

PREPARATION, STRUCTURAL CHARACTERISTICS AND CATALYTIC PROPERTIES OF LARGE-PORE RARE EARTH ELEMENT (Ce, La)/Al-PILLARED SMECTITES

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Abstract—Ce/Al- and La/Al-pillared smectites were prepared by cation exchange of bentonite, saponite and laponite with hydrothermally treated (130–160 °C for 16–136 h) solutions containing mixtures of aluminumchlorohydrate (ACH) and Ce³⁺- and La³⁺-salts. After calcination at 500 °C, the pillared products are characterized by basal spacings between 24.8 and 25.7 Å and surface areas of approximately 430 m² g⁻¹. The products are hydrothermally stable at 500 °C after 2 h in steam. The large basal spacings are due to the formation of a large Ce/La-bearing Al-polyoxocation, whose formation is favored by initially high Al concentrations $\geq 3.7 M$ and an OH/Al molar ratio of approximately 2.5. The Ce/Al or La/Al molar ratios can be as low as 1/30. ²⁷Al nuclear magnetic resonance (NMR) spectroscopy has shown that the polyoxocation has a higher Al^{tetrahedral}/Al^{octahedral} ratio than the Keggin structure Al₁₃, which may partly explain the higher stability compared to normal Al-pillared clays. Hydroconversion of n-heptane indicated that the activity of the Pt-loaded pillared products is higher than that of a conventional Pt-loaded amorphous silica-alumina catalyst. Selectivity is strongly dependent on the type of starting clay and its acidity. In industrial hydrocracking of normal feedstock, a Ni/W-loaded Ce/Al-pillared bentonite catalyst showed rapid deactivation due to coke-formation reducing the surface area and the pore volume. Additionally, coke-formation is facilitated by the relatively high iron content of the pillared bentonite (3.43 wt% Fe₂O₃).

Key Words—Al₁₃, Bentonite, Hydroconversion, Hydrocracking, Laponite, Montmorillonite, Pillared Clays, REE, Saponite.

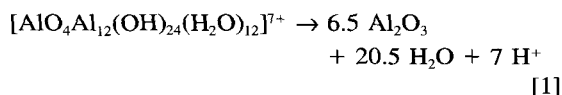
INTRODUCTION

Pillared clays are considered to be interesting 2-dimensional, shape selective, molecular sieves of a larger pore size range than zeolites. Barrer and MacLeod (1955) developed the idea of pillaring montmorillonite with organic compounds like N(CH₃)₄⁺ and N(C₂H₅)₄⁺. The catalytic potential of pillared clays was ignored for a long time, probably because of their limited thermal stability, although the molecular sieving properties of these materials were known. Starting in the late 1970s, the synthesis of relatively heat-stable, high-surface-area smectites pillared with inorganic polyoxocations, such as Al, Ti, Zr, Cr and Fe, was reported (Brindley and Sempels 1977; Lahav et al. 1978; Vaughan et al. 1979; Yamanaka and Brindley 1979).

The most widely used and extensively investigated polyoxocation for the preparation of pillared clays is the Keggin structure of the tridecameric Al₁₃ complex. This complex [AlO₄Al₁₂(OH)₂₄(H₂O)₁₂]⁷⁺ was firstly proposed by Johansson et al. (1960) based on structural information from X-ray diffraction (XRD) of basic aluminum sulfate. The presence of this complex in the basic aluminum sulfate was later supported by ²⁷Al magic angle spinning (MAS) NMR (Kunwar et al.

1984; Klopogge et al. 1992). Al₁₃ is formed by partial hydrolysis of Al(III) in a range of OH/Al molar ratios between 0.5 and 2.5 as shown by ²⁷Al NMR (Akitt et al. 1972; Bottero et al. 1980; Klopogge et al. 1992, 1993) and Small Angle X-ray Scattering (Rausch and Bale 1964; Bottero et al. 1982). Aluminumchlorohydrate or chlorhydrol (ACH) is a commercially available basic aluminum chloride solution prepared by the slow dissolution of Al metal in AlCl₃ or HCl solutions. These solutions, however, contain many polymeric species different from and mostly larger than Al₁₃ (Wang and Hsu 1994), which is thought to be due to the higher preparation temperature (Schönherr et al. 1983).

Recognition of the catalytic properties of Al-pillared clays started with the patent of Vaughan et al. (1979). The high cracking activity of these pillared clays is believed to be associated with the acidity introduced by the pillaring of the clay with the Al₁₃ polyoxocation and the following calcination. The calcination step causes dehydroxylation of the pillars, releasing protons according to the following overall reaction (Vaughan and Magee 1980):



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In these pillared clays, both Lewis and Brønsted acidity have been reported (Occelli and Tindwa 1983;

Schutz et al. 1987). At increasing temperatures, the Brönsted/Lewis acidity ratio decreased, and at temperatures above 400 °C, the acidity was mainly due to Lewis sites.

An improvement of the thermal stability of Al-pillared clays was reported by Tokarz and Shabtai (1985), who prepared pillared clay catalysts by first exchanging the clay with Ce^{3+} or La^{3+} , then exchanging these clays with refluxed, partly hydrolyzed Al(III) solutions. McCauley (1988) and Sterte (1991a, 1991b) found that hydrothermally stable (steaming, 815 °C) large-pore pillared smectites with basal spacings in the range between 25 and 28 Å could be prepared from refluxed or hydrothermally treated solutions containing mixtures of ACH and salts of rare earth elements (REE) such as Ce- or La-nitrate. These basal spacings are large compared to the values between 17 and 19 Å normally found for Al-pillared clays. Large-pore Ce/Al-pillared clays could be prepared from solutions having a Ce/Al molar ratio of approximately 1/88. At higher ratios, the formation of these large-pore pillared clays proved to be unsuccessful.

