into account this fact, Akitt *et al.* (1972) and Bottero *et al.* (1980) proposed the structure of the crystalline aluminum hydroxy-sulfate described by Johansson *et al.* (1960), $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, which is shown in Figure 3a. This entity consists of a central tetrahedral Al atom surrounded by 12 octahedral Al atoms.

With such a structural model, the crystallization of gibbsite in acidic medium, either by dialysis (Herbillon and Gastuche, 1962) or by aging hydroxy-Al solutions in the presence of clay (Barnhisel and Rich, 1963), from the tridimensional structure proposed by Akitt *et al.* (1972) is not straightforward. The bidimensional model of Hsu (1977), on the other hand, neither accounts for tetrahedral Al nor for the observed d-values. Although some uncertainties remain concerning the structure of these polymers, they appear to be characterized by a high degree of hydrolysis (OH/Al = 2.0, 2.4) and by the presence of Al in four-fold coordination. Note that if this polymeric Al is represented by the $Al_{13}$ polymer of Johansson *et al.* (1960), its size is consistent with the d-values of the pillared clays.

### *Characterization of the synthetic beidellites*

The synthetic beidellite produced in the sodium form was examined by XRD to monitor (unoriented sample) its crystallinity. The $NH_4$-exchanged material yielded a CEC of 94 meq/100 g (on the basis of the clay calcined at 900°C), essentially the same as that expected (96 meq/100 g) for beidellite having the formula: $0.67\ Na \cdot nH_2O(Si_{7.33}Al_{0.67})^{IV}(Al_4)^{VI}O_{20}(OH)_4$.

To ascertain the beidellitic nature of the clay, IR spectra of the $NH_4^+$-exchanged form were recorded in the OH-stretching region. Chourabi and Fripiat (1981) reported that $NH_4^+$ ions located in tetrahedral exchange sites (i.e., in clays having substitution in the tetrahedral layer) gave rise to a N–H stretching band at 3030 $cm^{-1}$.

Figure 4a shows the IR spectra of a clay wafer outgassed at room temperature and heated at 200° and 300°C. The bottom spectrum (room temperature) exhibits three absorptions at 3640, 3290, and 3030 $cm^{-1}$. The band at 3640 $cm^{-1}$ was attributed to the stretching vibration of OH groups within the octahedral layer;

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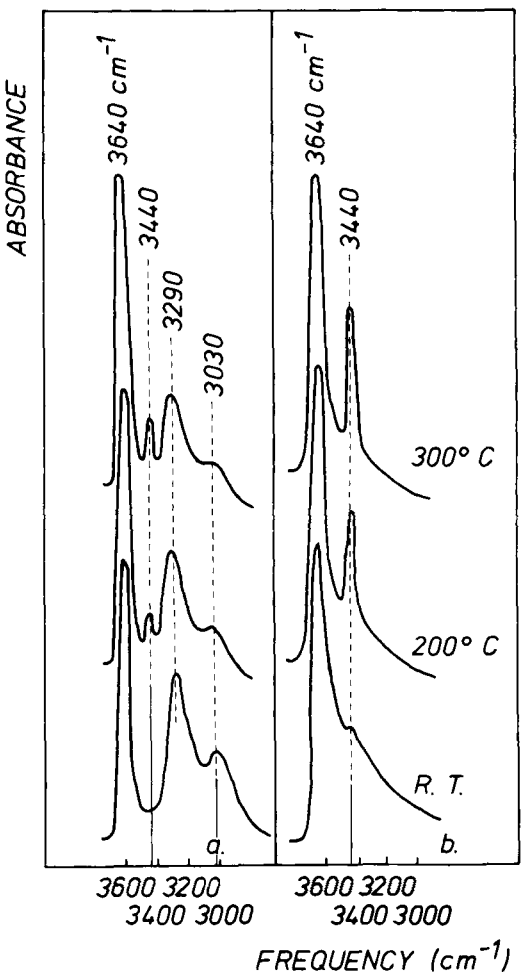



Figure 4. Infrared spectra of (a) $NH_4^+$-beidellite and (b) $H_3O^+$-beidellite after outgassing at room temperature, 200°C, and 300°C.

