

ENHANCED THERMAL STABILITY OF Al-PILLARED SMECTITES MODIFIED WITH Ce AND La

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Abstract—A commercial bentonite (primarily smectite) from Fischer Scientific Company (F bentonite) and a natural bentonite from Peru (P bentonite) were used in the preparation of pillared clays with polyoxymetal cations of Al that were subsequently modified with Ce and La. Several Al/metal ratios (5 and 9) were used to investigate the effects on the thermal and hydrothermal stability of these synthetic clays. The structure of these materials was studied by X-ray diffraction. Isotherms were determined by N₂ adsorption. Thermal stability was determined using thermogravimetric (TG) measurements and ammonia-TPD (temperature programmed desorption) was used to obtain acidity data. These materials exhibited basal spacings from 16 to 20 Å, with surface areas from 239 to 347 m² g⁻¹, with microporosity contributing from 50 to 80% of the total surface area. Pillared clays prepared from F bentonite generally showed larger basal spacings and surface areas than those prepared from P bentonite. Pillared clays modified with Ce or La did not show any apparent structural changes relative to the Al-pillared clays. Pillared clays modified with Ce and La had similar acid properties as Al-pillared clays. In contrast, the thermal and hydrothermal stabilities of these materials were greater than Al-pillared clays. However, Ce-pillared clay appears to be more effective than La-pillared clay in delaying the dehydroxylation of pillared clays with increasing temperature. The intercalation of Ce and La into Al-pillared clays improved the thermal stability, which may increase the utility of these materials as catalysts.

Key Words—Bentonite, Ce, La, Pillared Clays.

INTRODUCTION

An ion-exchange process involving the exchangeable cations of certain clays typically initiates the production of pillared clays. Na-rich montmorillonite can be pillared by different polyoxymetal cations. Upon calcination, the resulting materials contain metal-oxide pillars which separate the 2:1 layers. This modification allows internal surfaces to be accessible for greater chemical activity. The polyoxymetal cations probably aggregate to form cationic oligomers in solution. The size of these oligomers appears to control the size of the pore openings in the pillared clay. In principle, any metal oxide or salt forming polynuclear species upon hydrolysis can be inserted as a pillar. Most common ions used are polycationic species of Al (Shabtai *et al.*, 1984; Pinnavia *et al.*, 1984; Suzuki *et al.*, 1988; Sterte, 1991), Zr (Bartley and Buch, 1985; Burch and Warburton, 1986; Yang and Baksh, 1991), Ti (Sterte, 1986), Fe (Burch and Warburton, 1987; Yamanaka and Hattori, 1988), and Cr (Pinnavia *et al.*, 1985; Carrado *et al.*, 1986; Vaughan, 1987). These pillaring agents are prepared by hydrolysis of the corresponding salts in solution. These intercalated clays are commonly prepared from natural smectite clays because of the low-charge density on the 2:1 layers and swelling ability. Properties such as acidity, surface area, pore-size distribution, and hydrothermal stability are related to the method of synthesis and the nature of the host clay.

Pillared smectites have acid properties thereby making them potentially suitable in petrochemical cracking where they may replace zeolites. Pillared clays have microporosity which allows larger molecules, such as heavy oil fractions, to crack. However, pillared clays are deactivated more rapidly than zeolites by coke deposited during cracking, and they have a restricted hydrothermal stability. Synthetic pillared laminar silicates, including those pillared with polyoxycations of Al, are not sufficiently stable and collapse with a loss of surface area and catalytic activity at temperatures below 773 K.

To avoid sintering of the pillared clay, the thermal stability of the pillars must increase. One way to achieve this goal is to introduce mixed-oxide pillars. These materials have been used in isomerization and dehydrogenation reactions: Al-Ga (Viera Coelho and Poncelet, 1991), Al-Zr (Ocelli, 1986), Al-Fe (Oades, 1984; Lee *et al.*, 1989; Bergaya *et al.*, 1993), and Al-Cr (Lee *et al.*, 1989). Another possible method to obtain pillared clays with mixed-oxide pillars is to use transition-metal ions by impregnation (Gil and Montes, 1997), with the pillared clay acting as a substrate. Pillared clays have been prepared also by cation exchange, either before or after initial pillaring of the clay (Suzuki *et al.*, 1988; Carrado *et al.*, 1986). In other cases, pillared clays were prepared by first combining the transition-metal ion with the pillaring agent

and the resulting species subsequently used to pillar the clay (Occelli, 1986; Viera Coelho and Poncelet, 1991; Lee *et al.*, 1989; Bergaya *et al.*, 1993; Fetter *et al.*, 1995; Cañizares *et al.*, 1999).

