

EXCHANGEABLE ION AND THERMAL TREATMENT EFFECTS ON BASAL SPACINGS OF Al-HYDROXY PILLARED MONTMORILLONITES

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Abstract—Al-hydroxy intercalated clays (ALHICs) obtained from different parent clays were used to investigate the interactions between oligomers and clay surface layers.

The thermal stability of ALHICs obtained from natural, Cs-, Ca-, Ba-, Fe-, Cu- or Ce-montmorillonites has been investigated by studying the relationship between basal spacing and calcination temperature. X-ray diffraction has shown that the basal spacing of ALHICs obtained from Cu-montmorillonite calcined at 550°C is 13.4 Å, different from basal spacings of ALHICs obtained from Fe-montmorillonite (16.0 Å) and other parent clays (16.7 Å). Thermograms for ALHICs obtained from natural, Fe- and Ce-montmorillonites displayed distinct steps at 225 and 650°C, attributed to the dehydration of Al₁₃ oligomers, and the dehydroxylation of the surface layer, respectively. By contrast, thermograms of ALHICs obtained from Cu-montmorillonite displayed one step between 250 and 700°C for both dehydration and dehydroxylation. Mössbauer parameters showed that Fe³⁺ octahedra in octahedral sheets are distorted in pillared interlayered clay (PILC) obtained from Cu-montmorillonite and undistorted in that obtained from Fe-montmorillonite. The difference in thermal stability for the various ALHICs is attributed to the retention of some of the original cations after intercalation with Al₁₃ oligomers, which induces several interactions between the oligomers and the clay surface layers.

Key Words—Al-Hydroxy Intercalated Clays, ALHICs, Al₂O₃ Pillar, Basal Spacing, Cation Exchange Reaction, Homoionic Clays, Intercalated Clays, Montmorillonite, Pillared Clays, Surface Interactions, Thermal Stability.

INTRODUCTION

Several methods to prepare pillared clay minerals have been reported. These methods are based on the introduction of complex inorganic polycations into the interlamellar space of the clay. On heating, the intercalated inorganic species are converted into metal oxide clusters, generating a stable microporous structure (Kloprogge, 1998; Thomas, 1997). The molecular dimensions of the pillaring agent can determine the constant interlayer spacing in such structures (Lahav *et al.*, 1978). Several cations have been used as complex inorganic polycations, *e.g.* aluminum (Lahav *et al.*, 1978; Occelli and Tindwa, 1983), chromium (Pinnavaia *et al.*, 1985a), zirconium (Ohtsuka *et al.*, 1993) and iron (Govea and Steinfink, 1997). More recently, surfactants have been used together with aqueous silicate species to form a silica framework between the layers (Galarnau *et al.*, 1995). New mesoporous silica-pillared montmorillonites were prepared by intercalation of bulk organic cations into silica sol-exchanged montmorillonites (Han and Yamanaka, 1998).

Many papers have also been published on the interactions between Al-hydroxy oligomers and the montmorillonite layer in the Al oxide pillaring process of clays. Lahav *et al.* (1978) considered the basal spacing of <19.0 Å to be due to the partial overlap

between either the hydroxyl groups in the oligomeric species or between the montmorillonite oxygens and the hydroxyl groups in the oligomeric species. Bond formation and chemical bond stability between the pillars and clay silicate layers were previously discussed with regard to thermal stability (Pinnavaia *et al.*, 1985b; Plee *et al.*, 1985; Sterte and Shabtai, 1987). However, in the absence of these bonds in Al-pillared montmorillonites, stability was related to pillar density (Tokarz and Shabtai, 1985). Plee *et al.* (1987) investigated the influence of the structural charge on the pillaring process in montmorillonite, which has octahedral substitutions, and beidellite, which has tetrahedral substitutions. The basal spacing was practically the same for both types of pillared interlayered clays (PILCs). The main difference observed lies in the ordering of the pillars within the interlamellar space. According to Tichit *et al.* (1988), the presence of Ce³⁺ ions in the exchange positions of the pillared clay not occupied by the pillars increased thermal stability noticeably. These authors suggested that competitive ion exchange could be used to control pillar distribution and homogeneity.