The larger basal spacing of the (Ce,La)/Al-pillared clays is thought to be due to the formation of a large REE containing Al polyoxocation upon hydrothermal treatment or refluxing of the pillaring solution. Although the interlayer spacing was twice that of a normal Al-pillared clay, chemical analyses of the pillared clays indicated the presence of smaller amounts of Al and Ce or La than expected from a mere polymerization of the original Al_3 polyoxocation. Several others (Mendioroz et al. 1993; Trillo et al. 1993; González et al. 1992) have pillared montmorillonite in the presence of RE elements, but did not succeed in the formation of the large pores in the pillared clays. Instead, they found values known for normal Al-pillared clays. This might be explained by the larger reflux period and differences in the RE/Al molar ratio. Although the basal spacing was comparable to Al-pillared clays, González et al. (1992) observed an increased conversion and selectivity for cracking. For use as a heavy oil cracking catalyst, the larger basal spacing and improved (hydro)thermal stability are advantageous over conventional Al-pillared clays. McCauley (1988) found that the Ce/Al-pillared clays provided catalysts with higher Light Cycle Oil (LCO) selectivity and cracking than Y-type zeolites. Furthermore, he found that mixtures of these pillared clays and zeolites were compatible systems, exhibiting desirable synergisms such as the production of less C_1 – C_4 and more gasoline than expected from the single compounds.

This paper reports the preparation of large-pore RE/Al-pillared smectites. Furthermore, it aims to characterize the structure of these large-pore REE/Al-pillared smectites and to establish their catalytic properties for n-heptane hydroconversion and heavy oil (feedstock) hydrocracking.

MATERIALS AND METHODS

Starting Clays

Two natural, commercially available bentonites were obtained from BDH Industries (BDH bentonite) and ECC Ltd. (ASB350s). Both bentonites consist mainly of montmorillonite with minor amounts of quartz, cristobalite and feldspars. BDH bentonite had a general composition of 58.39% SiO_2 , 18.90% Al_2O_3 , 3.86% Fe_2O_3 , 2.65% MgO , 0.11% CaO , 0.14% K_2O and 2.56% Na_2O , and ASB350s had 54.75% SiO_2 , 23.43% Al_2O_3 , 2.57% Fe_2O_3 , 2.65% MgO , 0.83% CaO , 0.71% K_2O and 1.89% Na_2O . Laponite, a synthetic fluorohectorite, was obtained from Laporte Industries Ltd. The saponites were synthesized and described by Klopogge et al. (1993), Klopogge, Breukelaar et al. (1994) and Vogels et al. (1997).

On the bentonite, adsorbed organic compounds were oxidized in a 30% H_2O_2 solution for 24 h. After separation, the clay was washed twice in demineralized water and the <2- μm fraction was obtained by the conventional centrifugation method. The clays were brought in the Na form by washing 4 times with 1 M NaCl solution. Excess Na^+ and Cl^- were removed by washing at least 4 times with demineralized water. The presence of Cl^- was checked by the $AgNO_3$ method after each washing. After all these steps, minor amounts of quartz and cristobalite were still present, as shown by XRD. The laponite and saponites, which contained no secondary minerals, were not pretreated, but suspensions were directly prepared by the dispersion of 5 g of clay in 0.5 L demineralized water. All clay slurries used in this study contained 1 wt% clay.

Pillaring Agents

The ACH solutions were obtained from Reheis Chemical Company (23.8% Al_2O_3 , OH/Al molar ratio 2.5). Stock solutions containing 0.1 M and 1.0 M $Ce(NO_3)_3$ and 1.0 M $La(NO_3)_3$ were prepared and the amounts necessary to prepare the pillaring solutions were taken from these stock solutions. The pillaring solutions were prepared by hydrothermal treatment of ACH solutions together with $Ce(NO_3)_3$ and $La(NO_3)_3$ solutions. The treatments were carried out in Teflon liners, which fit into stainless steel pressure vessels that were slowly rotated for periods between 5 and 136 h at temperatures in the range between 120 and 165 °C. All solutions were in the range between 0.9 and 6.2 M Al^{3+} and had (Ce, La)/Al molar ratios ranging from 4.1 to 50.

Preparation of the Pillared Clays

To assure complete saturation of the clays, excess amounts of the hydrothermally treated pillaring solutions were added rapidly to the clay suspensions. Molar ratios ranging from 15 to 30 meq Al/g clay were obtained. The clay suspensions were allowed to ex-

Table 1. Experimental conditions.

RE	Al/RE molar ratio	Al conc (M)	OH/Al molar ratio	T(°C)	Time (h)	Solution	Clay	meq Al/g clay	T _{calc} (°C)	Basal spacing (Å)	Sample nr.
Ce	16.3	4.4	2.5	160	16	clear/prec.					
Ce	50.0	1.1	2.5	120	63	gel					
Ce	50.0	1.1	1.85	120	63	gel/clear	BDH	22.5	300	9.9	EBPB1
							BDH	22.5	400	10.0	EBPB2
Ce	8.2	2.8	1.85	160	12	prec.					
Ce	4.1	2.1	2.5	165	16	prec.					
Ce	41.2	2.1	2.5	165	16	gel/prec.					
Ce	42.4	5.4	2.5	135	64	clear/prec.					
Ce	42.4	6.2	2.5	135	64	clear/prec.					
Ce	15.0	4.3	2.5	130	136	clear	BDH	30	450	25.2	EBPB3
Ce	15.0	6.2	2.5	130	136	prec.					
Ce	15.0	4.3	2.5	150	18	clear	BDH	25	500	25.5	EBPB5
Ce	10.0	3.7	2.5	150	18	clear/prec.	BDH	25	500	25.3	EBPB4
Ce	30.0	0.9	2.5	160	16	gel					
Ce	25.0	4.9	2.5	130	64	clear	LAP	20	500	Delaminated	EBPB8
Ce	15.0	4.3	2.5	151	19	clear	BDH	25	500	25.7	EBPB7
Ce	30.0	5.1	2.5	160	16	clear					
Ce	15.0	4.3	2.5	142	22	clear	BDH	25	500	24.8	EBPB10
Ce	15.0	4.3	2.5	162	16	clear	ASB	20	500	24.8	EBPB11
Ce	10.0	3.7	2.5	162	16	clear	BDH	15	500	25.6	EBPB13
Ce	15.0	4.3	2.5	132	65	clear	NaSAP	20	500	Delaminated	EBPB16
							NSAP	20	500	Delaminated	EBPB17
							NSAP	20	500	Delaminated	EBPB18
La	8.2	2.8	1.85	160	12	prec.					
La	15.0	4.3	2.5	130	64	clear	BDH	25	500	25.4	EBPB6
						ACH	BDH	20	250	17.8	EBPB12

prec. = Precipitate; BDH = BDH bentonite; ASB = ASB350s bentonite; LAP = laponite; NaSAP = Na-saponite (LTSAPNa); NSAP = NH₄-saponite (LTSAP11A and LTSAP12A).

change for 24 h at room temperature under constant stirring, followed by washing 5 times with demineralized water to remove excess ions. After removal of the water, the clays were dried overnight at 120 °C. Finally, the exchanged clay samples were slightly ground and calcined at the desired temperature for 1 h (heating rate 50 °C/h). Table 1 gives a complete list of all experiments.

