USE OF COMPETITIVE ION EXCHANGE FOR INTERCALATION OF MONTMORILLONITE WITH HYDROXY-ALUMINUM SPECIES

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Abstract—Three montmorillonite samples, from Wyoming (particle size <0.2 μm, 4.6 wt. % Fe_2O_3), Greece (<14 μm, 6.5 wt. % Fe_2O_3), and Poland (0.5 wt. % Fe_2O_3, two fractions <2 μm and 2–10 μm) were intercalated with hydroxy-Al species. The amount of hydroxy-Al cations exchanged by the clays depended on the particle size: it decreased from 31 wt. % Al_2O_3 for 0.2 μm in size to 22.6 wt. % for >2 μm. The X-ray powder diffraction (XRD) pattern showed that most of the material was not intercalated after refluxing at 80°C for 2 hr; several redispersions of the pillared clay in hot water were required to obtain a single sharp XRD line at 18.6 Å. The diffusion of the Al cations therefore limited the cation-exchange process. The addition of NH_4^+ to the pillaring solution decreased the amount of Al fixed by the clay from 31 (no NH_4^+) to 26 wt. % (NH_4^+/Al = 10), but increased slightly the microporous volume of the resulting pillared material from 0.13 to 0.14 ml/g. The competition between NH_4^+ and Al-hydroxy cations for ion-exchange sites forced the Al species into the interlayer space and increased the homogeneity of the resulting pillared material. The influence of particle size on the amount of Al exchanged was then reduced. After calcination in air at 700°C the pillared Wyoming clay retained a microporous volume of 0.09 ml/g if no NH_4^+ was added, compared with 0.11 ml/g for a NH_4^+/Al ratio of 10. The Fe content of the clay affected the thermal stability of pillared clays at 800°C: for two samples prepared by competitive ion exchange (NH_4^+/Al = 10) the microporous volume increased from 0.06 ml/g for 6.4 wt. % Fe_2O_3 to 0.08 ml/g for 0.5 wt. % Fe_2O_3. The acidity of the pillared clay was determined by calorimetric adsorption of ammonia at 150°C, on samples calcined at 500°C. Pillared montmorillonite prepared using noncompetitive intercalation showed a weak acid strength: most sites adsorbed ammonia with an enthalpy of 65 kJ/mole. The intercalation of the same original clay using competitive ion exchange yielded a solid that possessed both weak (heat = 60 kJ/mole) and strong (120 kJ/mole) acid sties. Competitive ion exchange appears to be a simple means of preparation of large quantities of pillared clays of reasonable thermal stability and higher acidity than those obtained by conventional methods.

Key Words—Competitive ion exchange, Hydroxy-Al, Intercalation, Montmorillonite, Pillared clays, Thermal stability, X-ray powder diffraction.

Résumé—Trois montmorillonites provenant du Wyoming (taille des particules <0,2 μm, 4,6% en poids de Fe_2O_3), de Grèce (taille <14 μm, 6,5% Fe_2O_3) et de Pologne (0,5% Fe_2O_3, deux fractions ≤2 μm et 2–10 μm), ont été intercalées par des complexes cationiques hydroxylés de l'aluminium. La quantité d'Al échangée par l'argile dépend de la taille des particules: elle décroit de 31% Al_2O_3 pour une taille de 0,2 μm à 22,6% pour >2 μm. Le spectre de diffraction des rayons X montre que la majeure partie du matériau n'est pas intercalée après reflux à 80°C pendant 2 hr; plusieurs redispersions de l'argile intercalée, dans l'eau chaude, sont nécessaires pour obtenir une raie de diffraction individualisée et étroite à 18,6 Å. La diffusion des cations Al limite donc le processus d'échange ionique. L'addition d'ammoniaque à la solution d'intercalation décroît la quantité d'Al fixée par l'argile de 31% (sans NH_4^+) à 26% (NH_4^+/Al = 10), mais accroît légèrement le volume microporeux du produit final de 0,13 à 0,14 ml/g. La compétition pour les mêmes sites d'échange, entre NH_4^+ et les polycations Al_{13}^{7+} pousse les cations Al dans l'espace interfoliaire, et accroît l'homogénéité du matériau intercalé obtenu. L'influence de la taille des particules sur la quantité d'Al échangée est alors réduite. Après calcination dans l'air à 700°C, l'argile du Wyoming intercalée conserve un volume microporeux de 0,09 ml/g, quand elle est préparée sans compétition, et de 0,11 ml/g quand le rapport de compétition NH_4^+/Al = 10. Le contenu en fer de l'argile effecte la stabilité thermique à 800°C des argiles intercalées: pour deux échantillons obtenus par échange en compétition, avec NH_4^+/Al = 10, le volume microporeux croît de 0,06 ml/g pour 6,4% Fe_2O_3 à 0,08 ml/g pour 0,5% Fe_2O_3. L'acidité de ces argiles intercalées a été déterminée par calorimétrie, en utilisant l'adsorption d'ammoniac à 150°C sur des échantillons calcinés à 500°C. Les montmorillonites intercalées préparées par échange non compétitif présentent une acidité faible, la plupart des sites adsorbant NH_3 avec une enthalpie de