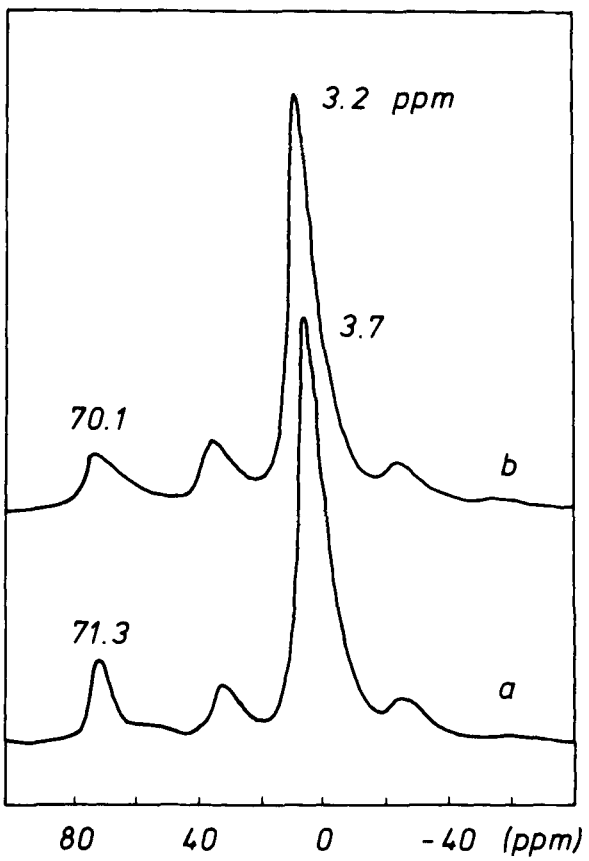
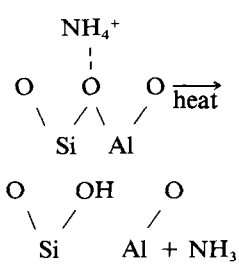



Figure 5. $^{27}Al$ magic angle spinning-nuclear magnetic resonance spectra of H-beidellite (a) dried at room temperature and (b) after calcination at 300°C.

the other two were assigned to N–H stretching of $NH_4^+$. The 3030 $cm^{-1}$ band appears only in 2:1 layer silicates where the cationic subsitutions are located within the tetrahedral layer. Heating the clay resulted in the development of a new band at 3440 $cm^{-1}$, which was attributed to silanol groups in the tetrahedral layer. A similar observation was reported by Uytterhoeven *et al.* (1965) and Ward (1967) upon heating $NH_4$-Y zeolite. These authors proposed that during the thermal decomposition of $NH_4^+$ ions, Si–O–Al bonds were broken by proton attack, as follows:




The spectra shown in Figure 4b were recorded on a wafer of H-exchanged beidellite (using a 0.05 M HCl as exchange solution) outgassed at room temperature and after heating at 200° and 300°C under vacuum. The spectrum of H-beidellite outgassed at room temperature contains two bands at 3640 and 3440 $cm^{-1}$ and is similar to the spectrum of Na-beidellite. Upon heating the sample, the intensity of the band at 3440 $cm^{-1}$ increased appreciably. That this band was more intense for H-beidellite than for the $NH_4$-form heated at 300°C suggests that water was removed (or $H_3O^+$ decomposed) at a lower temperature than the thermal decomposition of $NH_4^+$. Indeed (Figure 4a), the N–H stretching bands were clearly present after the sample was reacted at 300°C.

Figures 5 and 6 show the $^{27}Al$ and $^{29}Si$ MAS-NMR spectra recorded before and after calcination of H-beidellite at 300°C. The two signals at about 3 ppm and 70 ppm in Figure 5 correspond to Al in the octahedral and tetrahedral layer, respectively (Sanz and Serratosa, 1984). After the sample was calcined, these two signals were slightly shifted towards lower frequencies and decreased in intensity. In Figure 6, the signals showing