The interaction of clay minerals with cerium and lanthanide cations, not extensively studied previously, has attracted attention in the design of safe repositories for high-level radioactive nuclear waste material (Miller *et al.*, 1982). The presence of Ce in Al-pillared clays produces a substantial increase in the conversion of *n*-heptane and in the selectivity towards cracking products owing to the increase in the number of acid centers (Hernando *et al.*, 1996). Montmorillonite saturated with lanthanides shows, upon heating, a decrease in cation-exchange capacity, which was partially attributed to the migration of the lanthanide ions to octahedral sites of the 2:1 layers (Poyato *et al.*, 1987). Tokarz and Shabtai (1985) reported the synthesis and analysis of Ce³⁺ and La³⁺-containing montmorillonites pillared with hydroxy-aluminum oligocations. The calcination temperature affected both surface area and the position of the X-ray *d*(001) peak. Schoonheydt *et al.* (1993) showed that the addition of Ce³⁺ to the pillaring solutions with Ce/Al ≤ 1 had no significant effect on the *d*(001) values and the thermal behavior of the pillared clays. Despite these studies, the influence of Ce or La in Al-pillared clays on the thermal and the hydrothermal stability of these materials has not been extensively studied. In this paper, the physicochemical properties of Al-pillared clays modified with Ce or La were investigated. For starting materials, two different bentonites (rocks that are composed primarily of smectites) were used. We were interested in determining if thermal and hydrothermal stabilities were affected.

EXPERIMENTAL

Starting materials

Two different bentonites were used in this study, a purified-grade bentonite (Fisher Scientific Company, Loughborough, Oregon, USA; see Yang and Baksh, 1991; Cañizares *et al.*, 1999 and a natural Peruvian bentonite (Agregados Calcáreos Sociedad Anónima Company, Lima, Perú). Hereafter, the former is referred to as "F bentonite" and the latter is referred to as "P bentonite". Particle sizes of <2 μm were used. Before the pillaring process, both bentonites were pre-treated with acetic acid and H₂O₂ to remove free carbonates and organic compounds, respectively. As determined at the University of Lima following standard procedures, the chemical analysis (wt. %) of F bentonite is: SiO₂, 52.22; Al₂O₃, 16.81; Fe₂O₃, 3.84; Na₂O, 1.26; MgO, 0.88; CaO, 0.74; K₂O, 0.80; and the composition of P bentonite is: SiO₂, 62.76; Al₂O₃, 12.13; Fe₂O₃, 3.04; Na₂O, 2.13; MgO, 2.04; CaO, 1.79; K₂O, 0.54. The cation-exchange capacities (CEC) of the F and P bentonites were 97 and 92 meq/100 g of clay,

respectively. The CEC was determined by dispersing and then saturating with K⁺ ions using 1 N KCl. The exchanged amount of K⁺ was determined by atomic absorption.

Synthesis of Al-pillared clays

Al-pillared clays were synthesized by intercalating sodium clays with hydroxy-aluminum oligomeric cations. The pillaring solution was prepared (Shen, 1990) by the slow addition of a 0.2 M NaOH solution to a 0.1 M AlCl₃ solution under constant stirring until the desired OH/Al ratio was reached.

A suspension of 1 wt. % bentonite in deionized water was mixed with this oligomeric solution. Pillaring stoichiometries of 5 and 9 mmol Al/g clay were used. The mixture was allowed to react at room temperature for 12 h before washing by centrifugation with deionized water until chloride free (conductivity lower than 10 μS). Following air-drying, the resulting product was calcined for 2 h at temperatures ranging from 473 to 1073 K.

Modification with Ce and La

The Ce and La-containing solutions were prepared by the slow addition of 0.05 M Ce(NO₃)₃ or La(NO₃)₃ aqueous solutions to the pillaring solution as described above. The resulting solutions had Re³⁺/Al ratios (Re = Ce or La) of 1.8, 1.0, 0.55, and 0.11 for Ce and 1.8 and 1 for La. A suspension of 1 wt. % bentonite in deionized water was mixed with these solutions. Pillaring stoichiometries of 9 and 5 mmol of Al/g clay were used. The mixed solutions were aged at room temperature for 16 h. The mixture was allowed to react at room temperature for 12 h before washing by centrifugation with deionized water until chloride free. Following air-drying, the resulting product was calcined for 2 h at temperatures ranging from 473 to 1073 K.

Pillared clays with different Re³⁺/Al ratios are referred to as follows: bentonite F or P, Al, Al/clay ratio (mmol/g), Ce or La, Re(III)/clay ratio (mmol/g). For example, FAL9-CE5 corresponds to a sample of F bentonite pillared with 9 mmol of Al and 5 mmol of Ce per 1 g of clay.

Characterization methods

X-ray diffraction (XRD) patterns were obtained with a Philips model PW 1710 diffractometer using Ni-filtered CuKα radiation. To maximize the (001)-reflection intensity, oriented clay-aggregate specimens were prepared by drying clay suspensions on glass slides.