65 kJ/mole. L'intercalation de la même argile de départ par la méthode d'échange compétitif fournit un solide qui possède, en plus des sites faibles (enthalpie = 60 kJ/mole) des sites forts (120 kJ/mole). L'échange d'ions en compétition apparait comme une méthode simple permettant de préparer des quantités importantes d'argile intercalée présentant une stabilité thermique raisonnable et une acidité supérieure à celle obtenue par les méthodes conventionnelles.

INTRODUCTION

The preparation and properties of smectite pillared with Al-hydroxy oligomers (PILC) have been extensively investigated (Brindley and Sempels, 1977; Lahav *et al.,* 1978; Vaughan *et al.,* 1979; Jacobs *et al.,* 1982; Occelli and Tindwa, 1983; Pinnavaia *et al.,* 1984; Plee *et al.,* 1987; Schutz *et al.,* 1987). Several factors have been proposed to control the stability of the structure. Tichit *et al.* (1985) and Tokarz and Shabtai (1985) correlated the stability of Al-montmorillonite to the density of the pillars; however, the strength of the bond linking the pillars to the clay sheet was emphasized by Plee *et al.* (1985), Pinnavaia *et al.* (1985), and Sterte and Shabtai (1987). These authors related the high stability of beidellite pillared by Al species and of fluor-hectorite pillared by silico-aluminum species to the formation of a covalent bond. For montmorillonite pillared by hydroxy-Al species, bonding was supposed to be ionic, which resulted in weaker bonds. Tichit *et al.* (1988b) concluded that in this system the thermal stability of the PILC was controlled by the sintering of the pillars at <750°C. At >750°C, the clay structure itself appeared to be unstable. Several details of the preparation, such as the size of the particles of the original clay, were found to influence the stability of the resulting PILC (Tichit *et al.,* 1988a). Clay particles 0.2 μm in size fixed more Al than particles in the range 2–10 μm, which suggests that diffusion controlled the exchange of the Al-hydroxy cations and affected the distribution of the pillars within the particles. These authors postulated that the homogeneity of the distribution of the pillars controlled thermal stability.

How to improve the homogeneity of the distribution of the cations within a pellet of catalyst has been thoroughly investigated for noble metals in reforming catalysts (Brunelle, 1978; Ribeiro and Marcilly, 1979). A more homogeneous distribution can be reached by increasing the dilution of the solution of the noble metal. Similarly, a high dilution of the clay slurry increases the surface area of PILC (Vaughan *et al.,* 1979; Lahav *et al.,* 1978); however, the practical use of diluted slurries is questionable. The method usually employed to distribute homogeneously noble metals within a pelletted support is competitive ion exchange (Brunelle, 1978). The basic principle of competitive ion exchange is the addition to the exchange solution of a competitor ion, which tends to decrease the strength of the bond between the noble metal ion and the support. The interaction between the noble metal and the support is then converted into a reversible equilibrium, which

