Synthesis, Characterization, and Catalytic Properties of Pillared Montmorillonite with Aluminum/Cerium Polyoxycations

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This paper describes the preparation of pillared montmorillonite by means of mixed aluminum and cerium oligomers. When cerium was incorporated into the materials, the basal spacing increased up to 26 Å. Nuclear magnetic resonance studies indicated total absence of tetrahedral aluminum in the polyoxycations incorporated between the clay sheets. These results indicate that AlCe-pillared montmorillonite incorporates inorganic polyoxycations with a chemical nature different from that of the aluminum polyoxycation or Keggin ion $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$. The texture of the materials showed a high specific surface area and porosity, with generation of pores at the limit between the microporous and mesoporous zones. The number and strength of the acid sites in these materials were also high. The catalytic behavior of the materials in the hydrocracking and hydroisomerization reaction of *n*-heptane was compared with that of materials obtained from the same montmorillonite and intercalation of the Keggin ion. The AlCe-pillared samples showed increased conversion and improved the selectivity toward the products of cracking.

Introduction

Pillared clays in general and pillared montmorillonite in particular are clay minerals that have been modified by introducing large polyoxycations into their interlayer regions. The separation between layers can be kept stable and depends on the polyoxycation used. Heating these materials results in the formation of inorganic oxide clusters that prop open the clay layers permanently, thus generating a microporous structure with a high specific surface area. The inorganic polyoxycations most frequently used as pillaring agents are species of aluminum, zirconium, titanium, chromium, and iron.[1−5]

Since the introduction of pillared clays in the late seventies,[6] much research has been done to develop materials suitable as active components in catalysis and for other applications.[7] Pillared clays are versatile materials because the size and shape of their cavities can be varied over wide ranges and the constitution and chemical properties of the pillars can be altered. Pillared montmorillonites have been proposed as potential materials for cracking catalysts of heavy oil fractions[7] as they can be prepared with pore sizes larger than those of zeolites. The presence of acid centers on the surface of their layers as well as on their pillars makes these materials suitable also for use in other reactions of acid catalysis.[8]

To prevent the clay layers from sintering at the high temperature of the catalytic reactions, the stability of the pillars must be increased. One way to achieve this is to introduce mixed pillars into the materials.[9−12] Sterte[13] and McCauley[14] found that the incorporation of lanthanide elements in the preparation of the pillaring agent resulted in material whose basal spacing was larger than that in conventional materials.

The aim of the present study was to prepare and characterize montmorillonite pillared with aluminum and cerium under different synthesis conditions. The textural and structural parameters of the materials were compared with those of montmorillonite pillared only with aluminum. The chemical reactivity of the materials generated was evaluated and compared by means of their catalytic activity as metal−acid bifunctional catalysts in the hydrocracking−hydroisomerization reaction of *n*-alkanes (*n*-heptane).

Experimental Section

Starting Materials. The clay used as the raw material was a montmorillonite from Wyoming, supplied by Missouri Uni-

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Table 1. Amount of Cations Incorporated into the Pillaring Clay and Basal Spacing

samples	Al^{3+} incorp. (mequiv/g)	Ce^{3+} incorp. (mequiv/g)	$d(001)$, 25 °C (Å)	$d(001)$, 400 °C (Å)
AlCe-Wy-25	15.6	0.3	27.2	24.7
AlCe-Wy-50	12.0	0.1	26.1	24.5
AlCe-Wy-75	7.1	0.0	20.3	17.9
Al-Wy	6.8		20.0	18.8

versity (reference Wy-1) and denominated here as Wy. It was purified by fractional sedimentation, with the fraction <2 μm being collected. Its specific surface area is 33 m^2/g and its pore volume 0.042 cm^3/g at $P/P_0 = 0.98$. Its exchange capacity is 106 mequiv/100 g of clay.