Surface-area and pore-size distributions were determined by using nitrogen as the sorbate at 77 K in a static volumetric apparatus by using a Micromeritics ASAP 2010 sorptometer (Gregg and Sing, 1991). For this analysis, pillared clays were outgassed at 453 K

Table 1. Thermal stability of pillared clays as indicated by $d(001)$ values (Å).

Sample	298 K	473 K	573 K	673 K	773 K	873 K	973 K	1073 K
F BENT.	13.39	9.95	9.84	9.66	9.66	9.47	9.65	9.69
P BENT.	12.13	10.33	10.63	9.81	9.71	9.74	9.62	9.74
FAL5	19.00	18.34	18.34	18.00	17.99	n.d.p.	n.d.p.	n.d.p.
PAL5	18.84	18.18	18.18	17.67	15.68	n.d.p.	n.d.p.	n.d.p.
FAL9	19.00	18.08	18.33	17.67	17.36	n.d.p.	n.d.p.	n.d.p.
PAL9	19.06	17.96	16.90	17.05	16.07	n.d.p.	n.d.p.	n.d.p.
FAL9-LA5	18.99	17.66	18.20	17.48	17.48	17.49	17.66	17.14
FAL5-LA5	20.25	18.90	18.69	18.17	16.67	16.62	n.d.p.	n.d.p.
PAL5-LA5	19.44	16.50	16.20	15.91	15.49	16.20	n.d.p.	n.d.p.
FAL9-CE1	19.04	17.36	18.18	17.67	17.36	17.48	17.30	17.14
PAL9-CE1	19.06	17.67	17.67	17.36	16.62	17.30	n.d.p.	n.d.p.
FAL9-CE5	19.84	17.14	18.02	17.48	17.48	17.43	17.30	17.31
FAL5-CE5	18.99	18.67	18.39	18.02	17.52	17.01	17.30	17.43
PAL5-CE5	19.25	18.39	18.20	17.48	15.91	17.40	n.d.p.	n.d.p.
FAL5-CE9	19.19	18.20	18.39	18.02	17.20	17.66	17.82	17.48
PAL5-CE9	18.78	17.36	16.50	15.77	16.34	n.d.p.	n.d.p.	n.d.p.

n.d.p.: no diffraction peaks obtained in the pattern.

for 16 h under a vacuum of 5×10^{-6} Torr. Specific total surface areas were calculated by using the Brunauer, Emmett, and Teller (BET) equation (Gregg and Sing, 1991) and specific total pore volumes were determined from nitrogen uptake at a relative pressure of N_2 (P/P_0 , pressure/saturation pressure) = 0.99. The Horvath-Kawazoe method (Horvath and Kawazoe, 1983) was used to determine microporous surface area and volume. The Barret, Johner and Halenda (BJH) method (Barret *et al.*, 1951) was used to determine the distribution of mesopores. This method uses the N_2 desorption branch of the isotherm and relates the amount of adsorbate desorbed to the average size of pores affected by this desorption. After evaporation of the condensed liquid adsorbate (core), a layer is calculated from the thickness equation. The thickness of this layer decreases with each successive decrease in pressure. The measured quantity of gas desorbed in a step is composed of a quantity equivalent to the liquid core evaporated in that step plus the quantity absorbed from the walls of pores whose cores were evaporated in that and previous steps.

Thermogravimetric analyses (TGA) were performed on 10-mg samples with a Perkin Elmer TGA 7 thermogravimetric analyzer under an helium flow of 50 mL/min using a heating rate of 10 K min^{-1} from 273 to 1173 K. Total acid-site density of the samples was measured by temperature programmed desorption (TPD) of ammonia by using a Micromeritics TPD/TPR analyzer. Samples were housed in a quartz tubular reactor and pre-treated in flowing helium (99.999%) while heating at 15 K min^{-1} to 773 K. After 30 min at 773 K, the samples were cooled to 453 K and saturated for 15 min in an ammonia or methane (99.999%) stream. The sample was then allowed to equilibrate in a helium flow at 453 K for 1 h. Finally, ammonia was desorbed by using a linear heating rate of 15 K min^{-1} to 773 K. Temperature and detector

signals were simultaneously recorded. The unique area under the curve was integrated to determine the total acidity on the catalyst. The average relative error in the acidity determination was <3%. Infrared (IR) spectra were recorded between $4000\text{--}400 \text{ cm}^{-1}$ with a Perkin Elmer 16 PC-based spectrometer. The samples were crushed, mixed with KBr powder and pressed into wafers. A typical wafer concentration was 3 mg of pillared clay in 300 mg KBr. Hydrothermal-stability tests of different samples were performed in a fixed-bed reactor at atmospheric pressure. Each sample (0.2 g) was pretreated in the reactor under a 100 mL/min nitrogen flow from ambient temperature to 573 K and held at 573 K for ~1 h. Next, water vapor with a flow rate of 0.5 mL min^{-1} was added to the nitrogen flow. To avoid condensation of water, the line containing water-vapor was heated to a temperature higher than the saturation temperature. Samples were subjected to water vapor treatment for either 1 or 5 h. After water-vapor treatment, each sample was heated in the reactor with a nitrogen flow for 1 h. Then, the samples were dried at 373 K for 16 h and subsequently calcined at 473 K for 2 h.