favors a homogeneous deposition of the metal on the support. Any cation can play the role of the competitor, provided that it does not change the degree of polymerization of the Al oligomers. Species should be used that can be removed easily from the solid, such as NH_4^+, to compare clays of similar chemical compositions. $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ is currently widely accepted (Vaughan and Lussier, 1980; Vaughan *et al.,* 1981; Plee *et al.,* 1985, 1987; Pinnavaia *et al.,* 1984, 1985) as the pillaring species. This Al_{13} oligomer has been characterized in solutions by small angle X-ray scattering (Rausch and Bale, 1964) and by ^{27}Al nuclear magnetic resonance (NMR) (Akitt *et al.,* 1972; Bottero *et al.,* 1980). These NMR studies and the recent work of Schutz *et al.* (1987) established that the main factor determining the type of Al species in the pillaring solution is pH.

Drying has also been demonstrated to be a critical step of the preparation (Occelli, 1987; Vaughan and Lussier, 1980); drying in a thick bed compacts the clay into hard agglomerates, which are degraded by subsequent grinding. The pillared clays of the present study were therefore dried in very thin beds.

Natural clays usually contain Fe substituting for Al in the octahedral sheet, which cannot be removed without damaging the structure. Synthetic clays, such as beidellite or hectorite, are essentially free of Fe. The high stabilities observed for these synthetic materials may be due to the absence of Fe. The possible influence of Fe on the thermal stability of the PILC was therefore investigated by comparing montmorillonite of different origins, containing different amounts of Fe.

The extent to which acidity can be modified by the method of preparation is not known. Acidity should be directly related to the environment of the Al ions in the pillars, which could be modified by the preparation. The changes of the acidic properties induced by the preparation were therefore investigated.

EXPERIMENTAL

Three montmorillonite samples were used. Sample B was a suspension of Volclay montmorillonite refined by CECA (Honfleur, France) and consisted of particles <0.2 μm. Sample G, from Greece, was used in its original powdered form, the particle size ranging from 0.1 to 14 μm. Sample C, from Chmielnik, Poland, was converted into the Na-form and sedimented into <2- and 2–10-μm fractions. The chemical compositions of these clays are listed in Tables 1 and 2. XRD analysis showed no contamination of the original clays. The

Table 1. Chemical compositions (wt. % on a dry basis) of sample B and of pillared clays prepared from this material.[1]

		No competition			With competition		
	B	B1	B2	B3	B4	B5	B6
pH		6	6	4.2	6	6	6
NH_4/Al		0	0	0	2	10	50
Clay conc. (g/liter)		5	10	5	5	5	20
SiO_2	66.5	66.5	66.5	66.5	66.5	66.5	66.5
Al_2O_3	20.6	51.6	51.2	33.3	52.2	46.6	34.1
Fe_2O_3	4.6	4.8	4.2	nd	4.6	4.8	nd
MgO	2.8	1.8	1.8	nd	nd	nd	nd
Na_2O	4.5	nd	0.2	0.14	0.05	0.12	nd
K_2O	0.3	0.1	<0.1	0.3	nd	nd	nd
CaO	0.32	nd	<0.1	nd	nd	nd	nd
% Al_2O_3 fixed	0	31	30.5	12.6	31.5	25.9	13.5

nd = not determined.

[1] Chemical compositions of the pillared clays are referred to the initial silica content of the clay.

basal spacings of the initial clays were 12.5 Å for Wyoming and Chmielnick clays, used in their Na form, and 15.5 Å for the Greek clay used in its original form.