Synthesis. *Preparation of the Pillaring Agent.* The solutions of the pillaring agent with different Al/Ce ratios (Table 1) were prepared by adding suitable amounts of $CeCl_3 \cdot 7H_2O$ to 2.5 M Al solutions obtained from Locron $[Al_2(OH)_5Cl \cdot 2-3H_2O]$. These solutions were heated in a reactor autoclave for 72 h at 130 °C. The reactor reaches pressures of 3 bar. After the conditions returned to room temperature and atmospheric pressure, the reaction mixture was diluted with the quantity of water necessary to yield an Al concentration of 0.1 M. The pillaring agent with aluminum, the Keggin ion, $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, was obtained from a 0.1 M Al solution from Locron at room temperature. These different conditions of the synthesis for each pillaring agent were the optimum after several essays in the laboratory.

Pillaring Process. The solutions of pillaring agent were added with vigorous stirring to a clay slurry of 2.5 g/100 mL. The final proportion in all cases was 20 mequiv of Al/g of clay, with a solid/liquid ratio of 0.5%. The reaction mixture was stirred continuously for 24 h at room temperature. It was then washed by means of dialysis with distilled water, using 1 L of water/g of clay. Dialysis was continued with water being renewed every 24 h until the Cl^- ion concentrations decreased to the point where the conductivity of the water was <30 μS. Finally, the samples were freeze-dried. The materials obtained are denominated AlCe-Wy-25, AlCe-Wy-50, and AlCe-Wy-75 according to the proportion of cations used in the pillaring agent. The sample denominated Al-Wy was obtained in the same conditions from a pillaring agent prepared with solutions containing only aluminum. Samples were then calcined for 2 h at 400 °C to obtain the pillars.

Equipment and Methods. The following equipment and techniques were used for the physicochemical characterization of the materials.

X-ray Diffraction. The X-ray diffraction diagrams were obtained on powder with the particles oriented so as to increase the intensity of the (001) reflection. The apparatus used was a Philips PW-1700 diffractometer with Cu Kα radiation.

MAS NMR Spectra. Magic-angle spinning nuclear magnetic resonance (MAS NMR) measurements were recorded on a Bruker AMX 300 spectrometer equipped with a multinuclear probe. Powder samples were packed in zirconia rotors. ^{29}Si spectra were obtained at 59.60 MHz, with a pulse width of 4 μS, a spinning rate of 4.0 kHz, and a spectral width of 20 kHz. Chemical shifts are reported in ppm from tetramethylsilane. ^{27}Al spectra were obtained at 78.23 MHz, with a pulse width of 4 μS, a spinning rate of 3.0 kHz, and a spectral width of 50 kHz. Chemical shifts are reported in ppm from 0.1 M $[Al(H_2O)_6]^{3+}$.

Textural Parameters. The adsorption isotherm of N_2 at 77 K was determined in a Micromeritics ASAP 2000 with a micropore system. The specific surface area was determined by applying the BET equation to the isotherm.[15] The total volume was considered to be the volume of liquid N_2 adsorbed at a relative pressure of 0.98. Microporosity was deduced by the t-plot method[16] using the Harkins and Jura[17] thickness. Mesoporous volume was analyzed by the BJH method[18] by diameter of pore size >20 Å.

Acidity Study. The surface acidity was measured by means of gas-phase adsorption of pyridine using a pulse-chromatographic technique.[19] The amount of adsorbed amine (μmol/g of sample) was determined at 200, 300, and 400 °C. Pulses of 2 μL of a solution of 1 M pyridine in cyclohexane were injected into a flow of 20 mL/min of N_2 until the sample was saturated. All the samples, weighing 10 mg, were previously calcined in the reactor at 400 °C for 2 h. The temperature was then adjusted to that at which the amine adsorption was to be carried out. The residual pyridine was analyzed by gas chromatography.

The FTIR spectra of chemisorbed pyridine were obtained on a Perkin-Elmer Model 1605 spectrophotometer in the 1700−1400-cm^{-1} range. The self-supported sample wafers were outgassed at 400 °C for 2 h prior to pyridine adsorption. After adsorption of pyridine at room temperature, the samples were outgassed at 200, 300, and 400 °C and their spectra were recorded. This method allows evaluation of the presence and ratio of Brönsted/Lewis acid centers and their evolution with temperature.

