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Pillared Clays and Pillared Acid-Activated Clays: A Comparative Study of Physical, Acidic, and Catalytic Properties

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The preparation, characterisation, and catalytic properties of alumina-pillared materials derived from an acid-treated host clay matrix is described. Various levels of acid treatment are studied in order to ascertain the level of acid treatment which yields pillared materials with the most suitable physicochemical properties and thermal stability. The pillared acid-activated clays prepared possess basal spacing (19.3 Å after thermal treatment at 500°C) and surface areas (315–374 m^2/g) comparable to conventional pillared clays but significantly higher pore volume (0.33–0.48 cm^3/g), average pore diameter and surface acidity. The improvement in acidity is mainly of the Brønsted acid type. As a result of improved acidity, the pillared acid-activated clays are better catalysts compared to conventional pillared clays and they exhibit activity indicative of the presence of strong Brønsted acid sites in the temperature range 250–400°C.

INTRODUCTION

Pillared clays have attracted considerable attention as catalysts for a variety of acid-mediated reactions (1–7). They are prepared by intercalating polycations into the interlayer region of expandable clay minerals (usually montmorillonites) which following calcination are converted to metal oxide pillars, which are fixed to the layers of the clay to yield rigid cross-linked materials (8–10). Zirconia, chromia, and in particular alumina have been extensively used as pillars.

The catalytic properties of pillared clays are a result of the propping apart of the clay structure, thereby increasing the surface area and pore volume, and exposing much of the interlayer region (intracrystal surface area) and any acid sites therein to reactant molecules (11). Furthermore, in addition to expanding the layer structure, the metal oxide pillars are themselves also thought to possess a certain amount of acidity (12, 13). The combination of exposing the host clay sheets as well as the presence of the pillars yield materials, which on calcination, possess both Lewis and Brønsted acid sites (12), although at high temperatures (i.e., 400–500°C) the acidity of pillared clays is predominantly of the Lewis type (13). Indeed, infrared studies of pyridine molecules, adsorbed on pillared clays, have shown that Brønsted acid sites are thermally less stable, i.e., infrared evidence of the presence of Brønsted sites is lost at temperatures above 300 to 400°C. The generally accepted view of the acidity of pillared clays is that Lewis acid sites are mainly resident on the metal oxide pillars (14), whereas Brønsted acid sites are associated with structural OH groups present on the layers of the host clay (14, 15). Bodoardo *et al.* (16) have, however, more recently reported that the pillars contribute a significant amount of Brønsted acid sites.

To date, most attempts at improving and controlling the acidity of pillared clays have concentrated on changing the type of host matrix (17, 18) and varying the identity of the pillar (13, 19). Our synthetic programme has, however, focused on the acid modification of the clay mineral (host lattice) prior to pillaring (20–23). As most of the Brønsted acid sites on pillared clays are believed to be associated with the layers of the clay (14, 15), we have attempted to enhance the (Brønsted) acidity of the host matrix by acid treatment (24, 25) prior to pillaring. For example, we have already shown that the number of matrix protons (on the clay sheets), not associated with the interlayer cation, may be increased by acid treatment (26).

Here we report, in detail, the properties of alumina-pillared acid-activated clay (PAAC) catalysts. Preliminary work with "soft" low temperature (175–250°C) catalysis has shown that acid treatment before pillaring has beneficial effects on the catalytic properties of the final pillared (acid-activated) clay (27). We compare the catalytic activity of a range of pillared acid-activated catalysts (with the level of acid treatment prior to pillaring as the main variable) with a conventional pillared clay (PPE) and non-pillared calcined acid-activated clays (CAAC). The test reactions used are the dehydration of 1-butanol and the cracking/dehydrogenation of cumene. Both reactions may be used to characterise the acidity of solid acid cata-

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TABLE 1

Removal of Octahedral Ions with Increasing Levels of Acid Treatment

Acid-activated clay	Acid/Clay ratio	ReO[a] (%)
PE25	0.25	14.0
PE30	0.30	19.2
PE35	0.35	23.5
PE40	0.40	28.7
PE45	0.45	32.2
PE60	0.60	48.5

[a] ReO = amount of octahedral ions removed.

lysts, e.g., the dehydration of 1-butanol to dibutyl ether and butenes has been used to characterise the Lewis/Brønsted acidity of silica-aluminas (28). The conversion of cumene, on the other hand, is a model reaction in identifying the Lewis/Brønsted acid ratio of a catalyst; cumene is cracked to benzene and propene over Brønsted acid sites as opposed to dehydrogenation mainly to α-methylstyrene over Lewis acid sites (15). The relative amounts of benzene and α-methylstyrene in the product mix is a good indication of the type of acidity possessed by the catalyst. An important difference between the two reactions is that water is formed during the dehydration of butanol but not in the conversion of cumene.