According to Brown and Kevan (1988), three discrete sites are occupied by Cu²⁺ ions between montmorillonite layers, depending on the degree of hydration of the clay. Heating produces complete dehydration and Cu²⁺ ions enter the hexagonal cavity of the structure. The Cu²⁺ ions remain in this cavity as the dehydration temperature is raised, becoming irreversibly trapped in the cavity above 150–200°C. It has been suggested that the major

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axis of symmetry for Cu^{2+} ions are perpendicular to the silicate layers (Comets *et al.*, 1992). This should be expected, if Cu^{2+} is inside the hexagonal cavity, which defines the symmetry axes.

Rozenon and Heller-Kallai (1977) established relationships between some parameters of Mössbauer spectra of dioctahedral smectites and their structures. Smectites have three possible octahedral sites: *M1* with hydroxyl groups arranged in trans positions and two *M2* sites with hydroxyl groups arranged in *cis* positions. For a square bipyramidal arrangement of groups like $\text{FeO}_4(\text{OH})_2$, the absolute value of the ratio of the quadrupole splitting for the *trans* and the *cis* configuration, *K*, is 2. In samples with *K* values other than 2, the octahedra are supposed to be distorted, due to a more significant effect of the next nearest neighbors.

The aim of the present study is to compare the basal spacing of Al-hydroxy intercalated clays under different thermal treatments together with cation exchange (Na, Cs, Ca, Ba, Fe, Cu and Ce) in the parent clay. Particular attention was paid to the effect of Cu^{2+} ions on the orientation of the Al-hydroxy oligomers between montmorillonite layers with increasing calcination temperature. We have studied the effect of Al_{13} oligomers and surface layer interactions on the thermal stability of Al_2O_3 -PILCs, which was defined as the conservation of the typical 19 Å spacing after calcination.

EXPERIMENTAL PROCEDURE

The natural montmorillonite sample used, SWy-2, was supplied by the Source Clays Repository of The Clay Minerals Society, University of Missouri. Elemental analyses were performed by X-ray fluorescence (XRF) and neutron activation techniques. The major components are listed in Table 1. X-ray diffraction patterns show the characteristic reflection peaks for montmorillonite, as well as for quartz impurities ($2\theta = 26.59^\circ$). The solutions used in all experiments were prepared with deionized water treated in a Milli-UV-Plus system.

Solutions of $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ (Keggin cation)

Solutions were prepared following the method of Furrer *et al.* (1992). A volume of 178 mL of a 0.25 M

AlCl_3 solution was heated with an electrothermal mantle up to 80°C, and 320 mL of a 0.25 M NaOH solution were added at a rate of 2 mL/min, using an addition funnel with a pressure equalization arm. The mixture was stirred at 300 rpm. The concentration ratio ($[\text{NaOH}]/[\text{AlCl}_3]$) was 1.8. The solution obtained was aged for at least 1 week in a dark bottle.

The homoionic montmorillonites

Na-montmorillonite was submitted to ion exchange with a cation (cation = Cs, Ba, Ca, Fe, Cu, Ce) nitrate solution. Then, 20 g of Na-montmorillonite was added to 1 L of 1 M nitrate solution. The mixture was stirred for 8 h at 80°C. The ion-exchanged products were collected by centrifugation followed by five washes with deionized water until the pH of the supernatant solution was constant.

Pillaring process

Some of the homoionic montmorillonites were solvated with ethylene glycol before use (Govea and Steinfink, 1997). A 1 g/20 mL clay/water suspension was prepared from the samples and aged for 1 week. Pillared clay was prepared according to Occelli and Tindwa (1983). The suspension was heated up to 80°C under magnetic stirring at 300 rpm. The pillaring solution of $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ was added to this mixture at a rate of 2 mL/min using an addition funnel with a pressure equalization arm. The volume was that required to obtain an Al/montmorillonite ratio of 19 mmol Al/g montmorillonite. After 32 h of reaction at 80°C, the resulting product, Al-hydroxy intercalated clay (ALHIC), was aged for 1 week at room temperature. The product was washed by redispersing it in deionized water, and separated by centrifugation until it was chloride free (as tested by AgNO_3).