Catalytic Activity. The pillared clays obtained were impregnated with Pt and used in the hydroisomerization−hydrocracking of *n*-heptane. This process provides good evaluation of the number and strength of the acid sites. Two types of product can be obtained through this reaction: products of isomerization and products of cracking. In these bifunctional catalysts, the main role of the Pt is to dehydrogenate the alkane, which is then isomerized or cracked on the acid sites. The samples were impregnated with a 1% (w/w) ammoniacal complex of Pt. All samples were heated at 400 °C for 2 h under an air flow of 10 cm^3/min and then reduced in a flow of 10 cm^3/min of H_2 at 400 °C. The catalytic reactions were carried out in a continuous flow system at a pressure of 1.0 atm with a fixed bed of 200 mg of catalyst under a constant flow of 10 cm^3/min of H_2 saturated with *n*-heptane at 27 °C. The WHSV (weight hour space velocity) was 0.9 g of *n*-heptane. (g of catalyst·h)$^{-1}$. The reaction was performed under temperature-programmed conditions with a heating rate of 1 °C/min and the products were collected every 25 °C and were analyzed in a Varian 3000 gas chromatograph.

Results and Discussion

Table 1 shows the amount of aluminum and cerium cations incorporated (mequiv/g) into the pillaring products. For the AlCe-Wy-75 sample, the chemical analysis indicated an absence of cerium and the amount of aluminum incorporated was similar to that in the Al-Wy sample. However, in the other two samples, cerium was incorporated and the aluminum content was at least double that of the other materials.

X-ray Diffraction. Figure 1 shows the X-ray diffraction diagrams between 3° and 12° (2ϕ) of samples AlCe-Wy-25 and Al-Wy. The Al-pillared sample displays a $d(001)$ peak at 20.0 Å, associated with the basal spacing between the clay layers and characteristic of clays pillared with aluminum polyoxycations, the Keggin ion[12,20,21]. In contrast, sample AlCe-Wy-25, pillared with Al−Ce displayed peaks at 27.2 and 13.6 Å, which correspond to inorganic polyoxycations with sizes different from that of the Keggin ion. In the samples

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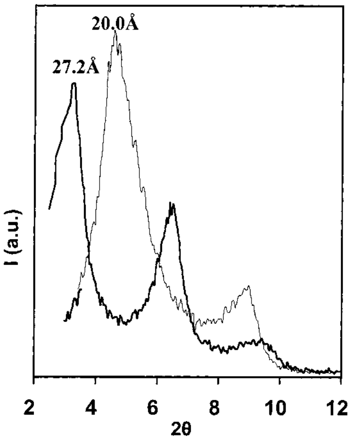

Figure 1. X-ray diffraction patterns of samples AlCe-Wy-25 and Al-Wy.

treated at 400 °C, the basal spacing was reduced to 24.7 Å for the AlCe-Wy-25 sample and 18.8 Å for the Al-Wy sample. The symmetry and intensity of the *d*(001) peaks confirm the existence of pillared materials at this temperature.

Table 1 gives the basal spacing data for all the samples. The samples incorporating only aluminum show similar values, whereas those incorporating aluminum and cerium have higher values, the difference being at least 5.7 Å. This would seem to indicate the presence of inorganic polyoxycations different from the Keggin ion between the clay layers when aluminum and cerium have been incorporated.

MAS NMR Spectra. *^{29}Si MAS NMR Spectra.* Figure 2 shows the ^{29}Si spectra obtained for samples AlCe-Wy-50 and Al-Wy, together with that of the original montmorillonite, Wy. All the spectra are very similar, showing a signal centered at 93.8 ppm. This signal is attributable to one ^{29}Si coordinated with three tetrahedral silica, Q^3(OAl), as reported in the literature[22,23] for the bidimensional framework of sheet silicates. The fact that this signal does not shift indicates that this bidimensional framework is maintained in the pillared materials. The signal at 107.9 ppm is attributable to one ^{29}Si coordinated with four silica, Q^4(OAl). It comes from the feldspar impurities already present in the initial montmorillonite sample, Wy.