Preparation of the pillared clays

The pillaring solution (OH/Al = 2) was prepared following the procedure described by Lahav et al. (1978). Mixed 0.2 M solutions of $AlCl_3 \cdot 6H_2O$ and NaOH were aged for three days at room temperature. The desired volume of intercalating solution was added dropwise, at room temperature, to the clay previously dispersed in deionized water (usually 5 g of clay per liter of water). The final pH was adjusted by adding either HCl or NH_4OH. The slurry was then stirred for 3 hr at 80°C, filtered, washed free of chloride in hot deionized water, and air dried in thin layers (<1 mm) at 60°C. As illustrated in Figure 1, washing modified the quality of the resulting PILC. For competitive ion exchange, a 1 M CH_3COONH_4 solution was added dropwise to the pillaring solution to obtain the desired NH_4/Al ratio. For NH_4/Al = 10, the pH increased from 4.2 to 5.94. A small amount of ammonia was then added to adjust the pH to 6, and the normal pillaring procedure was then applied, without additional aging of the solution.

The PILC were calcined in a shallow bed in a horizontal furnace swept by an air flow of 100 ml/min. The heating rate was 50°C/hr, and the desired temperature was maintained for 5 hr. A fresh sample was used for each calcination temperature.

Characterization studies

The position of the 001 XRD peak defined the interlayer distance. XRD patterns were recorded on a CGR Theta 60 instrument, using monochromatized $CuK\alpha$ radiation. Surface areas were obtained from nitrogen adsorption isotherms using BET methods. According to Plee et al. (1987), the interlamellar porosity can be approximated by the microporous volume, v_m, obtained by application of the Dubinin equation:

$$\log v = \log v_m - K(\log P_0/P)^2,$$

where v is the volume adsorbed at the relative pressure P/P_0, v_m is the volume of the pores <10 Å in size, and K is a constant.

^{27}Al-NMR spectra of the pillaring solutions were recorded at 65.18 MHz, using a Bruker AC 250 instrument. The liquid sample was placed in a 10-mm silica glass tube, which contained a capillary full of D_2O to

Table 2. Chemical compositions (wt. % on a dry basis) of samples C and G and of pillared clays[1] prepared from these clays.

Sample[2]	C	C1	C	C2	G	G1
Part. size	<2μm		2–10μm		0.1–14 μm	
SiO_2	53.1	53.1	51.4	51.4	61.7	61.7
Al_2O_3	17.4	36.6	17.2	36.8	20.1	41.2
Fe_2O_3	0.5	0.6	0.8	1.7	6.5	6.9
MgO	4.9	4.5	4.8	4.4	3.4	5.2
Na_2O	3.1	0.2	3.0	0.2	0.9	0.1
K_2O	0.1	0.1	0.1	0.1	3.1	1.7
CaO	0	0	0	0	2.0	0.1
Al_2O_3 fixed (wt. %)	0	19.2	0	19.6	0	21.2

[1] Conditions of preparation: 5 mmole Al/g clay; pH = 6; dilution = 5 g clay/liter; NH_4/Al = 10 for samples C1 and C2, and NH_4/Al = 0 for sample G1.

[2] See text for sample descriptions.

lock the magnetic field. Acid properties were determined by the adsorption of ammonia at 150°C, using the calorimetric method described by Auroux (1988). The heat of adsorption of ammonia was taken as a measure of the acid strength.

RESULTS

Nature of the pillaring agent

The standard solution of the hydroxy-Al compound (pH = 4.2), gave the ^{27}Al NMR spectrum reported in Figure 2a. According to Akitt *et al.* (1972) and Bottero *et al.* (1980), this spectrum can be interpreted by the presence of two species: the line at 0 ppm corresponding to octahedral Al (in the form of $Al(H_2O)_6^{3+}$, and the line at about 63 ppm corresponding to the tetrahedral Al included in the Al_{13} oligomer. Increasing the pH to 6 by the addition of NaOH induced a change of the spectrum: octahedral monomeric Al bands disappeared, and a broad band, centered at about 63 ppm, appeared superimposed on the sharp line that may be attributed to the formation of a larger polymer (Figure 2b). The addition of NH_4Cl instead of NaOH to reach pH = 6 did not modify the spectrum (Figure 2c). The addition of ammonium acetate to the standard solution (pH = 4.2) induced an increase of pH, which reached 5.94 for the ratio NH_4/Al = 10. As shown in Figure 2d, the NMR spectrum of this solution is comparable to that of the standard solution adjusted to pH = 6. These results agree with Bottero *et al.* (1980), who first concluded that the pH was the main factor controlling the nature of the Al species.