RESULTS AND DISCUSSION

X-ray diffraction

Table 1 gives $d(001)$ values of the pillared clays prepared after calcination at different temperatures. Basal spacings of untreated clays calcined at the same temperatures are given also for comparison. Note that the basal spacing decreases when the calcination temperature is increased owing to dehydroxylation of the pillars. The introduction of Ce or La produced an increase in the thermal stability. In general, although the basal spacings of both untreated clays were nearly equal after calcination at 473 K (9.95 Å: F bentonite and 10.33 Å: P bentonite), the basal spacings of pil-

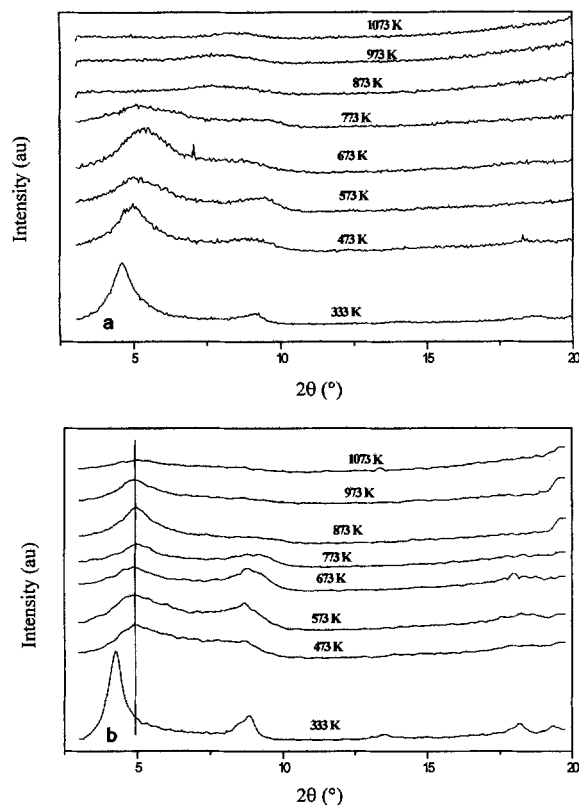


Figure 1. X-ray diffraction patterns of a) FAL9-CE1 and b) PAL9-CE1 samples calcined at different temperatures between 333–1073 K.

lared clays prepared from the F bentonite were greater than those of clays prepared from P bentonite. This result indicates that pillared clays of the F bentonite are thermally more stable than those prepared from P bentonite (Cañizares *et al.*, 1999). For the most stable pillared clays prepared from F bentonite, note that an

increase in temperature in the range 773–1073 K caused only a small decrease in $d(001)$.

For Al-pillared clays, the interlayer space is $\sim 9.4 \text{ \AA}$ at 298 K, which corresponds to the size of the Keggin cation. The other pillared clays showed, independently of the Re/Al ratio used, different basal spacings between 9–10 \AA .

Figure 1 shows the oriented clay-aggregate powder XRD patterns of FAL9-CE1 and PAL9-CE1 samples after heating between 333–1073 K for 2 h. The peak at $2\theta \approx 9^\circ$ suggests that a portion of the material was not pillared. In Al-pillared clays modified with Ce and La, increases in the calcination temperature caused the $d(001)$ peak to become broader and less intense, which made accurate measurement difficult and therefore, the $d(002)$ was used. After low-temperature calcination, the $d(001)$ peaks were sharp, indicating a relatively homogeneous pillaring process. After calcination at high temperatures, the products showed a gradual decrease in the $d(001)$ values. For pillared clays derived from P bentonite the $d(001)$ peak was not observed at $>873 \text{ K}$, indicating the collapse of the pillars and the near total destruction of the structure (Cañizares *et al.*, 1999).

BET analysis and pore-size distribution

The pillaring process increases the surface area to $230\text{--}350 \text{ m}^2\text{g}^{-1}$ relative to the untreated clay (Table 2). Micropores in the products represented $>50\%$ of the total surface area. The pillared clays showed a higher surface area than the untreated clays. In most cases the pillared clays prepared from F bentonite yielded higher surface areas than pillared clays prepared from P bentonite. This result may be attributed to the greater CEC of the F bentonite. The effect of the calcination temperature on the surface area of the most stable pillared clays is given in Table 3. Surface area decreased with calcination temperature, especially at 1073 K. Ce or

Table 2. Surface area, pore volume, and total acidity values of some pillared clays measured by ammonia TPD. Calcination conditions: 473 K for 2 h.