^{27}Al MAS NMR Spectra. The ^{27}Al spectra of the samples studied are shown in Figure 3. All display a central line close to 0 ppm, assigned to Al^{VI} of the octahedral layer of sheet silicates.[22-23] The spectrum for montmorillonite (Wy) shows a very weak signal around 60 ppm, attributable to Al^{IV} due to the replacement of Si by Al in the tetrahedral layer or to impurities in the starting materials. Sample Al−Wy, with pillars ($AlAl_{12}$), clearly shows a signal of higher intensity at 60 ppm due to the presence of tetrahedral aluminum in the central position of the oligomer ($AlAl_{12}$), surrounded by 12 octahedral aluminum.[12] In contrast, in the AlCe-Wy-50 sample, this signal is not altered with respect to the initial montmorillonite. This may indicate the absence of tetrahedral aluminum in the intercalated inorganic polyoxycations between the clay sheets in this sample.

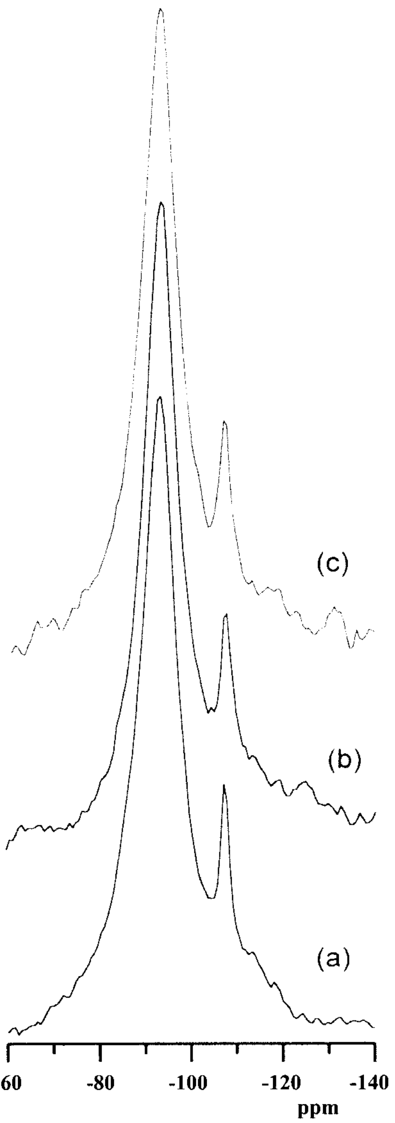

Figure 2. ^{29}Si MAS spectra: (a) Wy, (b) Al-Wy, and (c) AlCe-Wy-50.

Figure 4 shows the spectra of samples Al-Wy and AlCe-Wy-50 subjected to thermal treatment at 400 °C. The signal corresponding to the tetrahedral aluminum in sample Al-Wy is modified, deforming and shifting to a lower value, whereas this signal is not altered in sample AlCe-Wy-50. This result supports the absence of tetrahedral aluminum in the inorganic polyoxycations intercalated in sample AlCe-Wy-50.

Textural Analysis. Figure 5 shows the N_2 isotherms at 77 K for samples Al-Wy, AlCe-Wy-50 and the starting montmorillonite, Wy, after thermal treatment for stabilization at 400 °C. The isotherms are type IV, corresponding to mesoporous solids. All pillared samples in the zone of low values of P/P_0 (<0.1) present Langmuir adsorption isotherms (type I), which indicates the presence of micropores, generated in the pillaring process to intercalate inorganic polyoxycations between the clay layers. The AlCe-pillared samples showed a great increase in the volume of nitrogen adsorbed around $P/P_0 = 0.1$. This step in nitrogen adsorption, in a certain range of relative pressures, would be due to the pillars formed in the pillaring process, creating a greater interlayer space between the clay layers. Thus,