Catalyst Preparation

Pillared-clay-based catalysts were prepared for the hydroconversion of n-heptane and for an industrial hydrocracking test. For the hydroconversion experiments, the pillared clays were loaded with 0.8 wt% Pt by impregnation of a mixture of H₂PtCl₆ and a 65 wt% HNO₃ solution for 1 h. Then they were dried and reduced by calcination at 500 °C for 1 h (heating rate 50 °C/min, dwelling 1 h at 350 °C before heating to 500 °C). The catalysts were slightly ground and sized to 40–100 mesh. This procedure is comparable to the one used to prepare a hydroconversion catalyst based on Al-pillared beidellite (Klopogge, Booij et al. 1994). The catalyst used in the hydrocracking test was prepared by extrusion of 60 wt% pillared clay together with 40 wt% alumina. The catalysts were loaded with 3.6 wt% Ni and 15 wt% W by co-impregnation. For comparison, a commercially available amorphous sil-

ica/alumina catalyst ASA from American Cyanamid containing 50% SiO₂ and 50% Al₂O₃ is prepared the same way.

Analytical Techniques

One of the hydrothermally treated Ce/Al pillared solutions was investigated by ²⁷Al NMR spectroscopy. The spectrum was recorded on a Bruker AM 500 spectrometer operated at 130.3 MHz (332 FIDs, spectral width 125 kHz, pulselength 0.9 μs). The chemical shifts are reported relative (in ppm) to [Al(H₂O)₆]³⁺.

X-ray powder diffraction patterns were recorded on a Philips PW 1700 diffractometer using CuKα radiation. Elemental analyses were performed with wavelength dispersive X-ray fluorescence (XRF). The morphology of the products was investigated with a Philips EM 420 transmission electron microscope (TEM) operated at 120 kV. Surface areas were determined from N₂ adsorption/desorption isotherms, applying the BET equation (Carlo Erba Sorptomatic 1800). Pore volumes were estimated from the liquid volume adsorbed at a relative pressure of 0.98. The relative Brønsted acidity was determined from Infrared (IR) adsorption spectra of pyridine adsorbed onto the pillared products.

The hydrothermal stability of the RE/Al-pillared clays was tested by steaming 1.5 g of sample at 500

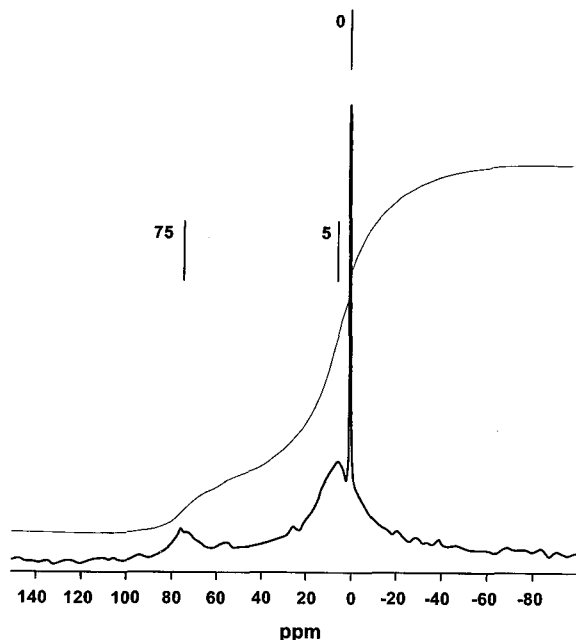


Figure 1. ^{27}Al NMR spectrum of a hydrothermally treated Ce/Al pillaring solution: 160 °C/15 h, Al/Ce ratio 10, (Al^{3+}) 3.7 M, OH/Al ratio 2.5.

°C for 2 h in a mixture of 50 wt% H_2O and 50 wt% N_2 (heating rate 200 °C, flow rate 6 g $\text{H}_2\text{O}/\text{h}$).

The n-Heptane hydroconversion experiments were carried out in a nanoflow tube reactor containing 0.15 g of the catalyst. Prior to the reaction, the catalysts were dried for 16 h at 120 °C and, subsequently, reduced in an H_2 flow (flow rate 2.24 Nml/min, total pressure 30 bar) at 400 °C for 2 h. The hydroconversion conditions were temperature approximately 330–340 °C, total pressure 30 bar, H_2 flow rate 2.24 nml/min, gas hourly space velocity (GHSV) 1020 Nml/g-h, and n- C_7 flow rate 0.15 g/h. The effluent was analyzed by on-line gas chromatography.

RESULTS

Thermal Treatment of the Pillaring Solutions

As shown in Table 1, under certain conditions clear solutions are formed, while in the solutions with an OH/Al molar ratio of 1.85 a white precipitate is observed. This precipitate was identified by XRD as pseudoboehmite ($\text{Al}_7\text{O}_{16}(\text{OH})_{16}\text{Cl}_3$). These solutions have not been used to pillar the smectites. To obtain clear solutions, a minimum aluminum concentration of 3.7 M and an Al/RE molar ratio of 30 is needed. Figure 1 shows the ^{27}Al NMR spectrum of such a solution after hydrothermal treatment [Al/RE molar ratio 10, (Al^{3+}) 3.7 M, OH/Al molar ratio 2.5, treatment 160 °C/15 h]. This spectrum exhibits 3 signals: 1) a sharp octahedral signal at 0 ppm assigned to monomeric Al; 2) a broad octahedral signal at approximately 5 ppm

(FWHM \pm 2690 Hz); and 3) a broad tetrahedral signal at approximately 75 ppm (FWHM \pm 1630 Hz). The characteristic signal due to Al_{13} at approximately 63 ppm is not observed after the hydrothermal treatment. The last 2 broad signals are thought to represent the polymer(s) probably formed during the hydrothermal treatment. The integrated peak areas indicate a ratio of approximately 81 octahedral Al to 14 tetrahedral Al, which is quiet near a ratio of $\text{Al}^{\text{VI}}/\text{Al}^{\text{IV}}$ of 6. Because no information on missing intensities or unobservable Al is available from these solutions, the above-mentioned ratio is only a rough approximation.