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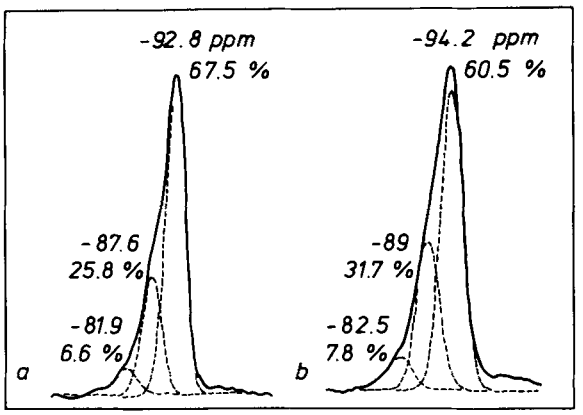


Figure 6. $^{29}$Si magic angle spinning-nuclear magnetic resonance spectra of a H-beidellite (a) dried at room temperature and (b) calcined at 300°C.

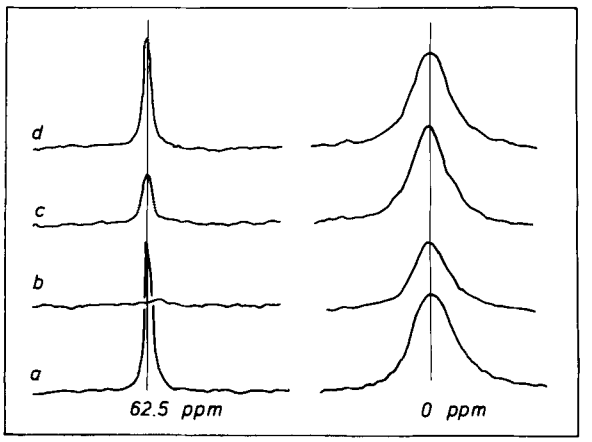


Figure 7. $^{27}$Al nuclear magnetic resonance signals of (a) hydroxy-Al solution having OH/Al = 2.0 and (b) supernatant solutions of the systems containing (b) 5, (c) 10 and (d) 15 meq Al/g of clay.

up at about −93, −88, and −82 ppm correspond (following Alma *et al.,* 1984) to Si bound to (0 $Al^{IV}$)(2 $Al^{VI}$), (1 $Al^{VI}$)(2 $Al^{VI}$), and (2 $Al^{IV}$)(2 $Al^{VI}$), respectively. The modifications brought about by the calcination were marked by a decrease of the signal due to Si near (0 $Al^{IV}$)(2 $Al^{VI}$) and an increase of the contribution of the two other signals.

From the IR and MAS-NMR data, the cationic substitutions in the tetrahedral layer of dioctahedral smectites appear to have generated acid sites created by proton-induced structural modifications. By propping the clay sheets apart with Al-OH pillars, these acid sites became accessible to organic molecules and could control catalytic transformations (Diddams *et al.,* 1984; Schutz *et al.,* 1987; Poncelet and Schutz, 1986).

*Hydroxy-Al pillared beidellite*

In a first series of experiments, adequate volumes of hydroxy-Al solutions with OH/Al molar ratio = 2 were added to beidellite suspensions to bring 5–30 meq Al/g of clay into the system. After stirring for 30 min, the suspensions were centrifuged. The total Al left in the supernatant solution was determined by atomic absorption, and the amount of monomeric Al was established by the ferron method and NMR spectroscopy. Both methods yielded similar results. The $Al^{IV}$ (involved in polymeric species) was determined by $^{27}$Al NMR spectroscopy. The total quantities of Al fixed by the clay were obtained by subtracting the amounts found in the equilibrium solutions from the total Al initially present.

The difference in the integrated intensities of the NMR signals at 0 and 62.5 ppm observed between the starting Al-OH solutions (diluted with distilled water to the same volume as those containing the clay) and the equilibrium solutions corresponded, respectively, to the amounts of monomeric Al and to the $Al^{IV}$-containing species sorbed by the clay during the ion exchange reaction. As can be seen from Table 2, the total Al fixed (monomeric + Al polymeric species) by the clay increased with the Al content in the starting solutions. By substracting the amount of monomeric Al from the total Al fixed by the clay, the proportion of Al involved in polymeric species and also the mean $Al^{VI}/Al^{IV}$ atomic ratio were estimated. About 90% of the intercalated Al was involved in polymeric species having $Al^{VI}/Al^{IV}$ atomic ratios of about 9 (vs. 12 for the $Al_{13}$ polymer).