Characterization studies

The oriented sample films were obtained by stirring a 1 g/200 mL clay/water suspension with a magnetic stirrer for 30 min. A glass slide fixed over a PVC support was inserted into the mixture and the clay sediment was allowed to spread spontaneously over the slide. Film samples were either dried at room temperature or calcined in a programmable 'Vulcan' furnace for

Table 1. Chemical composition (wt.%) of homoionic montmorillonites.

Exchangeable cation	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	MgO	TiO_2	Na_2O	
Natural	72.8	13.8	6.9	0.9	0.1	0.3	0.1	5.2	
Fe	73.1	14.4	11.5	0.03	0.05	0.3	0.1	0.4	
Ca	73.9	13.8	6.9	4.4	0.06	0.3	0.1	0.4	
Cu	70.8	13.1	7.1	0.05	0.05	0.3	0.1	0.4	CuO 8.1
Ce	70.3	13.5	7.7	0.05	0.04	0.2	0.09	0.4	Ce_2O_3 7.7
Ba	71.3	13.8	4.6	0.06	0.06	0.4	0.1	0.4	BaO 9.2

Table 2. Chemical composition (wt.%) of ALHICs obtained from homoionic montmorillonites.

Exchangeable cation	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	MgO	TiO ₂	Na ₂ O	
Natural	68.4	24.1	6.7	0.05	0.06	0.3	0.1	0.4	
Fe	68.7	21.0	9.5	0.05	0.05	0.3	0.1	0.4	
Ca	68.9	23.0	7.3	0.05	0.05	0.3	0.1	0.4	
Cu	64.0	22.9	8.5	0.06	0.06	0.3	0.1	0.4	CuO 3.6
Ce	67.9	23.7	6.5	0.05	0.05	0.3	0.1	0.4	Ce ₂ O ₃ 1.1
Ba	68.9	22.1	8.3	0.05	0.05	0.3	0.1	0.4	BaO 0.1

4 h at 400, 500 and 550°C. Calcination was performed under ambient conditions. The basal spacing of the resulting product, a pillared interlayered clay (PILC), was determined after calcination at each temperature and the subsequent cooling up to room temperature. X-ray powder diffraction patterns were obtained with CuK α radiation using a Rigaku diffractometer Geigerflex model.

Thermal analyses were performed using a 2950 TGA HR V5.3C apparatus, with argon flow of 100 mL/min and heating rate of 10°C/min.

Mössbauer spectra were obtained using a conventional constant acceleration spectrometer and a ⁵⁷Co (Rh) source at room temperature.

Chemical analyses

Chemical analyses were performed using XRF, atomic absorption, flame emission and ultraviolet and visible absorption spectroscopy.

The standards for XRF analysis were prepared using specpure (JMC) silicon dioxide, iron oxide, copper oxide, cerium oxide, barium carbonate or cesium chloride, and (Merk) aluminum oxide or calcium oxide. The homoionic and Al-hydroxy intercalated montmorillonites and the standards were calcined at 1050°C before use. The powdered samples were compressed into briquettes using high pressure with 5 g of boric acid as a binder. The XRF intensities of the samples were compared with those from standards of similar composition.

The cation exchange capacity (CEC) was determined by stirring the samples with 3 M ammonium acetate (pH = 7). The mixture (1 g/60 mL clay/solution) was stirred using a magnetic stirrer for 8 h at room temperature, and then filtered. The resulting solid was washed with alcohol and dried at 110°C for 4 h before use, and treated with 60% w/w NaOH in a Kjeldahl flask. The ammonia released was collected in a 0.025 M HCl solution, and titrated with 0.025 M NaOH solution. The supernatant solutions were analyzed for Na⁺ and K⁺ by flame emission (Digimed NK-2004) and Ca²⁺, Ba²⁺, Mg²⁺ and Fe³⁺ by atomic absorption spectroscopy (Perkin Elmer-AAAnalyst 300) and spectrophotometry with 4-(pyridyl-2-azo) resorcinol, PAR, according to

Bobrowska-Grzesik and Grossman (1996) and Gomez *et al.* (1992).