Pillared Smectites

Figure 2 depicts the XRD patterns of the pillared smectites after calcination. Sample EPBP2 pillared from a gel containing solution has a basal spacing corresponding to a non-pillared smectite with a collapsed interlayer containing probably only H^+ or Al^{3+} as interlayer cation (Figure 2a). This indicates that, after the hydrothermal treatment of the pillaring solution, all of the Al polymers are present in the gel. Pillaring from clear solutions results in expanded basal spacings in the range between 24.8 and 25.7 Å for both types of bentonites (Figure 2b). The XRD patterns of the BDH bentonites reveal 2 sharp reflections at 2θ values of 22.0° for cristobalite and 26.6° for quartz. These minerals are absent in ASB350s. Steaming at 500 °C for 2 h resulted in an increase in intensity and a decrease in linewidth of the basal reflection caused by an increased crystallinity, indicating a more regularly pillared structure (Figure 3). The pillaring of laponite and saponite resulted in the disappearance of the basal reflections, indicating delamination (Figure 4).

In Table 2, BET-surface areas, T-areas and pore volumes calculated from N_2 adsorption/desorption isotherms of 2 pillared BDH-bentonites and the starting BDH-bentonite are shown (starting material data supplied by M. Crocker, KSLA). Interlayer spacings have been calculated from the basal spacings, assuming an average layer thickness of 9.6 Å. The pillared bentonites have slit-like pore geometries without any microporosity (pores smaller than 20 Å). The large average pore diameters in the range between 60 and 70 Å are interpreted as being caused by the macroporosity created by the clay particle aggregation in a “house-of-cards-like” structure (edge-to-face and edge-to-edge arrangements of particles as observed by TEM).

The chemical analyses reveal that the pillared bentonites contain appreciably higher amounts of Al and small amounts of rare earth elements (REE) (Table 3). Assuming that the chemical composition of the clay layers does not change upon pillaring and that all Ce is incorporated into the pillar structure, the Al/Ce molar ratio in the pillars can be calculated. The chemical data indicate that much less Ce is incorporated than was originally present in the solution. Molar ratios of

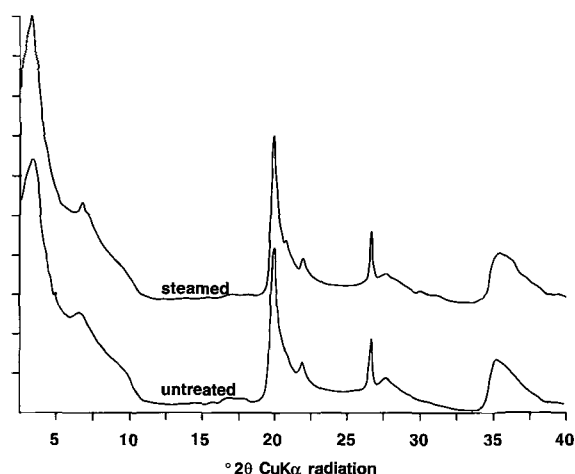
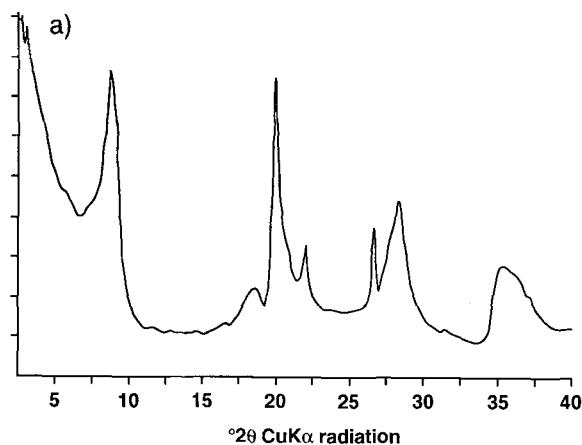


Figure 3. XRD pattern of pillared bentonite EBPB13 prior to and after steaming at 500 °C for 2 h.

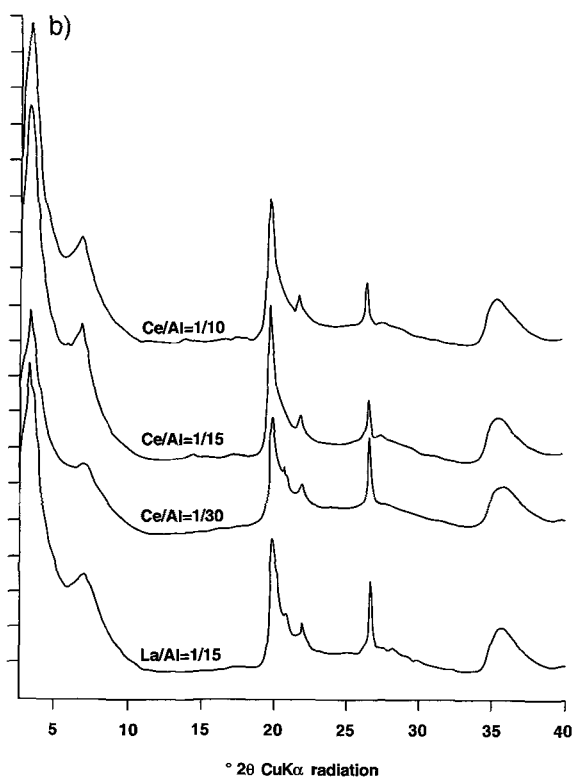


Figure 2. XRD patterns of pillared smectites: a) BDH-bentonite pillared with gel containing solution (EBPB2); b) BDH-bentonite pillared with solutions having an Al/Ce ratio of 10 (EBPB4), 15 (EBPB3) and 30 (EBPB10) and Al/La ratio of 15 (EBPB6).