CHEMICAL COMPOSITION OF THE PILLARED CLAYS

The chemical analyses of the PILCs are reported in Tables 1 and 2. The amounts of Al fixed by the clay depended on several factors: size of the particles, pH, concentration of the slurry, and concentration of competing ions in the pillaring solution. The influence of pH and dilution of the clay agree with those reported by Plee *et al.* (1987). All three original clays had CECs of 80–100 meq/100 g. In the absence of competition, the lesser amount of alumina fixed by sample G1 compared with sample B1 can be accounted for by diffusional limitations in the kinetics of exchange intro-
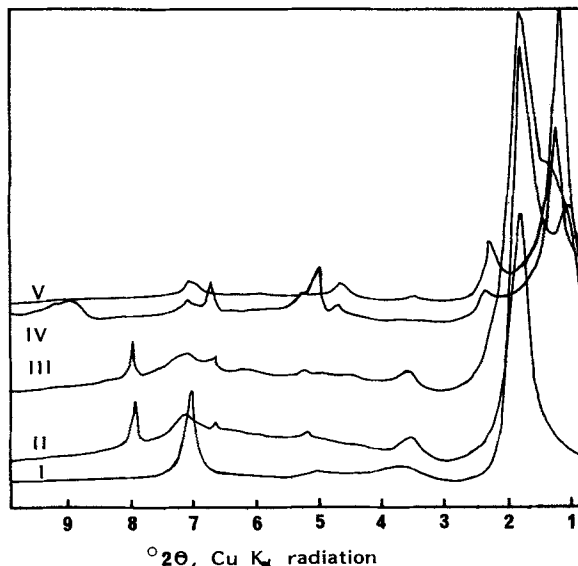

Figure 1. X-ray powder diffraction patterns of clay samples at different points in the preparation: I, original Wyoming montmorillonite clay (sample B); II, this clay (sample B1) after ion exchange at room temperature; III, refluxed at 80°C; IV, washed twice; V, washed four times.

duced by a larger particle size. Using competitive intercalation, the comparison of samples B4, B5, and B6 shows that the amount of Al retained by the clay decreased as the ratio NH_4/Al increased, as expected from the theory of ion exchange. For a ratio $NH_4/Al = 10$, the amount of Al exchanged by the clay was less, but independent of the granulometry of the clay, as evidenced by the composition of samples C1 and C2.

CHARACTERIZATION OF THE TEXTURE OF THE PILLARED CLAYS

Pillaring increased basal spacings to 19–20 Å. These spacings decreased to 17.6 Å after the PILCs were calcined >400°C. Within experimental error, all the PILCs studied here had the same spacing. The main difference was in the width of 001 line, which was narrower for

Table 3. Interlayer 001 spacings determined on pillared clays prepared from small (sample C1) or large (sample C2) particles of the same parent clay.[1]

Sample[2]	d-values (Å)				
	001	002	003	004	006
C1	18.2	9.6	6.14	4.74	3.15
C2	17.7	9.71	6.27	4.75	—

[1] Samples calcined at 500°C.
[2] See text for sample descriptions.

Table 4. Surface areas measured by nitrogen adsorption at 77 K for pillared clays calcined at different temperatures.

Sample[1]	Surface areas (m²/g)				
	300°C	500°C	600°C	700°C	800°C
B1		309	—	230	122
B2	300	320		213	107
B4		270	187	162	25
B5		320		254	150
C1	360		276	242	170
C2	302			166	
G1	350	340		250	140

[1] See text for sample descriptions.