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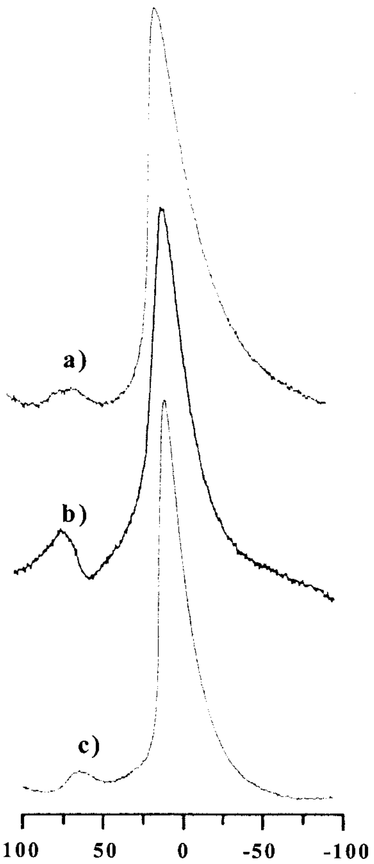

Figure 3. ^{27}Al MAS spectra: (a) Wy, (b) Al-Wy, and (c) AlCe-Wy-50.

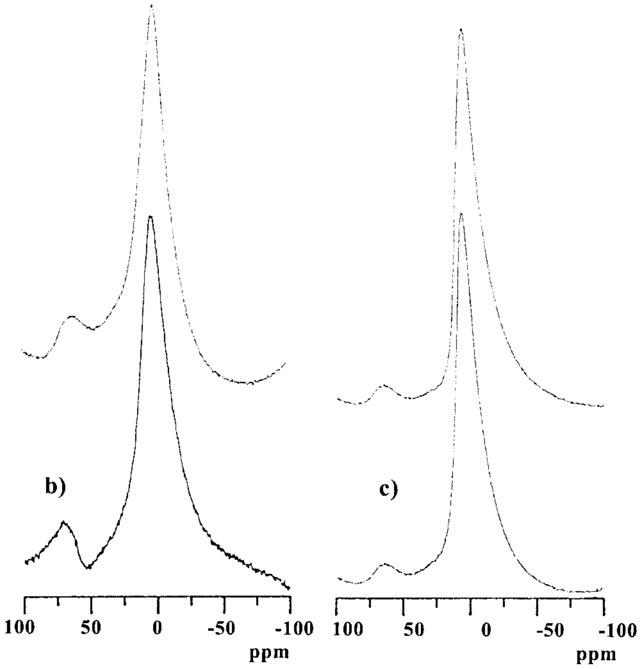

Figure 4. ^{27}Al MAS spectra at room temperature and 400 °C from bottom to top: (b) Al-Wy and (c) AlCe-Wy-50.

the existence of larger diameter pores produces nitrogen adsorption to high relative pressures. This adsorption is at the limit between microporous and mesoporous size, corresponding to a diameter of 20 Å in the classification of Dubinin.[24]

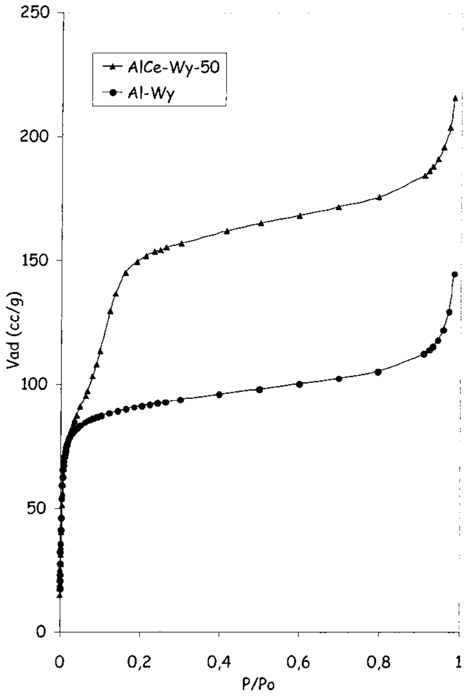

Figure 5. N_2 adsorption isotherms of the samples at 77 K: Al-Wy and AlCe-Wy-50.