62.9 and 57.8 are observed instead of 10 (EBPB4) and 15 (EBPB11 and 13).

TEM photographs show that the pillared bentonites exhibit a “house-of-cards-like” structure with particles aggregated in an edge-to-face, edge-to-edge, and face-to-face orientation (Figure 5). This type of aggregation explains the observed large average pore sizes found by N₂ adsorption/desorption. Basal spacings cal-

culated from the lattice fringes for sample EBPB5, for example, are in the range 16.5 to 22.5 Å, which is slightly smaller than observed with XRD.

Hydroconversion and Hydrocracking Experiments

Hydroconversion experiments for n-heptane were first carried out at a reactor temperature of 340 °C. At this temperature, all of the Pt-loaded Ce/Al-pillared clay catalysts prepared from EBPB3, -4 and -5 yielded 100% conversion. Therefore, the reaction temperature was lowered to 330 °C and all experiments were rerun with the Pt-loaded Ce/Al-pillared clay samples EBPB5, -11 and -13 (Table 4).

Pyridine adsorption on EBPB5 showed that a linear relationship exists between the number of Brønsted acid sites, as shown by the intensity of the IR absorption band at 1545 cm⁻¹, and the conversion. The Brønsted acidity is much higher than in the amorphous silica/alumina ASA commercial catalyst.

The industrial hydrocracking test, using a Ni/W-loaded catalyst based on the pillared clay EBPB13, shows that the initial activity of the Ce/Al-pillared clay catalyst is slightly better than other catalysts like Ni/W-loaded amorphous silica/alumina ASA. The pillared clay catalyst deactivated very rapidly, whereas the ASA based catalyst showed practically no deactivation. The selectivity for the middle-distillates for the pillared clay catalysts is slightly lower than for the ASA catalyst, being 71 and 74 wt%, respectively, at 40% conversion. Investigation of the pillared clay catalysts after the hydrocracking test showed that the hydrogenation function of the catalyst was still intact, but that the surface area and pore volume were significantly reduced due to coke formation, making the active site inaccessible for the feedstock hydrocarbons.

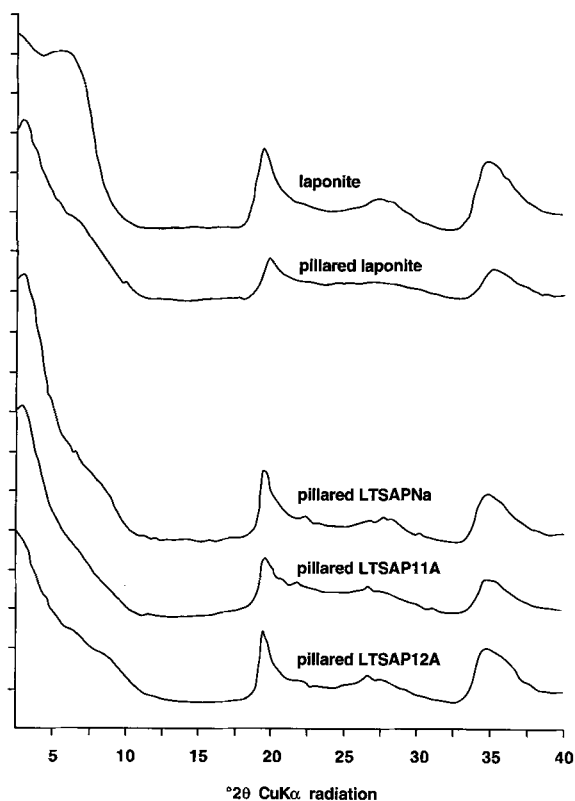


Figure 4. XRD patterns of laponite and its pillared analogues (Al/Ce ratio 25, EBPB8) and pillared saponites (Al/Ce ratio 15, EBPB 16, 17 and 18).

DISCUSSION

Structure of the Ce/Al-Pillared Smectite

The formation conditions of the Ce/Al polyoxocation responsible for the formation of pillared clays with basal spacings larger than 24.8 Å seem to be mainly determined by the Al(III) concentration and the OH/Al molar ratio in the pillaring solutions. Concentrations that are too low and/or OH/Al molar ratios result in the formation of fibrous boehmite. The results presented in Table 1 indicate that the time and temperature at which the solutions are hydrothermally treated are not very critical, because pillared clays could be prepared from solutions treated at conditions ranging from 16 h at 160 °C to 136 h at 130 °C.

A few years ago, Fu et al. (1991) investigated the aging processes in alumina sol-gels. The ^{27}Al NMR

Table 3. Chemical compositions (wt% oxides) of the starting bentonites BDH and ASB350s and their pillared derivatives.

	BDH-bent	EBPB4	EBPB13	ASB350s	EBPB11
SiO ₂	58.39	47.05	50.05	54.75	42.35
Al ₂ O ₃	18.90	28.53	29.85	23.43	29.67
Fe ₂ O ₃	3.86	3.29	3.43	2.57	2.14
MgO	2.65	1.99	2.16	2.65	1.49
CaO	0.11	—	—	0.85	—
K ₂ O	0.14	—	—	0.71	—
Na ₂ O	2.56	—	—	1.89	—
Ce ₂ O ₃	—	0.84	0.89	—	0.83

observations after prolonged aging showed, in addition to the well-known tetrahedral signal at 63 ppm of the Al₁₃, 2 other tetrahedral resonances at 70.2 and 75.6 ppm. The 75.6-ppm resonance became dominant with increasing aging time. These 2 additional resonances were attributed to polymeric species formed upon prolonged aging at elevated temperatures. They proposed a model in which the signal at 70.2 ppm is assigned to a species Al₂₄O₇₂ formed by the loss of one octahedron per Al₁₃ unit, and the linkage of 2 of these reduced Al₁₃ species. The 75.6-ppm signal was, along the same line of reasoning, attributed to an even larger species formed by the linkage of the Al₂₄O₇₂ species. These large Al species were more thermally stable than the Al₁₃ polyoxocation, which was thought to be due to the higher Al^{IV}/Al^{VI} ratio. Turner (1976) and Tsai and Hsu (1985) found that these larger Al species were much more resistant to attack by acid or ferron than the Al₁₃ species.