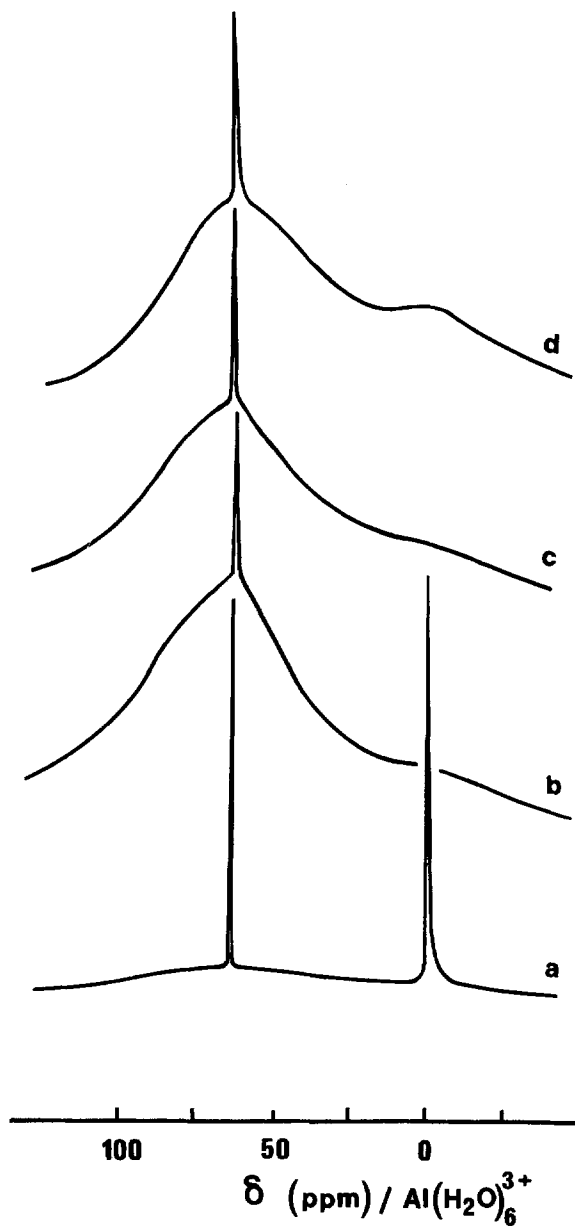Figure 3. X-ray powder diffraction patterns of samples B4 and B5 after calcination at different temperatures.

Figure 2. ^{27}Al nuclear magnetic resonance spectra of pillaring solutions: (a) standard hydroxy-Al solution at pH = 4.2; (b) adjusted to 6 with NaOH. Solutions having NH_4/Al = 10 at pH = 6 were obtained from the standard solution by adding (c) NH_4Cl or (d) CH_3COONH_4.

Table 5. Microporous volumes (ml/g) of pillared clays calcined at different temperatures.

Sample[1]	500°C	700°C	800°C
B1	0.13	0.09	0.05
B4	0.12	0.07	
B5	0.14	0.11	0.06
C1		0.12	0.08

[1] See text for sample descriptions.

samples prepared by competitive ion exchange, thus showing a greater crystallinity. The d(001) values of samples C1 and C2 are reported in Table 3. For a regular structure the product $l \times d$ (i.e., the Miller index l times the lattice spacing d) should be constant; the deviations from constancy are a measure of the regularity of the structure. Sample C1, prepared from smaller particles than sample C2, showed a more regular structure, which suggests a greater homogeneity of the sample.

The surface areas of PILCs dehydrated at different temperatures are listed in Table 4; the microporous volumes are listed in Table 5. After the samples were calcined at 500°C, this area increased as a function of the amount of Al introduced. The Al content of the PILCs, however, was not the unique factor controlling the surface area, as shown by a comparison of samples B2 and B5, or samples C1 and C2 (Table 4).