Ion exchange in Fe-montmorillonites was determined according to Han *et al.* (1997). Fe-montmorillonites were dispersed in either 0.2 N or 2.0 N HCl in solution for 19 h at room temperature to leach out the Fe species. After filtration, the Fe species in the supernatant solution were determined by either AAS or spectrophotometry.

RESULTS AND DISCUSSION

The compositions of the homoionic montmorillonites and ALHICs are presented in Tables 1 and 2, respectively. The Al₂O₃ concentrations of ALHIC are ~9% greater than those of homoionic montmorillonite. The elemental analyses of the samples obtained from different parent clays are very similar, indicating a similar Al uptake by the parent clay from the pillaring solution (Sterte, 1991). This could be explained by the fact that when excess Al is offered in the form of Al₁₃⁷⁺, ion exchange is incomplete and is accompanied by precipitation and polymerization of Al₁₃⁷⁺ on the clay surface (Schoonheydt *et al.*, 1994).

Exchangeable cation concentrations before and after exchange with oligomers Al₁₃⁷⁺ are listed in Table 3. A proportion of the original ions was retained in the PILC when the exchangeable cation in the parent clay was either Fe³⁺ or Cu²⁺, but in the PILC obtained from the other homoionic montmorillonites, it was within 5% of the limits of experimental error. These different amounts of original cations exchanged depended on the CEC of

Table 3. Cation concentrations (meq/100 g) for montmorillonite, in the starting homoionic montmorillonite and in the ALHICs.

Starting cation	Exchangeable cations (meq cation/100 g of clay)	
	Before	After
Ca	77	4
Cu	90	38
Cs	82	3
Ce	91	10
Fe	54	25
Ba	82	1

Table 4. Cation exchange capacity (CEC) determined using the Kjeldahl method with ammonium acetate (3 M, pH = 7) as an ion-exchanger.

Montmorillonite	Meq of NH_4^+ /100 g of clay
Natural	77±1
Fe	61±1
Cu	75±2
Ca	73±1
Ba	61±3

Samples were divided into three replicates.

the homoionic clays, which was determined according to the Kjeldahl method and are listed in Table 4. Their values are in the range 61–75 meq of NH_4^+ /100 g clay interval. One phenomenon that may be responsible for high cation concentration is precipitation of hydroxide onto clay particles. It is possible that in the preparation of homoionic montmorillonites, a quantity of ions exceeding the CEC is adsorbed by montmorillonites during the exchange reaction.

X-ray power diffraction patterns ($4^\circ \leq 2\theta \leq 30^\circ$) of ALHICs (air-dried at room temperature) and pillared clays after calcination at 550°C for 4 h in air are shown in Figure 1. The basal spacing measurement for an ALHIC from Cu-montmorillonite dried at room temperature was 17.3 Å. A 19.0 Å basal spacing value was obtained by increasing the Al/montmorillonite ratio from 19 mmol/g to 38 mmol/g in the pillaring process. The basal spacing of the clays increased by 19.0 Å upon intercalation with Al_{13}^{7+} oligomers. A comparison between XRD patterns of the pillared clays after calcination at 550°C with those of ALHIC dried at room temperature reveals that the peak intensity is approximately the same for both. A variation is observed in the position of the peaks, which rose at sharper higher angles at 550°C, notably for PILC obtained from Cu-montmorillonite.

The ALHICs were thermally treated by drying either at room temperature or over a range of calcination up to 550°C. The variations of basal spacing with temperature for the different cations in homoionic montmorillonites are given in Table 5. It was observed that the basal spacings of PILCs were greater than those for parent clays which collapsed (9.4 Å) after calcination at 550°C. The PILCs obtained from Cs-, Ca-, Ba- or Ce-montmorillonites had constant basal spacing values of ~16.7 Å, larger than those of PILCs obtained from Fe- or Cu-montmorillonites. In general, basal spacing decreased as calcination temperature increased. If thermal stability is defined as the conservation of the typical 19.0 Å spacing after calcination at 550°C, then the pillared montmorillonites should be considered thermally unstable, since ALHICs presented a different behavior under thermal treatment.