Figure 7 shows the $^{27}$Al signals at 0 (monomeric $Al^{VI}$)

Table 2. Total Al fixed, momoners, and $Al^{IV}$ adsorbed on beidellite for different systems prepared with increasing amounts of Al/g of clay.

| Amount of Al (meq/g of clay) | Total Al fixed (nmole/g) | Monomeric Al fixed (mmole/g) | $Al^{IV}$ fixed (mmole/g) | $Al_T$ − monomeric Al fixed (mmole/g) | $Al^{VI}/Al^{IV}$ ratio |
|---|---|---|---|---|---|
| 5 | 1.51 | 0.08 | 0.13 | 1.43 | 10 |
| 7.5 | 1.71 | 0.08 | 0.16 | 1.58 | 9 |
| 10 | 1.75 | 0.12 | 0.18 | 1.62 | 8 |
| 12.5 | 1.81 | 0.11 | 0.18 | 1.74 | 9 |
| 15 | 1.86 | 0.11 | 0.17 | 1.80 | 9 |
| 20 | 1.95 | 0.18 | 0.18 | 1.85 | 9 |
| 30 | 2.27 | 0.27 | 0.24 | 1.99 | 7 |

Table 3. Total Al and monomers adsorbed, and pH of Al-OH solutions before and after addition of the clay suspensions.

| OH/Al in solution | Total Al fixed ($Al_T$) (mmole/g) | Monomeric aluminum fixed (mmole/g) | pH of Al-OH solution | pH of supernatant solution |
|---|---|---|---|---|
| 1.2 | 1.22 | 0.25 | 3.92 | 3.82 |
| 1.6 | 1.58 | 0.11 | 4.02 | 3.90 |
| 2.0 | 1.70 | 0.10 | 4.10 | 4.05 |
| 2.4 | 2.22 | 0.01 | 4.35 | 4.29 |

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Table 4. Residual cation-exchange capacities (CEC) values determined before and after washing pillared clays and determination of exchangeable Al and Na for pillared beidellites prepared with different Al-OH solutions.

| OH/Al in solution | CEC before washing (meq/g) | CEC after washing (meq/g) | Exchangeable Al (meq/g) | Exchangeable Na (meq/g) |
|---|---|---|---|---|
| 1.2 | 0.41 | 0.34 | 0.42 | 0.01 |
| 1.6 | 0.44 | 0.34 | 0.40 | 0.01 |
| 2.0 | 0.37 | 0.35 | 0.39 | 0.01 |
| 2.4 | 0.28 | 0.26 | 0.33 | 0.01 |

Table 5. Basal spacings of pillared beidellite prepared with different concentrations of Al at OH/Al molar ratio of 2.0.

| Al introduced (meq Al/g) | d-values (Å) observed after drying at: | | |
|---|---|---|---|
| | Room temp. | 110°C | 400°C |
| 5 | 19.0 | 18.4 | 17.4 |
| 10 | 19.0 | 18.4 | 17.6 |
| 15 | 19.0 | 18.8 | 17.6 |
| 20 | 19.5 | 18.8 | 17.6 |
| 30 | 19.5 | 18.8 | 17.6 |

and 62.5 ppm ($Al^{IV}$ involved in polymeric forms) of the starting hydroxy-Al solution and of the supernatant solutions of the systems containing initially 5, 10, and 15 meq Al/g of clay. As can be seen, the equilibrium solution of the slurry containing 5 meq Al/g of clay was completely exhausted in $Al^{IV}$-based polymeric species, and partially in monomeric $Al^{VI}$ species. In contrast, slurries containing 10 and 15 meq Al/g initially had all of their monomeric $Al^{VI}$ left in the supernatant solution. For these systems, the basal spacings of the pillared clays were 19 Å (dried at room temperature), 18 Å (after drying at 110°C), and 17.6 Å (after calcining at 400°C) and, thus, were independent of the amount of Al initially introduced in the suspension.