The observed tetrahedral Al signal at 75 ppm and the octahedral signal at 5 ppm observed in this paper are tentatively assigned to a species present after hydrothermal treatment of REE containing ACH solutions with a structure comparable to that described by Fu et al. (1991). They observed an Al^{VI}/Al^{IV} ratio of approximately 8.4, which is somewhat higher than the value of approximately 5.8 observed in this paper based on surface integrals of the 2 signals, but also significantly lower than the theoretical value of 11 based on their model. The interpretation of the ratio in this paper is open for discussion, because no information on NMR-invisible Al is available: it can be significantly higher or lower (Klopprogge 1992).

Chemical analyses of the pillared clay revealed that the pillars contain approximately 1 Ce atom per 58 to 62 Al atoms, which is less than in the initial pillaring

Table 2. Surface areas and pore volumes of RE/Al-pillared BDH bentonites.

Sample	BET-area (m ² g ⁻¹)	T-area (m ² g ⁻¹)	Pore vol. (cm ³ g ⁻¹)	Micropore vol. (cm ³ g ⁻¹)	Avg. pore diameter (Å)	Interlayer spacing (Å)
BDH-bent.	54	31	0.10	n.d.	n.d.	n.d.
EBPB6	426	478	0.24	0.00	70	15.8
EBPB7	431	438	0.23	0.00	60	16.1

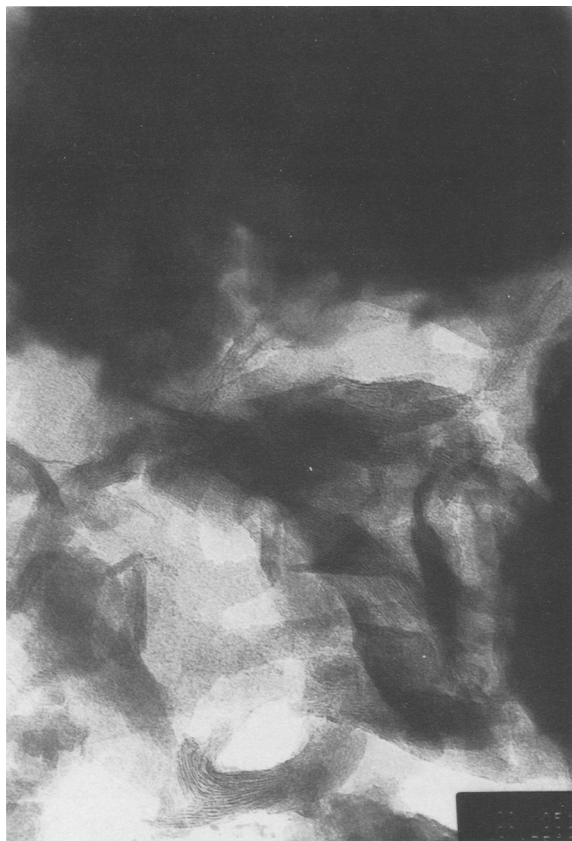


Figure 5. TEM photograph of Ce/Al-pillared bentonite EBPB5 (1 cm = 43 nm).

solution. McCauley (1988) reported that at least 1 Ce atom has to be present per 52 Al atoms to obtain pillared clay structures with large pores. On the basis of this observation in combination with the fact that the observed interlayer spacing of approximately 15 to 16 Å is equivalent to about 10 superimposed oxygen layers, he proposed a structure in which 1 Ce atom in tetrahedral coordination is surrounded by 4 Al₁₃ units more or less comparable to the model of Fu et al. (1991). Sterte (1991a, 1991b) calculated from his chemical analyses of La/Al-pillared clays that approximately 1 La atom was present per 14 to 17 Al atoms, which is much higher than that observed by McCauley (1988) and in this paper. This may be explained by the presence of free La³⁺ in the interlayer due to the excess La present in the solution with an Al/La molar ratio of 5.

The large differences in the Al/RE molar ratios observed in large-pore pillared clays by various authors and the fact that several scientists (Mendioroz et al. 1993; Trillo et al. 1993; González et al. 1992) did not succeed in the formation of large-pore pillared clays in the presence of Ce and La, but only in Al-pillared clays, indicate that there is little consistency about the formation and structure of RE/Al pillars. The Al/Ce

Table 4. Results of the hydroconversion experiments.

Sample	Clay	Conversion (wt%)	Selectivity i-C ₇	C ₁ -C ₄ conversion (wt%)
EBPB5	BDH	85.19	47.35	29.14
EBPB13	BDH	86.04	50.53	28.24
EBPB11	ASB350s	85.50	84.04	13.13

ratio and the ²⁷Al NMR chemical shifts observed in this paper do not rule out the structure proposed by McCauley (1988) or Fu et al. (1991). However, the Al^{VI}/Al^{IV} ratio of 5.8 seems to be too low compared to the expected value of 12, based on McCauley's model, and is closer to the value of 8.4 reported by Fu et al. (1991). If the value near 5.8 is significant, it can be suggested that, upon refluxing or hydrothermal treatment of RE containing Al pillaring solutions, polymerization consuming 4 Al₁₃ units takes place around 1 RE atom. This occurs with a change of 1 Al-octahedron in each of the 4 Al₁₃ units to a tetrahedral configuration, to obtain a better fit of the Al₁₃ units in the new structure. This would result in an Al^{octahedral}/Al^{tetrahedral} ratio of 5.5.

Pillaring bentonites with RE/Al polyoxocations yielded pillared products with basal spacings in a relatively narrow range between 24.8 and 25.7 Å. Increasing the meq Al/g clay to values above 15 does not significantly change the basal spacing nor the regularity of the pillar distribution. Pillaring results in a strong increase in BET surface area from 54 m² g⁻¹ to values of approximately 430 m² g⁻¹, together with a doubling of the pore volume due to the formation of macropores. These macropores are at least partly due to the formation of the so-called "house-of-cards-structure" of the aggregates. Steaming at 500 °C resulted in increased crystallinity, which is in contrast to observations on Al-pillared clays. Vaughan (1988), for example, found that even under mild hydrothermal conditions (at 600 °C) the pore structure of the Al-pillared clay completely collapsed. On the other hand, McCauley (1988) observed that under much more severe steaming conditions (100% steam at 815 °C for 5 h) the surface areas of some Ce/Al-pillared clays were still as high as 280 m² g⁻¹.