The results presented in Table 5 show that ethylene glycol had no observable effect since the samples submitted to thermal treatment had been divided into

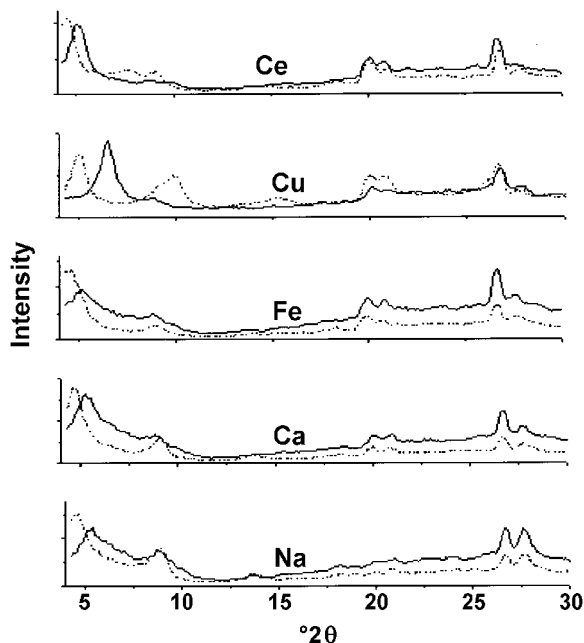


Figure 1. X-ray powder diffraction traces of ALHICs (dotted lines) air-dried at room temperature and pillared clays (solid lines) calcined at 550°C for 4 h in air. The cation originally present in the parent clay is indicated on the curves.

four replicates, each with a different concentration of ethylene glycol (0–5% wt.%). The differences in basal spacing values were within the range attributed to experimental error. In addition, PILC basal spacing values were not affected by either cation charge (Cs^+ , Ca^{2+} and Ce^{3+}) or size (Ca^{2+} , Ba^{2+} , Cs^+ , effective ionic radii 114, 149 and 181 pm, respectively). No direct correlation could be established between the cation used and the basal spacing measured. However the lowest basal spacing value for PILC obtained from Cu-montmorillonite suggests that the clay layers are more susceptible to structural change by this cation.

Thermogravimetric (TG) analysis and differential thermogravimetric (DTG) analysis curves are shown in Figure 2. Weight loss could be observed in all TG curves around 100°C, which may be attributed to the loss of surface-adsorbed water (González *et al.*, 1992). In

Table 5. Average basal spacing (Å) for ALHICs and PILCs obtained from homoionic montmorillonites.

Parent clays	ALHIC	Basal spacing		
		400°C	500°C	550°C
Natural	19.6±0.3	17.7±0.3	17.3±0.3	16.7±0.3
Cs	19.3±0.3	18.0±0.3	17.7±0.3	16.7±0.3
Ca	19.3±0.3	18.4±0.3	17.5±0.3	16.7±0.3
Ba	18.6±0.2	17.7±0.3	16.7±0.3	16.7±0.3
Fe	19.3±0.3	17.8±0.2	16.5±0.7	16.0±0.5
Cu	17.2±0.3	14.0±0.2	13.8±0.1	13.6±0.1
Ce	18.6±0.3	17.5±0.6	16.9±0.2	16.8±0.3

Samples were divided into three replicates.