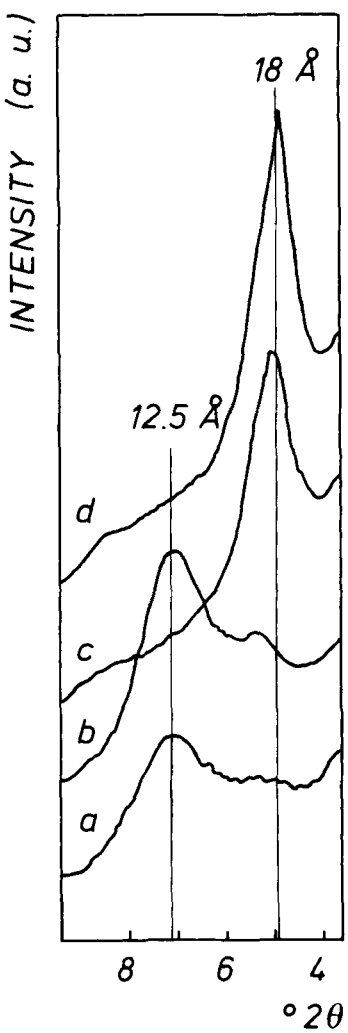


Figure 8. X-ray powder diffractograms of pillared beidellite (a) before washing and after (b) one, (c) two, and (d) three washings, for samples dried at 110°C. CuKα radiation.

In a second set of preparations, beidellites were pillared with hydroxy-Al solutions containing different OH/Al molar ratios, the total Al content in the final suspension being 20 meq Al/g clay. As shown in Table 3, the total amount of Al taken up by the clay increased as the OH/Al ratio of the pillaring solution increased, whereas the proportion of monomeric Al decreased to nearly 0 for the system with OH/Al = 2.4.

The differences between the pHs of the starting solutions (diluted with distilled water to volumes equal to those of the clay-systems) and the supernatant solutions implies that the aluminum polymers partly hydrolyzed in the presence of the clay. This process may be represented as follows:

$$Al(OH)_n^{y+} + mH_2O \rightarrow Al(OH)_{n+m}^{(y-m)+} + mH^+.$$

That Al is hydrolyzed in the presence of clay surfaces was also reported by Brown and Newman (1973). This further degree of polymerization of Al supplied protons and resulted in higher OH/Al ratios of the polymeric species fixed on the clay surface.

The residual CEC was determined on $NH_4^+$-exchanged sample, before and after washing the pillared clays. As seen in Table 4, washing the pillared clays resulted in lower CECs, especially for samples prepared with Al-OH solutions having OH/Al = 1.2 and 1.6. From the amount of exchangeable Al the charge per Al atom in the non-exchangeable polymers was calculated as follows:

$$X = \frac{CEC - CEC\ residual}{Al_{tot.} - Al_{exch.}}.$$

Except for the clay pillared with a hydroxy-Al solution having OH/Al = 1.2, in which much of monomeric Al was adsorbed, the net charge per Al atom was 0.4–0.35, which corresponds to an OH/Al molar ratio of the polymer of 2.6–2.65, i.e., values larger than

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Table 6. Basal spacings of pillared beidellites prepared with Al-OH solutions with different OH/Al molar ratios.

| OH/Al in solution | d-values (Å) observed after drying at: | | |
|---|---|---|---|
| | Room temp. | 110°C | 400°C |
| 1.2 | 19.0 | 18.8 | 17.0 |
| 1.6 | 19.0 | 18.8 | 17.6 |
| 2.0 | 19.0 | 18.8 | 17.6 |
| 2.4 | 19.0 | 18.8 | 17.6 |

Concentration of Al = 15 meq/g clay.

those found in the starting solutions. Barnhisel (1977) reported a value of 2.7 for the mean OH/Al ratio of the Al-OH polymers intercalated between the clay sheets. Thus, from the values of the residual CEC and the amounts of exchangeable Al, the OH/Al molar ratio of the polymeric species fixed in the clay surface was clearly >2.4.

Figure 8 shows the change of the d(001) values of unwashed beidellite after pillaring and of the same sample after washing with 250 ml distilled water per gram of clay. This illustration clearly indicates that the Al-OH polymers intercalated in the interlamellar space were not initially structured, but that their organization between the clay sheets and the fraction of clay that was pillared improved with the number of washings, perhaps by the elimination of anions.