Sample	Surface area (m^2/g)	External area $P/P_0 = 0.99$ (m^2/g)	Pore volume (cm^3/g)	Micropore volume (cm^3/g)	mmol NH_4/g clay
F BENT.	34.7	24.1 (69.4) ¹	0.0878	0.0053 (6.0) ²	0.1224
P BENT.	62.7	47.0 (74.9)	0.1744	0.0084 (4.8)	0.1181
FAL5	319.4	61.1 (19.1)	0.1800	0.1010 (56.1)	0.3442
PAL5	239.1	58.1 (24.3)	0.2106	0.0722 (34.3)	0.3680
FAL9	289.9	55.4 (19.1)	0.1654	0.0919 (55.6)	0.4256
PAL9	239.1	58.9 (24.6)	0.2130	0.0718 (33.7)	0.3095
FAL9-LA5	353.2	62.1 (17.6)	0.1964	0.1136 (57.8)	0.4058
FAL5-LA5	306.8	55.1 (18.0)	0.1777	0.0987 (55.5)	0.3482
FAL9-CE1	262.4	49.8 (19.0)	0.1719	0.0949 (55.2)	0.3776
FAL9-CE5	305.5	53.4 (17.5)	0.1810	0.0985 (54.4)	0.4340
FAL5-CE5	318.8	54.7 (17.2)	0.1749	0.1031 (59.0)	0.4634
FAL5-CE9	346.7	59.7 (17.2)	0.2005	0.1119 (55.8)	0.3749

¹ The numbers in parentheses are the percentages of total surface area contributed by the external surfaces.

² The numbers in parentheses are the percentages of total pore volume contributed by the micropores.

Table 3. Effect of calcination temperature on the surface area (m^2/g) of some pillared clays.

Sample	473 K	573 K	773 K	873 K	1073 K
FAL9-LA5	353.2	284.5 (80.5) ¹	273.2 (77.3)	252.8 (71.6)	126.0 (35.7)
FAL9-CE5	305.5	304.8 (99.8)	267.2 (87.5)	240.6 (78.8)	188.8 (61.8)
FAL5-CE5	318.8	305.9 (96.0)	295.6 (92.7)	248.4 (77.9)	76.6 (24.0)
FAL5-CE9	346.7	299.3 (86.3)	274.3 (79.1)	221.4 (63.9)	146.1 (42.1)

¹ Figures in parentheses are percentages of surface area measured at 473 K.

La increases the thermal stability of a pillared clay, and Ce in general produces a pillared clay that is more stable than a pillared clay with La.

Figure 2 shows nitrogen adsorption isotherms for the untreated and pillared clays with Ce (Figure 2a) and La (Figure 2b). The isotherms correspond to Type II (Gregg and Sing, 1991) in the classification of Brunauer, Deming, Deming, and Teller (BDDT). The hysteresis loops correspond to Type H3 in the International Union of Pure and Applied Chemists (IUPAC) classification. Among materials with this type of hysteresis are those with slit-shaped pores and particle aggregates of plates with spaces between parallel plates (Monkaya and Jones, 1995). This result is consistent with the expected structure of a pillared phyllosilicate. The microporosity consists mainly of pores

of $<20 \text{ \AA}$ in diameter, which is consistent with the XRD data. At $P/P_0 < 0.4$, where monolayer formation of N_2 is produced, the adsorption isotherm curves of the pillared and the untreated clays are parallel.

To analyze the microporosity of the pillared clays, nitrogen adsorption over a pressure range is given by Dubinin-Radushkevich plots [$\log V$ versus $\log^2(P_0/P)$] for F bentonite and the derived pillared clays (Figure 3). The untreated F bentonite (Figure 3) showed a near unimodal distribution of micropore sizes. In contrast, the pillared clays show two linear portions that suggest a bimodal distribution of micropore sizes. However, the deviation from linearity at low pressures may be related to restricted diffusion of nitrogen into very narrow micropores at very low adsorption temperatures (Rodríguez-Reinoso *et al.*, 1989). Deviations from linearity at high pressures may be related also to the presence of larger micropores (Masters and McEnaney, 1983).