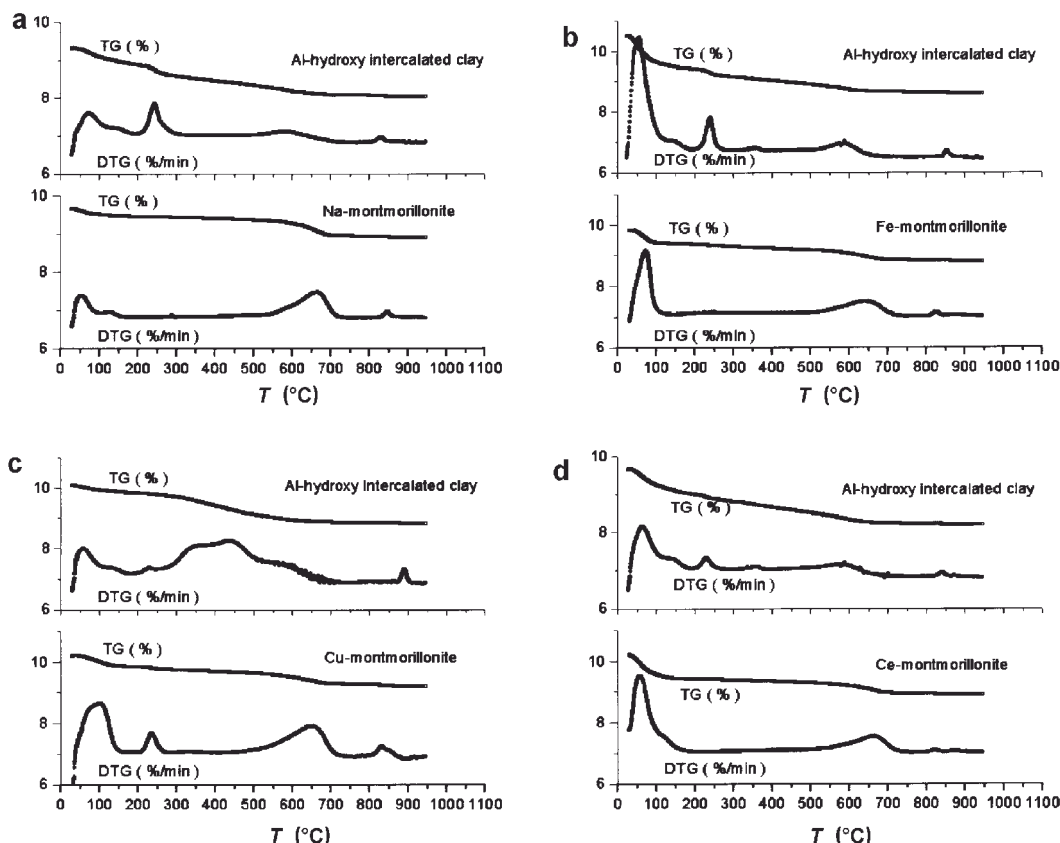


Figure 2. TG and DTG spectra of homoionic montmorillonites and Al-hydroxy intercalated montmorillonites for: (a) Na-/ALHIC(Na); (b) Fe-/ALHIC obtained from Fe-montmorillonite; (c) Cu-/ALHIC obtained from Cu-montmorillonite; and (d) Ce-/ALHIC(Ce).

addition, weight loss was observed in TG curves for homoionic montmorillonites around 650°C, due to dehydroxylation of the silicate layers of the clay. When TG curves of ALHICs were compared with those of homoionic montmorillonites, a new peak appeared at 225°C, which could be attributed to the dehydration of pillars (Han *et al.* (1997). The peak attributed to the dehydroxylation of silicate layers occurred at a lower temperature (600°C) than that of homoionic montmorillonites did.

In the Cu-montmorillonite TG curve, weight loss was observed at ~225°C, and this additional peak may be attributed to the loss of the Cu(II) coordinated water molecules H-bonded to the basal oxygen (Comets *et al.*, 1992). In addition, in the TG curve of ALHIC obtained from Cu-montmorillonite, only a slight plateau is visible at 225°C and the principal effect observed occurred between 250 and 700°C, with a maximum at 430°C. Although no reaction between pillars and the tetrahedral sheet is expected for smectites without tetrahedral substitutions (hectorite, montmorillonite) (Plee *et al.*, 1985), new Al–O–Si bonds should be formed between the oligomers and the surface layer induced by Cu(II) with the subsequent loss of water (Pinnavaia *et al.*, 1985b).