In contrast to the RE/Al-pillared bentonites, the XRD patterns of the RE/Al-pillared saponites and laponite showed that these clays exhibited a delaminated structure without long-range layer stacking as indicated by the absence of basal reflections. However, short-range stacking of a few clay sheets cannot be ruled out. The results of Occelli et al. (1984, 1987) for Al-pillared laponite suggest that some short-range layer stacking occurs.

Catalytic Properties of the RE/Al-Pillared Smectites

The results of the n-heptane hydroconversion experiments show that the activity of the Ce/Al-pillared

clay catalyst is higher than that of the amorphous silica/alumina ASA. These results are in agreement with the data obtained from the IR spectra of the catalysts with chemisorbed pyridine, showing that the Brønsted acidity of the pillared clay is much higher. The conversion at 330 °C is more or less comparable for all Ce/Al-pillared bentonite catalysts, but the selectivity for *i*-C₇ does show large differences. The BDH-bentonite-based catalysts show a much lower selectivity of approximately 50%, whereas the ASB350s-bentonite-based catalysts have a selectivity of about 84%. Furthermore, The ASB350s-based catalysts show a favorably lower C₁–C₄ conversion of approximately 13 wt% in contrast to the 29 wt% for the BDH-based catalysts. This lower light gas production is probably related to the lower iron content in the ASB350s-bentonite. According to Occelli (1986), iron can facilitate secondary cracking of heavier hydrocarbons to light gases (and may also promote some coke formation) at the expense of the gasoline formation.

The initial activity of the RE/Al-pillared clay catalysts in the industrial cracking test was slightly higher than the amorphous silica/alumina ASA. However, the rapid coke formation caused very rapid deactivation and the activity soon dropped below the level of the ASA catalyst (but the hydrogenation component remained intact). Occelli and Lester (1985) investigated the coke forming reactions in Al-pillared bentonite catalysts. They found that the combination of the pores formed upon pillaring and the Lewis acidity facilitates coke formation due to the sorption of aromatics and condensation. The still larger pores in the RE/Al-pillared clays also facilitate the diffusion of high molecular weight hydrocarbons into the interlayer: therefore, a similar coke forming process is assumed to be responsible for the deactivation. Additionally, at the temperatures used during hydrocracking, Fe present in the clay structure can be active in dehydrocyclization and cracking reactions, resulting in the formation of coke. Lussier et al. (1980) showed that reduction of the Fe content in pillared clays resulted in reduced coke levels. The relatively high Fe content of the Ce/Al-pillared BDH-bentonite may therefore be responsible for some additional coke formation.

CONCLUSIONS

Pillaring of bentonites with hydrothermally treated or refluxed and partly hydrolyzed Al(III) solutions containing RE elements such as Ce or La results in the formation of hydrothermally stable pillared clays with basal spacings of approximately 25 Å and high surface areas. These materials show conversion levels around 85% in the hydroconversion of *n*-heptane. The selectivity is strongly influenced by the iron content of the starting bentonite. The best selectivity and lowest light gas productions are found when the clay has a low Fe content. In hydrocracking reactions, rapid

deactivation due mainly to strong coke formation is observed. Pillaring saponite or laponite results in a delamination of the clay structure.

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REFERENCES

- Akitt JW, Greenwood NN, Khandelwahl BL, Lester GD. 1972. ²⁷Al NMR studies of the hydrolysis and polymerization of the hexa-aquo-aluminum cation. *J Chem Soc Dalton Trans*:604–610.
- Barrer RM, MacLeod DM. 1955. Activation of montmorillonite by ion exchange and sorption complexes of tetraalkylammonium montmorillonites. *Trans Faraday Soc* 51: 1290–1300.
- Bottero JY, Cases JM, Fiesinger F, Poirier JE. 1980. Studies of hydrolyzed aluminum chloride solutions: 1. Nature of aluminum species and composition of the aqueous solutions. *J Phys Chem* 84:2933–2934.
- Bottero JY, Tchoubar D, Cases JM, Fiesinger F. 1982. Investigation of the hydrolysis of aqueous solutions of aluminum chloride: 2. Nature and structure by Small Angle X-ray Scattering. *J Phys Chem* 86:3667–3672.
- Brindley GW, Sempels RE. 1977. Preparation and properties of some hydroxy-aluminium beidellites. *Clay Miner* 12: 229–237.
- Fu G, Nazar LF, Bain AD. 1991. Aging process of alumina sol-gels: Characterization of new alumina polyoxocations by ²⁷Al NMR spectroscopy. *Chem Mater* 3:602–610.
- González F, Pesquera C, Benito I, Mendioroz S, Poncelet G. 1992. High conversion and selectivity for cracking of *n*-heptane on cerium-aluminium montmorillonite catalysts. *J Chem Soc: Chem Commun*:491–493.
- Johansson G. 1960. On the structure of some basic aluminum salts. *Acta Chem Scand* 14:771–773.
- Kloprogge JT. 1992. Pillared clays. Preparation and characterization of clay minerals and aluminum based pillaring agents [dissertation]. Utrecht, The Netherlands: Univ of Utrecht. 349 p.
- Kloprogge JT, Booij E, Jansen JBH, Geus JW. 1994. Synthesis of Al-pillared beidellite and its catalytic activity in the hydroconversion of *n*-heptane. *Catalysis Lett* 29:293–297.
- Kloprogge JT, Breukelaar J, Geus JW, Jansen JBH. 1994. Characterization of Mg-saponites synthesized from gels containing amounts of Na⁺, K⁺, Rb⁺, Ca²⁺, Ba²⁺, or Ce⁴⁺ equivalent to the CEC of the saponite. *Clays Clay Miner* 42:18–22.
- Kloprogge JT, Breukelaar J, Jansen JBH, Geus JW. 1993. Development of ammonium-saponites from gels with variable ammonium concentrations and water content at low temperatures. *Clays Clay Miner* 41:103–110.
- Kloprogge JT, Geus JW, Jansen JBH, Seykens D. 1992. Thermal stability of basic aluminum sulfate. *Thermochim Acta* 209:265–276.