Table 2. Textural Parameters of the Samples

samples	S_{BET} (m^2/g)	$V_{ad}(P/P_0=0.98)$ (cm^3/g)	V_{mp} (cm^3/g)	V_{msp} (cm^3/g)	D (Å)
AlCe-Wy-25	373	0.312	0.196	0.111	33.5
AlCe-Wy-50	411	0.337	0.223	0.109	32.8
AlCe-Wy-75	277	0.189	0.100	0.086	27.3
Al-Wy	346	0.226	0.131	0.090	26.1
Wy	33	0.042	0	0.040	50.9

Table 2 presents the values for specific surface area, S_{BET}, volume of N_2 adsorbed at $P/P_0 = 0.98$, V_{ad}, microporosity volume, V_{mp}, deduced from the t-plot, mesoporosity volume, V_{msp}, from the BJH method, and average pore diameter (D) of the different samples after thermal treatment at 400 °C.

An increase both in the adsorbed volume, V_{ad}, and in the micropore volume was observed in all the pillared samples in relation to the initial montmorillonite. This is a consequence of the creation of micropores between the clay sheets in the pillaring process. This increase is much greater in the pillared samples incorporating aluminum and cerium. However, the mesopore volume showed little variation in the two types of pillared materials, and the adsorption isotherms of sample Al-Wy and AlCe-Wy-50 are parallel from $P/P0 > 0.2$. This indicates that the nitrogen adsorbed from this point to $P/P_0 = 0.98$ was similar in both types of sample. In contrast, the specific surface area of the AlCe-pillared samples increased, but to a lesser degree than the micropore volume, which showed a 2-fold increase over the Al-pillared samples. As a result, the average pore diameter of the AlCe-pillared samples is larger. These textural parameters indicate the presence of larger pores between the clay sheets, originating in the pillaring process, and that this correlates with the increase in basal spacing.

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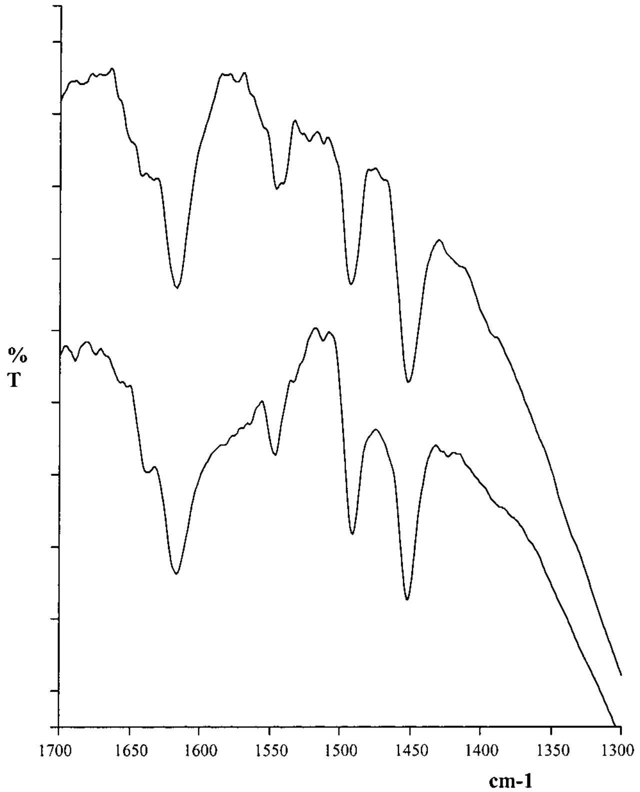

Figure 6. IR spectra of adsorbed pyridine: Al-Wy (bottom) and AlCe-Wy-50 (top).