The assumption above could be explained by the competition of the solvated ions and their interactions with the montmorillonite layers and by the crystal field theory (Huheey, 1978). Iron(III) has a tendency to resist spin pairing, but its high ionic charge favors octahedral coordination and an increase in the effective field of the ligands. In the absence of crystal field stabilization, which is precluded by the electronic structure of Fe³⁺, the tendency to form more covalent Fe–O bonds is a decisive factor in determining the distribution of Fe³⁺ ions among the available sites (Rozenon and Heller-Kallai, 1977). On the other hand, better evidence for the presence of Jan-Teller effects in transition metal compounds comes from structural studies of solids containing Cu(II). Thus, in this case, only Cu²⁺ ions will enter the pseudo-hexagonal cavity by virtue of their ability to undergo tetragonal distortion from octahedral symmetry.

In Mössbauer spectra performed at room temperature, this difference is reflected by a pronounced effect on the Fe³⁺ octahedra in the octahedral sheets of the clay. Figure 3 shows Mössbauer spectra of samples of natural montmorillonite, homoionic montmorillonites (Fe or Cu) dried either at room temperature or calcined at 350°C, and pillared clays calcined at 550°C. The spectra can be

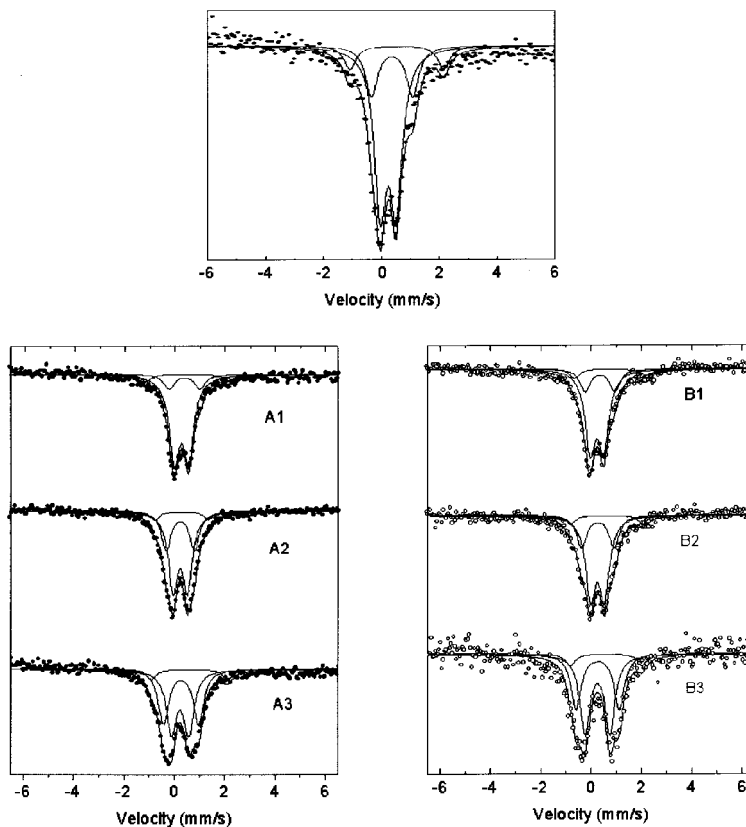


Figure 3. Mössbauer spectra of natural montmorillonite and their ionic exchanged products: Fe (A1), dried at room temperature (A2), calcined at 350°C; Cu (B1), dried at room temperature (B2), calcined at 350°C; and pillared clays obtained from (A3) Fe-montmorillonite, and (B3) Cu-montmorillonite.

resolved into three doublets: two corresponding to trivalent Fe in sites *M1* and *M2* and a third to a divalent Fe, all in octahedral coordination. The Mössbauer parameters, quadrupole splitting, QS, and isomer shift, IS, and the ratio *K*, the absolute value of the quadrupole splitting ratio of the *trans* and *cis* configurations, and the ratio $[AM1/AM2]$, which indicate preference of Fe^{3+} ions by *M1* or *M2* sites, are listed in Table 6.