The progressive structuring of the pillars in the interlamellar space may be envisioned as follows:

Polymers in Al-OH solution [OH/Al =2.0, 2.4] —clay addition→ Polymers intercalated [OH/Al = 2.7 d(001) = 12.5 Å] —washing→ Pillars [OH/Al = 2.7 d(001) = 18 Å]

The effect of washing on the d(001) value was repeatedly observed, and no explanation can be proposed from our experimental data. Such an observation, to our knowledge, has not been reported in the literature, perhaps because the washing step in similar investigations was generally carried out to complete removal of the excess salt. Consequently, transitory spacings could not be detected.

The evolution described above might be only an artefact. If not, it raises a question as to the true nature of the pillaring species and/or on its mechanism of formation between the clay sheets. That $Al^{IV}$ containing species were present in hydroxy-Al solutions as well as in the interlamellar space of a 18-Å pillared clay (Plee *et al.*, 1985b) was clearly established by NMR methods. As mentioned above, the $Al_{13}$ polymer has been considered by several authors as the pillaring species mainly because it is the only (crystalline) "polymer" known to contain Al in four-fold coordination and because the dimensions of the unit-cell were consistent with the observed spacings. Both arguments still remain indirect ones, and our data cannot rule out this assignment. To account for the transitory spacings, the $Al^{IV}$-containing species, not being a stable entity, as is the crystalline $Al_{13}$ polymer of Johansson *et al.* (1960), would, upon intercalation in the interlamellar space, undergo partial hydrolysis, possibly due to some surface acidity of the clay sheets. Washing would not only remove anions but also result in a sufficient increase of the local pH so that the conditions of the formation of an $Al_{13}$-like polymer would be satisfied. This interpretation is, of course, speculative and requires additional experimental evidence.

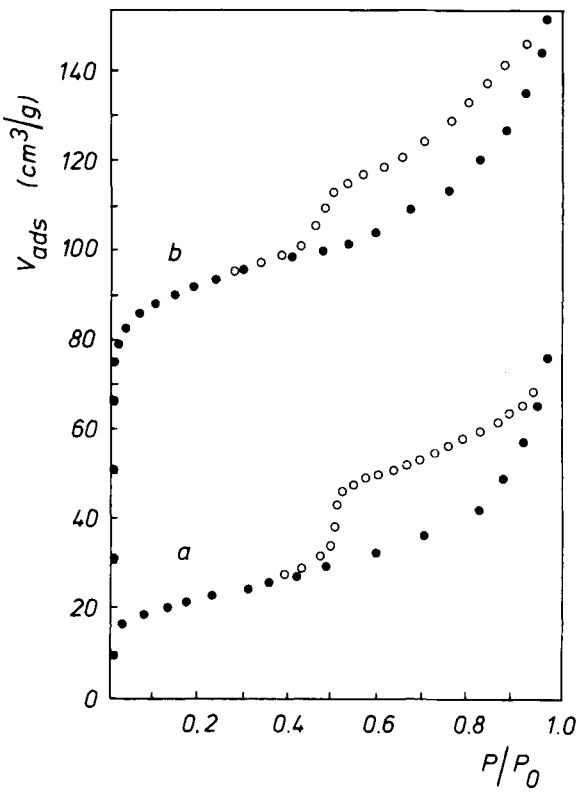


Figure 9. $N_2$ adsorption-desorption isotherms of (a) Na-beidellite and (b) pillared beidellite calcined at 400°C.

*Characterization of the pillared beidellite d-values.* The values of d(001) of the beidellites pillared with different quantities of Al and for various OH/Al molar ratios in the pillaring solutions are given in Tables 5 and 6. Spacings of 17.6 Å were obtained for the clays calcined at 400°C. Substracting 9.6 Å (the thickness of the clay sheet) from these values yields a value of about 8 Å for the height of the Al-OH pillars, namely four layers of oxygens.