EXPERIMENTAL

A Peruvian calcium montmorillonite (designated PE) supplied by Laporte plc was used as the starting material. The structural formula of the anhydrous montmorillonite is

$$Ca_{0.24}[Si_{3.93}Al_{0.07}][Al_{1.42}Fe_{0.15}Mg_{0.43}]\ O_{10}(OH)_2.$$

The montmorillonite was treated with concentrated (98%) sulphuric acid to yield acid-activated clays (PE25 to PE60, see Table 1) acid-treated to various levels as follows. The montmorillonite was slurried with water and then mixed with the acid at predetermined acid/clay (w/w) ratios so as to form a 20% (w/w) clay slurry which was maintained at 95°C for 16 h with constant stirring. At the end of the reaction time the activation was stopped by addition of a large amount of cold water. The solid recovered by filtration was washed with hot water (30 ml/g) before being air-dried and subsequently ground to a particle size in the range 120–160 μm. Samples used to determine the elemental composition were washed until free of SO_4^{2-} ions, as tested by $BaCl_2$.

Aluminium chlorhydrate (ACH) solution (Albright and Wilson) was used as the source of the pillaring species. The solution containing 50% (w/w) aluminium chloride pentahydroxide dihydrate $[Al_2Cl(OH)_5 \cdot 2H_2O]$ had an OH/Al ratio of 2.5 and was 6.4 *M* in aluminium. The pillared materials were prepared by adding the raw or acid-activated clay to the stirred pillaring reagent at 80°C. The concentration of the ACH pillaring reagent was 0.06 *M* and the clay was added to the solution at a solution/clay ratio of 50 ml/g corresponding to an Al/clay ratio of 6 mmol/g. Exchange was then carried out at 80°C for 1 h with constant stirring. The resulting slurry was repeatedly centrifuged in fresh deionised water and reslurried until free of Cl^- ions (as tested by $AgNO_3$). The obtained solids were then redispersed in a minimum amount of deionised water and air-dried to obtain the precursor-pillared clays, which were calcined for 4 h in air at 500°C to yield the pillared clays.

A Philips PW 1710 diffractometer utilising Cu$K\alpha$ radiation was used to obtain powder X-ray diffraction (XRD) patterns. Surface area, pore volume, and pore size distributions were obtained using a Micromeritics ASAP 2000 analyser. The samples (previously calcined in air for 4 h at 500°C) were degassed, under vacuum, for 8–10 h at 200°C prior to analysis. Elemental compositions were determined using a Philips PW 1400 X-ray fluorescence spectrometer fitted with a rhodium target X-ray tube. Brønsted acidity (proton concentration) was determined using the method outlined by Breen (29). In this method, thermogravimetric analysis (TGA) of clays following cyclohexylamine adsorption is used to determine the number of protons capable of interacting with the base. The weight loss between 240 and 420°C is used to compute the acidity in terms of millimoles cyclohexylamine desorbed. A relatively high lower temperature (240°C) is chosen so that differences in the amount of physisorbed base or nonexchanged water do not affect the computed values. All the clays (see Table 2) analysed using this

TABLE 2

Amount of Alumina Incorporated and Surface Acidity of Various Pillared Clays

Pillared clay	Alumina incorporated (Alp) (mmol/g)	Surface acidity (mmol H^+/g)[a]
PPE	1.50	0.43
PPE25	1.37	0.57(0.37)[b]
PPE30	1.32	0.60(0.39)
PPE35	1.28	0.64(0.36)
PPE40	1.20	0.66(0.35)
PPE45	1.14	0.65(0.34)
PPE60	1.15	0.58(0.29)

[a] mmol H^+ per g of clay at 240°C.

[b] Figures in parentheses are surface acidity for calcined nonpillared acid-activated clays.

method were calcined (500°C in air for 4 h) prior to analysis.

FTIR spectra of chemisorbed pyridine were obtained using a Nicolet 205 FTIR spectrometer. Each sample (25–30 mg) was pressed (for 2 min at 10 ton/cm^2 under vacuum) into a self-supporting wafer of diameter 13 mm. The wafers (of precursor-pillared material or acid-activated clay) were calcined in air at 500°C for 3 h followed by exposure to pyridine vapour at ambient temperature and heating at 100°C for 1 h to allow the pyridine to permeate the wafers. To remove physisorbed base, the wafers were held under vacuum (10^{-3} Torr) at 250°C for 1 h. The wafers were then allowed to cool to ambient temperature following which three subsequent 1 h thermal treatments at 150, 250, and 350°C were performed and the corresponding spectra were recorded at 150, 250, and 350°C, respectively after each thermal treatment. It is important to note that in an attempt to mimic conditions similar to those used for catalysis these latter thermal treatments and associated IR measurements were performed at atmospheric pressure.

Two test reactions were performed, namely 1-butanol dehydration and the conversion of cumene. In both cases a pulse microreactor was used with a helium flow of 25 ml per minute. For the butanol dehydration, the catalyst bed (0.05 g; 30–60 mesh) was activated for 4 h at 400°C under helium (25 ml per minute). The volume of one butanol pulse was 5 μl (54.6 μmol). For cumene conversion, the catalyst bed (0.05 g; 30–60 mesh) was activated for 1.5 h at 500°C under helium (25 ml per min). The volume of one cumene pulse was 2 μl (14.4 μmol). Products were separated and analysed with a Carlo Erba HRGC 5300 gas chromatograph on line with the microreactor.