A bimodal distribution occurs in Figure 4 where the micropore-size distributions of the pillared clays were calculated using the slit-like model of Horvath-Kawazoe (Horvath and Kawazoe, 1983). The micropore distributions for F bentonite and derived Al-containing pillared clays are shown before and after modification with Ce (Figure 4a) and La (Figure 4b). This model was calculated using a parallel-plate distribution and requires the evaluation of constants as determined

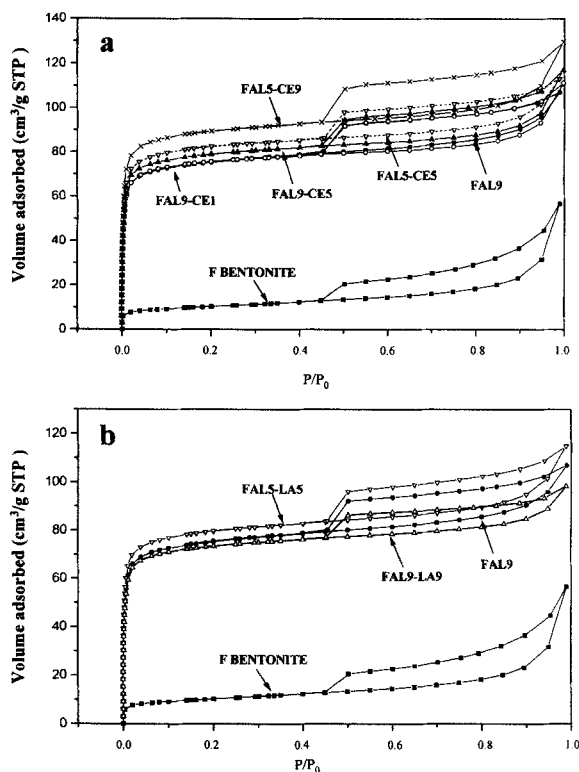


Figure 2. Comparison between nitrogen-adsorption isotherms of different Al-pillared clays modified with a) Ce and b) La. STP = standard temperature and pressure.

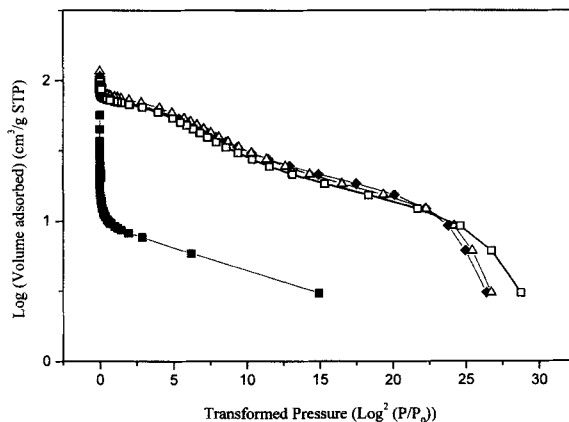


Figure 3. Dubinin-Radushkevich plots. F bentonite (■); FAL9 (◆); FAL9-CE5 (△); FAL9-LA5 (□).

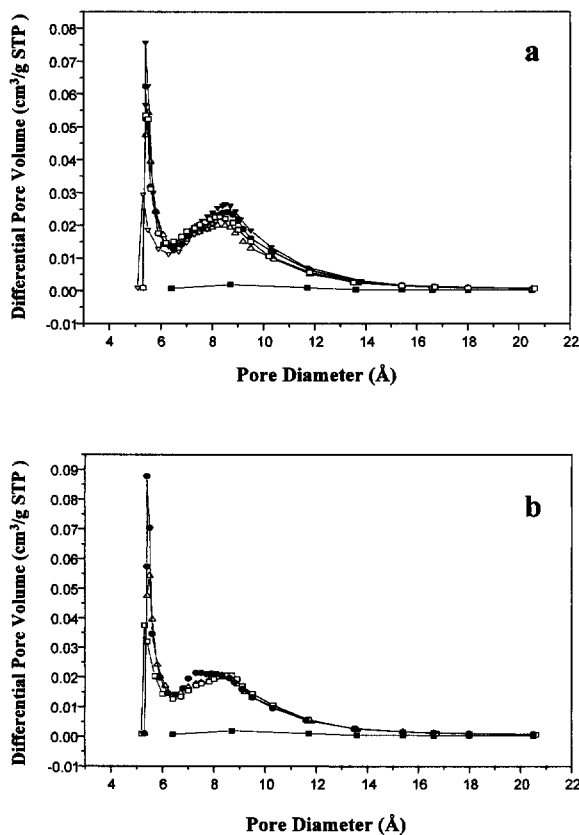


Figure 4. Micropore size distribution for different Al-pillared clays modified with Ce and La. a) F bentonite (■); FAL9 (Δ); FAL9-CE1 (▽); FAL5-CE5 (●); FAL5-CE9 (▼); FAL9-CE5 (□). b) F bentonite (■); FAL9 (Δ); FAL9-LA5 (□); FAL5-LA5 (●).

from physicochemical data of the gas/solid system. Each pillared clay has a pore diameter maximum at ~ 5.5 Å and a secondary maximum at ~ 8.5 Å. Similar trends were reported by Cañizares *et al.* (1999) for pillared clays containing single and mixed-oxide pillars. According to Gil and Montes (1994), the maximum at 5.5 Å is associated with basal spacings.