- Klopogge JT, Seykens D, Geus JW, Jansen JBH. 1993. The effects of concentration and hydrolysis on the oligomerization and polymerization of Al(III) as evident from the ^{27}Al NMR chemical shifts and linewidths. *J Non-Cryst Solids* 160:144–151.
- Klopogge JT, Seykens D, Jansen JBH, Geus JW. 1992. A ^{27}Al nuclear magnetic resonance study on the optimization of the Al_{13} polymer. *J Non-Cryst Solids* 142:94–102.
- Kunwar AC, Thompson AR, Gutowski HS, Oldfield E. 1984. Solid state aluminum-27 NMR studies of tridecameric Al-oxo-hydroxy clusters in basic aluminum selenate, sulfate and the mineral Zunyite. *J Magn Reson* 60:467–472.
- Lahav N, Shani U, Shabtai J. 1978. Cross-linked smectites. I: Preparation and properties of some hydroxy-aluminum montmorillonite. *Clays Clay Miner* 26:107–115.
- Lussier RJ, Magee JS, Vaughan DEW. 1980. Pillared interlayered clay catalysts preparation and properties. In: Wanke SE, Chakrabarty SK, editors. 7th Canadian symposium on catalysis. Preprint. Edmonton: Alberta, Canada. p 88.
- McCauley JR, inventor; Katalistiks International, assignee. 1988 Mar 4. Stable intercalated clays and preparation method. International patent PCT/US88/00567. 127 p.
- Mendioroz S., González F, Pesquera C, Benito I, Blanco C, Poncelet G. 1993. Preparation of thermalstable pillared clays. In: Guczi L et al., editors. New frontiers in catalysis. Proceedings of the 10th International Congress on Catalysis; Budapest, Hungary. Amsterdam: Elsevier Science. p. 1637–1640.
- Occelli ML. 1986. New routes to the preparation of pillared montmorillonite catalysts. *J Mol Catal* 35:377–395.
- Occelli ML, Landau SD, Pinnavaia TJ. 1984. Cracking selectivity of a delaminated clay catalyst. *J Catal* 90:256–260.
- Occelli ML, Lester JE. 1985. Nature of active sites and coking reactions in a pillared clay mineral. *Eng Chem Prod Res Dev* 24:27–32.
- Occelli ML, Lynch JL, Senders MV. 1987. TEM analysis of pillared and delaminated hectorite catalysts. *J Catal* 107: 557–565.
- Occelli ML, Tindwa RM. 1983. Physicochemical properties of montmorillonite interlayered with cationic-oxyaluminum pillars. *Clays Clay Miner* 31:22–28.
- Rausch WV, Bale HD. 1964. Small Angle X-ray Scattering from aluminum nitrate solutions. *J Phys Chem* 40:3391–3394.
- Schönherr S, Görz H, Bertram R, Müller D, Gessner W. 1983. Vergleichende Untersuchungen an unterschiedlich dargestellten basischen Aluminiumchlorid-lösungen. *Z Anorg Allg Chem* 502:113–122.
- Schutz A, Stone WEE, Poncelet G, Fripiat JJ. 1987. Preparation and characterization of bidimensional zeolitic structures obtained from synthetic beidellite and hydroxy-aluminum solutions. *Clays Clay Miner* 35:251–261.
- Sterte J. 1991a. Preparation and properties of large pore RE/Al-pillared montmorillonite. A comparison of RE-cations. In: Poncelet G, Jacobs PA, Grange P, Delmon B, editors. Preparation of catalysts V. Amsterdam, The Netherlands: Elsevier Science. p 301–310.
- Sterte J. 1991b. Preparation and properties of large pore La-Al-pillared montmorillonite. *Clays Clay Miner* 39:167–173.
- Tokarz M, Shabtai J. 1985. Cross-linked smectites IV: Preparation and properties of hydroxyaluminum-pillared Ce- and La-montmorillonites and fluorinated NH_4^+ -montmorillonites. *Clays Clay Miner* 33:89–98.
- Trillo JM, Alba MD, Alvero R, Castro MA, Muñoz A, Poyato J, Tobías MM, Lagaly G. 1993. Montmorillonite intercalated with Al(III), La(III) and alumina pillars: structural aspects and reactivity. *Solid State Ionics* 63–65:457–463.
- Tsai PP, Hsu PH. 1985. Aging of partially hydrolyzed aluminum solutions of sodium hydroxide/aluminum ratio = 2.2. *Soil Sci Soc Am J* 49:1060–1065.
- Turner RC. 1976. Effects of aging on properties of polynuclear hydroxy aluminum cations. *Can J Chem* 54:1528–1534.
- Vaughan DEW. 1988. Pillared clays—a historical perspective. *Catal Today* 2:187–198.
- Vaughan DEW, Lussier RJ, Magee JS, inventors. 1979 Nov 27. Pillared interlayer clay materials useful as catalysts and sorbents. US patent 4,176,090.
- Vaughan DEW, Magee JS. 1980. Preparation of molecular sieves based on pillared interlayer clays (PILC). In: Rees LVC, editor. Proceedings of the 5th International Conference on Zeolites; Naples, Italy. London: Heyden Pr. p 94–101.
- Vogels JMJ, Breukelaar J, Klopogge JT, Jansen JBH, Geus JW. 1997. Hydrothermal crystallization of ammonium-saponite at 200 °C and autogeneous water pressure. *Clays Clay Miner*: In press.
- Wang W, Hsu PH. 1994. The nature of polynuclear OH-Al complexes in laboratory-hydrolyzed and commercial hydroxyaluminum solutions. *Clays Clay Miner* 42:356–368.
- Yamanaka S, Brindley GW. 1979. High surface area solids obtained by reaction of montmorillonite with zirconyl chloride. *Clays Clay Miner* 27:119–124.

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