The thermal stability of the texture at T > 700°C was affected by several factors (Tables 4 and 5). The influence of the method of preparation, using the same parent clay B, is shown in Table 5 by the variations of the microporous volume for samples prepared under different conditions. In addition to decreasing the amount of Al exchanged into the clay, competitive ion exchange increased the stability of the microporous structure. The average pore size, h, estimated from the values of the total pore volume, V, and the surface
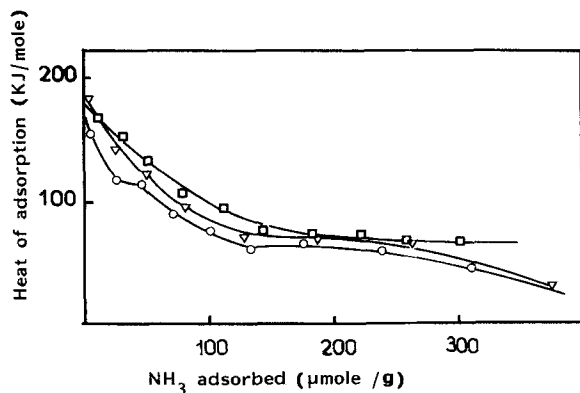
Figure 4. Differential heats of adsorption vs. coverage for the adsorption of NH_3 at 150°C on samples B1 (▽), B5 (O), and C1 (□).
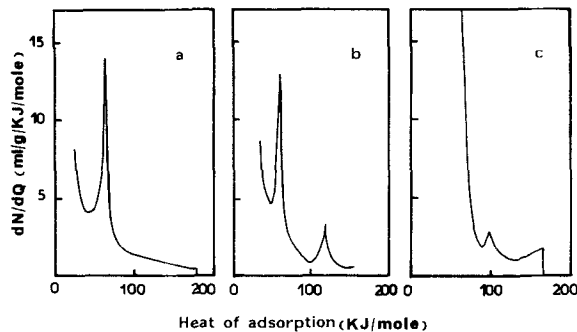

Figure 5. Distribution of acid strengths for (a) sample B1, (b) B5, and (c) C1, expressed as the fraction (dN/dQ) of site adsorbing ammonia with the energy Q.

area, S, for flat pores by h = V/S, increased only slightly, from 6.3 Å after calcination at 500°C, to 7 Å at 700°C and 8.2 Å at 800°C. These values reflect a good retention of the microporosity. The persistence of the 001 XRD line to 800°C (Figure 3) confirms the high stability of the structure.

Acidity measurements

The differential heats of adsorption of ammonia, measured at 150°C, are plotted as a function of the extent of adsorption in Figure 4. The distribution of acid strengths should reflect the type of bond linking the pillars to the clay and the interactions between the pillars. Figure 5 shows these distributions for samples B1, B5, and C1. The differences appear to be a function of the method of preparation.

DISCUSSION

Ion exchange is thought to be a fast process; hence, diffusional limitations are likely to control the kinetics. The diffusion of the Al_{13} cation, which has a kinetic radius of about 10 Å (Bottero *et al.*, 1982) should therefore be restricted in the interlayer space of smectites. This restriction is evidenced, in the absence of competition by: (1) the higher degree of exchange observed for small particles (sample B1) compared to large particles (sample G1) and (2) the fact that the degree of exchange reached a plateau, corresponding to 31% Al_2O_3 fixed, if the concentration of the solution was doubled, as for samples B1 and B2. The presence of an intense line at 12.5 Å in the XRD pattern of sample B1 (Figure 1) demonstrates that a major fraction of the material was not intercalated after refluxing at 80°C for 2 hr. Several redispersions of the PILC in hot water were needed to complete the process and to obtain a single sharp 001 XRD line centered at 18.6 Å.

The high selectivity of the clay for Al_{13} cations, reported by Plee *et al.* (1987) apparently precluded a good

distribution of the pillars. The cations did not diffuse into the core of the particle and remained in a shell, as is well known for noble metals. At the same pH, the NMR results suggest that the presence of a large excess of NH_4 ions did not noticeably modify the ^{27}Al spectrum. Thus, the distribution of Al between the different species in the pillaring solution was not altered, and the ammonium ions acted as competitor ions, without changing the nature of the pillars. Competitive ion exchange did occur inasmuch as the amount of Al fixed by the clay decreased as the NH_4^+/Al ratio increased. Moreover, although in the absence of competition, small particles were more exchanged than large particles, the identical compositions of samples C1 and C2 shows that the use of competitive ion exchange decreased diffusional limitations. Thus, the pillars were better distributed. The smaller surface area of sample C2, however, suggests that the NH_4/Al ratio was insufficient to reach a statistical distribution of the pillars in the structure if the size of the particle was >2 μm. The presence of some interstratification supports this contention.