The accuracy of the calculated interaction parameter and the accessibility of the micropores are important in the determination of the average value of the micropore distribution. To a first approximation, the micropore distribution average is an accessibility fraction. The interlayer spacings obtained by XRD contain only one-dimensional information.

Pore-size distributions were measured for F bentonite and pillared clays modified with Ce or La. In the untreated clay, a pore distribution contains mostly pores of 20 and 30 Å in size. Remaining pores (mesopores) have diameters of >200 Å. In contrast, pillared clays with pores mostly of >20 Å in diameter and fewer pores of ~ 200 Å in diameter were observed.

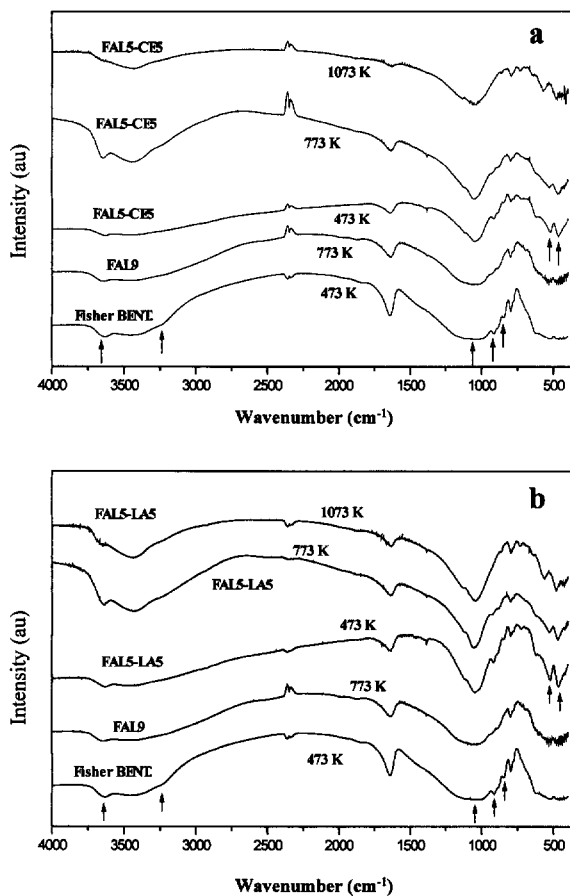


Figure 5. IR spectra for F bentonite and Al-pillared clays modified with a) Ce and b) La.

Infrared studies

The effect of heating temperature on the untreated clay and derived pillared clays was characterized using IR spectroscopy. All spectra were taken in the transmission mode and were recorded between 4000–400 cm^{-1} . The IR spectra of the FAL5-CE5 and FAL5-LA5 samples calcined at 473, 773, and 800 K were measured at room temperature (Figure 5). The spectra of the F bentonite calcined at 473 K and the derived Al-pillared clay calcined at 773 K are shown also. Several IR bands were affected by the pillaring process: the shoulder at about 3200 cm^{-1} decreased in intensity as did the Si-O band at 1047 cm^{-1} and two bands increased in intensity at 528 and 462 cm^{-1} . The latter bands are related to different Si-O and Si-O-Al vibrations (Stubican and Roy, 1961) probably owing to the formation of Si-O-Al bonds by reaction of hydroxy aluminum ions (Lou and Huang, 1988).

The calcination at 773 K of pillared clays modified with either Ce or La caused the following changes in the IR spectra. There was an intensity reduction of the main peaks, especially in the stretching mode of the

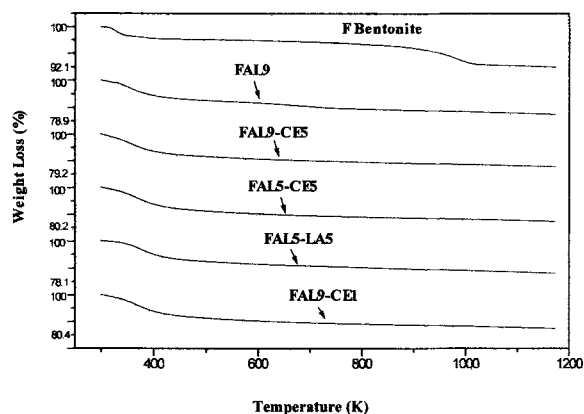


Figure 6. TGA curves for F bentonite and Al-pillared clays modified with Ce and La.

hydroxyl groups at 3627 cm^{-1} . This is attributed to the condensation of terminal hydroxyl groups from the polymeric ions in the pillars with the structural hydroxyl groups in the 2:1 layers (Tichit *et al.*, 1988). Also, there was an intensity reduction of Al-OH-Al and Al-OH-Mg vibrational modes at 910 and 842 cm^{-1} , respectively, accompanied by a broadening of the band centered at 1047 cm^{-1} , which is similar to ion-exchanged clays (Tennakoon *et al.*, 1986). However, when pillared clays modified with Ce or La were calcined at 1073 K , no peaks at 910 , 842 , 523 , and 462 cm^{-1} were present. The resulting materials behaved similarly to the Al-pillared clay that was calcined at 773 K .