Table 3. Surface Acid Properties of the Samples

samples	μmol of pyridine/g 200 °C	300 °C	400 °C
AlCe-Wy-25	391	261	129
AlCe-Wy-50	403	275	134
AlCe-Wy-75	349	230	89
Al-Wy	360	241	96
Wy	21	15	0

Acidity of Samples. The surface acidity in the starting montmorillonite and pillared clays is given in Table 3 as the amount of Py adsorbed up to saturation at different temperatures. Comparison of the acidity data for the pillared samples (Table 3) with the acidity values for the starting montmorillonite shows a remarkable increase in the acid sites generated in the samples by the pillaring process. These values indicate a larger number of total acid centers, as seen in the data of μmol/g of adsorbed Py. Table 3 also shows that the samples incorporating Al/Ce have greater acidity than those incorporating only aluminum. As the temperature increased, so the surface acidity gradually decreased, because only the strongest acid sites were able to retain the adsorbed Py. Nevertheless, at high temperatures, the samples incorporating Al/Ce retained more acid sites than did the Al-Wy sample. This increased acidity in the AlCe-pillared samples is associated with an increase in the number of the strongest acid centers.

Figure 6 presents the infrared spectra in the region 1700−1300 cm^{-1} of pyridine adsorbed on samples Al-Wy and AlCe-Wy-50. The samples treated at 200 °C after pyridine adsorption exhibit the bands at 1447 and 1615 cm^{-1}, which are assigned to Lewis centers and a band at 1490 cm^{-1}, attributed to both Lewis and Brönsted acid sites.[25] There are also small bands at 1547 and 1641 cm^{-1} due to Brönsted acid sites.

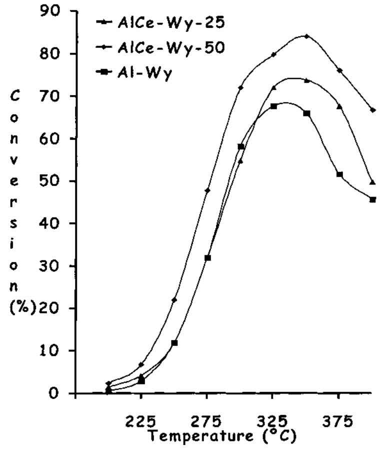

Figure 7. Total conversion of *n*-heptane vs reaction temperature.

Analysis of the spectra of the pyridine adsorbed on the surface of the samples with increasing pyridine desorption temperature (200, 300, and 400 °C) reveals that the ratio of Brönsted/Lewis (B/L) centers increased in the AlCe-pillared samples, as evaluated above with regard to the intensity of the appropriate bands.

From the study of the acidity of the samples, we can conclude that the AlCe-pillared samples not only present greater acidity than those samples pillared only with aluminum but also have a greater number of strong acid centers. These strong centers are linked to the Brönsted acid centers generated because the B/L ratio was greater in the pyridine spectra when the desorption temperature was increased.

Catalytic Activity. In Figure 7, the percentage of total conversion for samples AlCe-Wy-25, AlCe-Wy-50, and Al-Wy (data for sample AlCe-Wy-75 are not shown because they are similar to those for sample Al-Wy) is plotted as a function of the temperature in the reaction of hydroisomerization−hydrocracking of *n*-heptane. The AlCe-pillared samples present higher percentages for conversion of *n*-heptane than the sample incorporating aluminum. This is true over the whole temperature range for the AlCe-Wy-50 sample and from 300 °C for the AlCe-Wy-25 sample. This increase of the total conversion is related to the higher amount of acid sites in the AlCe-pillared samples (Table 3).

The greatest differences in the behavior of the catalytic activity are seen when the process is analyzed for selectivity between cracked and isomerized products. Figure 8 shows the percentage of cracking conversion for the samples in relation to reaction temperature. Table 4 gives the percentages for total conversion, cracking and isomerization, and the percentage of cracked selectivity between 300 and 400 °C. The fact that the conversion varies over a large range could not allow making a kinetic or thermodynamic study, but it is possible to compare the different chemical behaviors of the materials. The selectivity percentage toward cracking products is greatly increased in the AlCe-pillared samples. The cracked conversion percentage ranges from a maximum of 11.6% for sample Al-Wy to