*Surface area and porosity.* The adsorption-desorption isotherms established at liquid $N_2$ temperature for Na-

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Table 7. Basal spacings and surface areas ($S_0$) of pillared beidellite calcined at different temperatures.

| Temperature (°C) | d(001) (Å) | $S_0$ ($m^2/g$) | |
|---|---|---|---|
| | | Langmuir | B.E.T. |
| 300 | 18.0 | 410 | 329 |
| 400 | 17.3 | 420 | 320 |
| 500 | 17.0 | 312 | 254 |
| 600 | 16.7 | 290 | 240 |
| 700 | 16.2 | 286 | 230 |

beidellite and pillared beidellite calcined at 400°C are shown in Figure 9. As can be seen, the volumes adsorbed by pillared beidellite were greater than those adsorbed by Na-beidellite. The adsorption isotherms were of the type I, which are typical of microporous systems. The specific surface area of the pillared beidellite obtained on samples calcined at 400°C and calculated from B.E.T. equation was 320 $m^2/g$ (76 $m^2/g$ for unpillared beidellite).

The sum of the pore areas, calculated from the desorption isotherms by the method of Pierce (1953), for pillared beidellite and for Na-beidellite are similar and corresponded to the external surface area (66 and 77 $m^2/g$, respectively).

The microporosity was calculated according to the method of Dubinin (1975), using the experimental values between $10^{-3}$ and $10^{-1}$ p/po. Microporous volume of 0.15 $cm^3/g$ was obtained for pillared beidellite (0.17 $cm^3/g$ after correction for the weight of the pillars). If the theoretical free interlamellar volume is 0.24 $cm^3/g$ (8 Å × 300 $m^2/g$), the fraction of this volume occupied by the intercalated material corresponds to about 30%.

Table 7 lists the d-values and the specific surfaces ($S_0$) (Langmuir and B.E.T.) of pillared beidellites calcined at increasing temperatures. The main decrease in the interlamellar distances between 300° and 500°C was probably due to the dehydroxylation of the pillars. The pillared beidellite calcined at 700°C exhibited a d-value of 16.2 Å and a $S_0$ value >200 $m^2/g$.

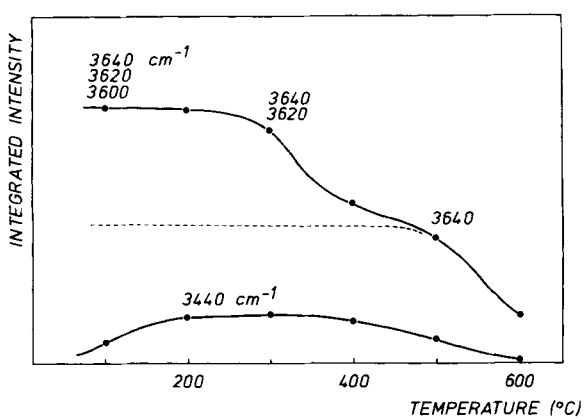


Figure 10. Evolution of the integrated intensity of the OH-stretching bands of pillared beidellite as a function of outgassing temperature.

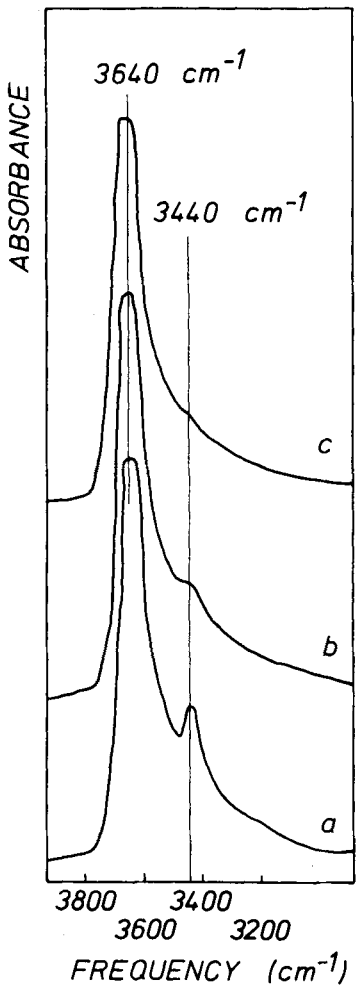


Figure 11. Infrared spectra of pillared beidellite (a) outgassed at 300°C and (b, c) after adsorption of pyridine.