Characterization of pillared clays modified with Ce or La did not show any apparent structural changes relative to the Al-pillared clay samples. The Ce and La cations are not part of the pillars. These cations delay dehydroxylation of these samples, probably by blocking the hexagonal cavities of the tetrahedral sheets or by strengthening the interaction of the Al pillars with the structure. According to Hernando *et al.* (1996), Ce and La may be in a form different from an exchangeable cation, such as simple or oligomeric cations. This conclusion is based on the lack of catalytic activity of either the Ce homoionic sample or Na-rich montmorillonite, whereas the pillared clay modified with Ce shows catalytic capabilities.

Thermogravimetric analysis and ammonia temperature programmed desorption

Thermogravimetric (TG) curves for F bentonite and associated pillared clays are shown in Figure 6. For both F and P bentonites, weight loss occurred in two steps. Weight loss of $\sim 2.3\text{ wt. \%}$ initially occurred from 298 to 423 K probably owing to H_2O physically adsorbed on clay surfaces. Between 423 – 773 K , the weight remained nearly constant with a loss in weight of 0.92 wt. \% . An additional 4 wt. \% was lost between 773 – 1173 K probably owing to the partial dehydroxylation of the 2:1 layer. An inflection point occurred between 973 – 1073 K for both untreated clays owing to rapid dehydroxylation of the clay structure. Pillared clays, however, showed a more continuous loss of weight, which monotonically decreased with temperature. About 50% of the water was surface adsorbed and was lost at temperatures below 423 K . Loss of water associated with the micropores of the pillared clays (dehydroxylation of hydroxide groups associated with interlayer pillars) occurred above 423 K . At 773 K , weight loss is attributed to dehydroxylation of the 2:1 layer and loss of any remaining hydroxyls from the pillars. Between 773 – 1173 K , additional loss in weight (3 – 4.5 wt. \%) is observed with a very little weight loss above 973 K .

TG curves showed that modified pillared clays lose more weight than the corresponding unpillared clay. The unpillared clays lost little weight ($\sim 1\text{ wt. \%}$) between 423 – 873 K and some loss in weight ($\sim 4\text{ wt. \%}$) occurs at 973 K , whereas pillared clays showed a steady weight loss (7 – 9 wt. \%) between 423 – 1173 K .

Ammonia TPD results are shown in Table 2. For most samples, the desorption temperature maximum was near 573 K . Total acidity of untreated material increased three-fold or more owing to the pillaring process. Acidity of pillared clays was previously related to the hydroxylation used (Cañizares *et al.*, 1999). According to Ocelli and Tindwa (1983), this acidity is primarily caused by Lewis sites on the pillars and by Brønsted sites in the 2:1 layer in the clay. Pillared clays modified with Ce or La have similar acidity values regardless of the Ce or La/Al ratio used. On the basis of the IR data, Ce or La is incorporated into

Table 4. Effect of hydrothermal treatment on basal spacing and surface area.

Sample	$d(001)$ (Å)			Surface area (m^2/g)		
	0 h	1 h	5 h	0 h	1 h	5 h
FAL9	18.08	17.26	16.67	289.9	219.1 (75.6) ¹	155.8 (53.7)
FAL9-LA5	17.66	17.41	17.31	353.2	206.5 (58.5)	164.0 (46.4)
FAL9-CE5	18.67	17.45	17.31	318.8	290.9 (91.2)	257.4 (80.7)
FAL5-CE5	18.20	16.98	17.14	346.7	285.6 (82.4)	241.9 (69.8)
FAL5-CE9	17.14	17.01	16.66	305.5	224.9 (73.6)	193.6 (63.4)

¹ Figures in parentheses are percentages of surface area measured at 0 h.

the pillared clays so as not to produce a structural change.

Hydrothermal analysis

The results compiled in Table 4 allow comparison to BET surface area and $d(001)$ values for each sample. Note that with hydrothermal treatment, the basal spacings for each sample decrease slightly. Although the collapse of the pillars was not observed, the XRD peaks for samples heated under humid conditions were broader than untreated samples. In contrast, the N_2 -adsorption data reflect a greater decrease in the surface area of the samples.

As observed, the reduction of BET area in the unmodified samples and in that modified with La (53.7 and 46.4% for 5 h of hydrothermal treatment) was greater than that in pillared clays modified with Ce. This result is similar to that previously obtained in the thermal stability study above. The presence of Ce associated with the pillars is more effective than La in delaying dehydroxylation of pillared clays. Likewise, the hydrothermal stability is increased by increasing the Al/Ce ratio.

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