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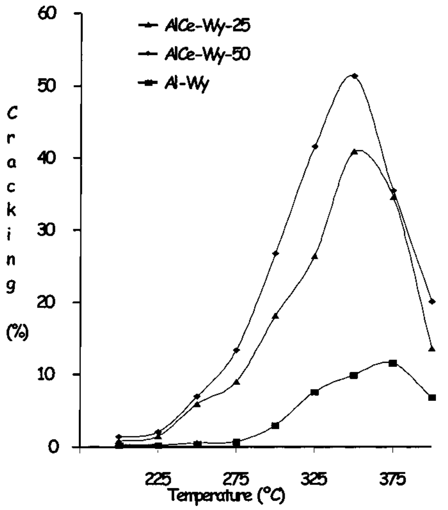

Figure 8. Cracking conversion of *n*-heptane vs reaction temperature.

Table 4. Conversion and Selectivity of the Samples

	temperature (°C)				
	300	325	350	375	400
	AlCe-Wy-25				
conversion	54.9[a]	72.0	73.7	67.6	49.7
isomerization	36.8[b]	45.6	32.8	32.9	36.1
cracking	18.1[c]	26.4	40.9	34.6	13.6
selectivity	33.0[d]	36.7	55.5	51.2	27.4
	AlCe-Wy-50				
conversion	71.9	79.8	84.0	76.0	66.7
isomerization	45.2	38.2	32.7	40.5	46.6
cracking	26.7	41.6	51.3	35.5	20.1
selectivity	37.1	52.1	61.1	46.7	30.1
	AlCe-Wy-75				
conversion	57.1	65.3	64.9	50.7	43.9
isomerization	52.3	56.2	54.3	40.3	37.8
cracking	4.8	9.1	10.6	10.4	6.1
selectivity	8.4	13.9	16.3	20.5	13.9
	Al-Wy				
conversion	58.2	67.6	65.9	51.6	45.6
isomerization	55.2	60.1	56.0	40.1	38.9
cracking	2.9	7.5	9.9	11.6	6.8
selectivity	5.0	11.2	15.0	22.5	14.9

[a] (mol %) Total conversion of *n*-heptane. [b] (mol %) Conversion to isomerization products. [c] (mol %) Conversion to cracking products. [d] (mol %) Selectivity toward cracking.

40.9% and 51.3% for AlCe-Wy-25 and AlCe-Wy-50, respectively. There is a significant shift of selectivity toward the cracked products over the whole range of temperatures. The largest difference (41.4%) occurs between sample Al-Wy and AlCe-Wy-50 at 350 °C.

The presence of Ce in the samples increased both *n*-heptane conversion and selectivity toward cracking. These results must be interpreted in light of two commonly accepted assumptions. First, hydroisomerization and hydrocracking of hydrocarbons takes place through the formation of carbocations as intermediate species, the number of these being formed corresponding to the number of acid centers and their strength. Second, hydroisomerization requires milder conditions of temperature and acid strength than hydrocracking.[26−27] In the AlCe-pillared samples, there is a larger number of acid centers and a higher B/L ratio with increasing temperature. This indicates a greater number and strength of Brönsted acid centers, which seems a plausible explanation of the greater selectivity toward cracking.

Conclusions

Montmorillonite pillared with aluminum and cerium incorporates between the clay layers inorganic polyoxycations with a chemical nature different from that of the aluminum polyoxycation denominated the Keggin ion. This was shown by the NMR studies that indicated total absence of tetrahedral aluminum in the polyoxycation incorporated between the sheets. XRD also showed an increase in the basal spacing up to 26 Å.

These materials exhibit modified textural characteristics. They show increased specific surface area and a modified porous structure, through generation of pores at the limit between microporosity and mesoporosity. The pores are larger than those generated in the Al-pillared material, which clearly displays microporous characteristics.

In addition, the AlCe-pillared materials present more acid centers, the centers active in reactions catalyzed by acids. This increase is greater in the number and strength of the Brönsted acid centers.

These changes are reflected in the improved reactivity of these materials in the hydroisomerization−hydrocracking reaction of *n*-heptane, with increased conversion and a greater selectivity toward the products of cracking.

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