In supported metals (Ribeiro and Marcilly, 1979), good distributions can be obtained using either dilute solutions of the precursor salt or competitive ion exchange. Washing the intercalated clay is therefore equivalent to the use of a dilute solution obtained by partial dissolution of the Al_{13} cations fixed by the solid. The progressive changes of the XRD spectra in Figure 1 confirm that washing was critical to improving the distribution of the pillars within the particle.

Thus, the surface area of the PILC is related to the distribution of the pillars. Tichit *et al.* (1988a) proposed that the thermal stability of the PILC is also related to that distribution. Indeed, the results reported in the present study are consistent with theoretical predictions: using the same parent clay B, the microporous volume and the surface area retained at >700°C increased if competitive ion exchange was used, even if the number of pillars decreased, as shown by comparing sample B5 with the other samples. Repeated wash-

ing also increased the stability, as evidenced by sample G1, which retained a surface of 140 m²/g at 800°C. Competitive ion exchange however, notably improved the preparation, inasmuch as the concentration of the clay slurries increased without loss of quality of the products.

Competitive ion exchange can be used in different forms; the competitor ion can be added to the pillaring solution, as used here, or exchanged first into the solid. Tokarz and Shabtai (1985) reported the intercalation of montmorillonite samples previously exchanged by Ce^{3+} or La^{3+} ions. This procedure was competitive ion exchange, because the PILC retained an amount of rare earth elements, which depended on the Al concentration of the pillaring solution. The residual Ce^{3+} content was about 30% of the CEC, demonstrating a strong bond between the lanthanide and the clay. The presence of Ce^{3+} ions at the exchange positions of the PILC not occupied by the pillars noticeably increases the thermal stability and stabilizes Lewis acidity (Tichit *et al.*, 1988c). Therefore, two effects probably cooperated in the stabilization of these La-Al-clays: a good distribution of the pillars, and the presence of La^{3+} ions at the cationic sites of the PILC.

The stability of samples G1, B5, and C1 at 800°C can also be correlated with the Fe_2O_3 content of the clay. The detrimental influence of Fe was noted at >700°C in dry air. Tichit *et al.* (1988b) reported that the clay structure itself was destroyed at this temperature, and Mössbauer spectrometry demonstrated that the environment of Fe^{3+} cations was distorted. In the present study, the iron-free clay was more stable, which is consistent with the known lower stability of Fe–O–Si bonds compared with Al–O–Si bonds. The greater stability of pillared synthetic beidellite can therefore be accounted for, in part, by the absence of Fe in the structure.

Competitive intercalation also altered the distribution of acid strengths of the PILCs. Sample B1, prepared using noncompetitive ion exchange, showed the presence of only a few strong acid sites and many sites of intermediate acidity (60 kJ/mole). Sample B5, prepared by competition ion exchange using very small particles of clay, exhibited a quite different pattern, having many sites of higher acidity (120 kJ/mole). The adsorption of NH_3 on pillared beidellite showed the presence of many strong acid sites (160 kJ/mole). Sample B5, therefore, appears to be closer to beidellite than conventional Al-pillared montmorillonite. For pillared beidellites, Fripiat (1988) proposed that the Al_{13} cation retains its individuality; thus, strong acidity due to the tetrahedral Al of the pillar should exist. Competitive ion exchange favored a good distribution of the Al_{13} cations in montmorillonite and should have resulted in a greater retention of their individuality. Thus, the hypothesis used for beidellites may also explain the higher acidity of sample B5. Sample C1 prepared by

competitive ion exchange using particles of 2-μm size showed less acidity than sample B5: both the number of strong acid sites and their strength decreased. The difficulty of obtaining an ideal dispersion of the Al_{13} cations appeared to have increased with the particle size of the clay. A poor dispersion most likely resulted in clustering of Al_{13} cations, which enabled dehydroxylation to alumina of lower acidity.

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