Exchange of interlayer cations has a small effect on *K* values, while the $[AM1/AM2]$ ratio indicates a strong preference of Fe^{3+} ions for *M2* sites. Heating Fe- and

Cu-montmorillonites gives *K* values of 1.96 and 2.06, respectively, while the $[AM1/AM2]$ ratio increases to values close to 0.5, indicating a random distribution of Fe^{3+} between *M1* and *M2* and that suggests an undistorted structure. On the other hand, the $[AM1/AM2]$ ratio is >0.5 for pillared samples, which indicates Fe^{3+} ions occupying less covalently bonded *M1* sites rather than Fe^{3+} ions in *M2* sites. The *K* ratio shows that Fe^{3+} octahedra are both distorted for PILC obtained from Cu-montmorillonite and undistorted for that obtained from Fe-montmorillonite. These results are in line with

Table 6. Mössbauer parameters for natural montmorillonite, Fe- and Cu-montmorillonites dried at room temperature and calcined at 350°C, and for the PILC obtained.

Samples	Fe^{3+} in <i>M1</i> (<i>trans</i> configuration)		Fe^{3+} in <i>M2</i> (<i>cis</i> configuration)		Fe^{2+}			<i>K</i>	$AM1/AM2$
	IS	QS	IS	QS	IS	QS	A(%)		
Natural mont.	0.48	1.39	0.35	0.54	0.64	3.22	10	2.57	0.32
Fe-mont.	0.47	1.24	0.35	0.57	0.60	3.31	7	2.18	0.18
Fe-mont. (350°C)	0.35	1.12	0.36	0.57	0.40	2.12	7	1.96	0.52
PILC (Fe)	0.38	1.40	0.34	0.68	0.70	3.01	8	2.06	0.89
Cu-mont.	0.45	1.20	0.35	0.68	0.85	2.85	9	1.76	0.28
Cu-mont. (350°C)	0.34	1.40	0.35	0.68	0.70	2.85	8	2.06	0.42
PILC (Cu)	0.34	1.70	0.35	1.12	0.70	2.85	8	1.52	0.70

Isomer shift, IS; quadrupole splitting, QS (in mm/sec); $AM1/AM2$ = ratio between the amount of Fe^{3+} in the *M1* and *M2* sites; *K* = quadrupole splitting ratio of *trans* and *cis* configurations.

the insertion of Cu^{2+} ions in hexagonal cavities, which allows their proximity to Fe sites in octahedral sheets (Gounis *et al.*, 2000).

Thereafter, the difference between PILCs obtained from Na-, Ce- or Fe-montmorillonites and that obtained from Cu could obviously be explained by the different structures of the intercalated species (Plee *et al.*, 1985). According to Botero *et al.* (1987), in the solid state, the formation of Al trihydroxides may occur through structural rearrangement without redissolution steps of Al_{13} units into homogeneous octahedral domains from which the perturbed-symmetry Al tetrahedrals disappeared.

CONCLUSIONS

There appear to be different mechanisms of interaction between Al_{13} oligomers and the surface layer under thermal treatment depending on the cation in the parent clay. In the first mechanism the ionic exchange is completed between the original ions and the Al_{13} oligomers. In this case, thermal stability decreases due to the partial overlap between either the oligomeric species themselves or between the montmorillonite surface layers and the oligomeric species. This can be observed for PILCs obtained from natural and Ca-, Ba- or Ce-montmorillonites. In the second mechanism, a proportion of original ions is retained due to partial substitution. If the original ions are Fe, the thermal stability of the PILC is lower than that in the previous case, because of the lower stability of Fe–O–Si interactions on calcination in comparison to those involving Al–O–Si (Figueras *et al.*, 1990). If the original ions are Cu, they will interact with montmorillonite layers at temperatures in excess of 100°C. These recessed Cu^{2+} cations induce the dehydroxylation of surface layers and Al_{13} oligomers at temperatures rising continuously from 250 to 700°C. In this case, Mössbauer spectroscopy could detect the difference between the behavior of retained Fe and Cu ions. According to Botero *et al.* (1987) this would lead to the formation of crystallized trihydroxides, such as bayerite, gibbsite or nordstrandite, given that the mechanism proposed occurs in the solid state. Thereafter, the Al_{13} oligomers can change structurally or form a monolayer between the interlayers with a basal spacing of $\sim(9.4 + 4.7) 13.6 \text{ \AA}$ (Lahav *et al.* 1978).

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