*Infrared spectroscopy.* The IR spectra of a self-supporting wafer of pillared beidellite were recorded in the OH-stretching region, using an IR cell in which the sample could be outgassed and heated. Figure 10 shows the evolution of the integrated intensity of the bands near 3640 and 3440 $cm^{-1}$ as a function of outgassing temperature. The dotted curve in this illustration refers to the evolution of the 3640-$cm^{-1}$ band of $NH_4^+$-beidellite treated in a similar way. Obviously, the pillars in the interlamellar space contributed to the 3640-$cm^{-1}$ absorption.

The band at 3640 $cm^{-1}$ contained, in fact, at least two or three contributions (3640, 3620, 3600 $cm^{-1}$) which could not be integrated separately. The integrated intensity of the high-frequency band decreased between 300° and 400°C due to the dehydroxylation

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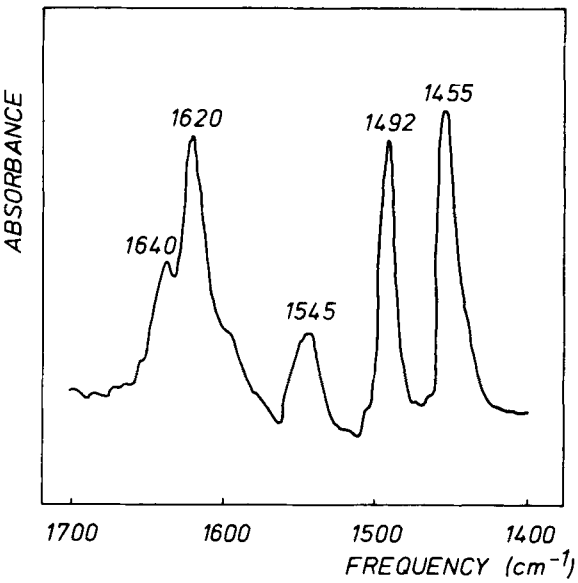


Figure 12. Infrared spectrum after adsorption of pyridine and outgassing at 150°C on pillared beidellite previously evacuated at 300°C.

of the pillars. Moreover, a second loss of integrated intensity took place between 500° and 600°C, probably due to the dehydroxylation of the octahedral layer. The band at 3440 $cm^{-1}$ appeared after the pillared beidellite was heated at 100°C, i.e., after removal of adsorbed water. This band was assigned, as mentioned above, to Si–OH groups created by the breaking of Si–O-$Al^{IV}$ bonds. These OH groups constituted Brönsted acid sites which were transformed into Lewis sites when the pillared clay was heated at temperatures >400°C.

Figure 11 shows the spectrum in the OH-stretching region of the pillared beidellite outgassed at 300°C and after adsorption of increasing amounts of pyridine. The disappearance of the band at 3440 $cm^{-1}$ implies that the acid sites were available to pyridine. Simultaneously, the bands characteristic of pyridinium and pyridine in interaction with Lewis-type sites developed at 1545 and 1455 $cm^{-1}$, respectively, as shown in Figure 12. The Lewis sites were probably associated with the intercalated pillars.

## SUMMARY AND CONCLUSIONS

Hydroxy-Al solutions having OH/Al molar ratios between 0.8 and 2.4 were investigated by several methods. Both monomeric and polymeric forms of Al were evidenced by NMR in proportions that varied with the molar ratio of the solutions. The average OH/Al ratio in the polymers was found to be 2.0–2.4 and Al was found in four-fold coordination. Nearly all the Al was involved in polymeric species in the solution having a OH/Al ratio of 2.4. These polymers were selectively intercalated in the interlamellar space of beidellite where they further hydrolyzed so that their average OH/Al ratio was 2.6–2.65. After the intercalated clays were washed, basal spacings of 18.8 Å (at 110°C) and 17.6 Å (at 400°C) were obtained. The pillared beidellites developed surfaces of 300 $m^2/g$ and pore volumes of 0.17 $cm^3/g$.

Infrared spectroscopy of adsorbed pyridine showed the presence of both Brönsted and Lewis acidities. The Brönsted acidity was accounted for by the proton attack of Si–O-Al bonds of the tetrahedral layer and formation of silanol groups responsible for the OH-stretching band at 3440 $cm^{-1}$, whereas the Lewis acidity was associated with the Al of the pillars. The OH groups of the pillars contributed to the OH-stretching band near 3640 $cm^{-1}$.

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