RESULTS AND DISCUSSION

Physical Properties of the Pillared Materials

Acid activation of a montmorillonite clay proceeds via removal of octahedral ions and any isomorphously substituted tetrahedral ions. The extent of removal of these ions is dependent on the activation temperature, the strength of acid used, the acid to clay ratio (a/c), and the duration of the activation. Montmorillonites from different deposits, however, are attacked to different levels by the same acid treatment. It is therefore necessary to have a convenient way of describing the severity of acid treatment. In Table 1 the severity of acid treatment is expressed as percentage of octahedral ions (Al, Fe, Mg) removed (ReO). The ReO values for the acid-activated clays were obtained from elemental analysis of thoroughly washed (SO$_4^{2-}$ free) samples. An approximately linear relationship is observed between the acid/clay ratio and ReO, indicating that for the montmorillonite studied, the extent of acid leaching is proportional to the amount of acid used. For the study reported here, an upper ReO limit of 48.5 was chosen in order to limit the metal ion removal to less than 50% and thereby ensure that the resultant (acid-activated) materials retained montmorillonitic (layer-like) behaviour (25).

Table 2 gives (in mmol/g) the amount of alumina incorporated (Alp) by the pillared parent clay (PPE) and the various pillared acid-activated clays. It also indicates the surface acidity of the calcined PPE along with that of calcined pillared and calcined (nonpillared) acid-activated clays. The amount of alumina incorporated (Alp) generally reduces with increasing severity of acid treatment. This may be due, in part, to the reduction of the cation exchange capacity of the clays (30) and consequently a tendency to incorporate less of the pillaring cation. Furthermore, the layer structure of the clay is progressively disrupted with increasing acid treatment, thereby reducing the ability to intercalate the pillaring species. PE60, despite being acid-treated to a greater extent, exhibits anomalous behaviour by incorporating amounts of alumina similar to PE45.

Figure 1 shows the powder XRD patterns (between 0 and 15° 2θ) obtained for some of the acid-activated clays (PE25, PE35, and PE45), the corresponding precursor-pillared acid-activated clays (air-dried at 25°C), and the pillared acid-activated clays after calcination (for 4 h in air) at 500 and 600°C. The equivalent patterns for the raw clay (PE) are shown for comparison. A comparison between the raw clay with the acid-activated clays reveals that the basal spacing of the acid-activated clays (15.1 Å) is slightly lower than that observed for the raw clay (15.8 Å). The most probable explanation for this observation is that during the acid activation process the interlayer cations in the raw clay (Ca) are replaced by H$^+$ and/or lattice ions (e.g., Al) (31). A lower extent of hydration

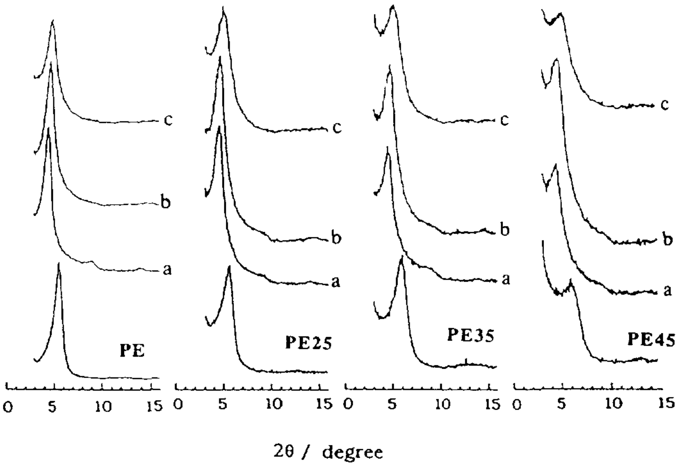

FIG. 1. Powder XRD patterns of the raw (PE) and acid-activated (PE25, PE35, and PE45) clays before and after pillaring and thermal treatment at (a) 25°C, (b) 500°C, and (c) 600°C.

for the new interlayer cations may lead to the presence of less interlamellar water and therefore lower interlayer spacing. It is interesting to note that, despite the gradual reduction in the intensity of the basal reflection, the basal spacing is the same for all the acid-activated clays (probably an indication that the interlayer cations are the same in all cases). The intensity of the basal reflections observed for the activated clays (along with the presence of higher order *hk* reflections at 2θ values of 19.8, 34.8, and 53.6, not shown) are a clear indication that the montmorillonitic structure of the parent clay is partially preserved despite the acid treatment.

The XRD patterns of the precursor-pillared materials indicate an expansion of the layer structure. Furthermore, the basal spacing obtained for the precursor-pillared acid-activated clays (~19.6 Å) is the same as that for the precursor-pillared clay suggesting that the pillaring species is likely to be similar in both cases. For the pillared materials (calcined at 500 or 600°C), the intensity of the basal reflection for PPE25 and PPE35 (see Fig. 1) suggests that these materials are fairly well ordered. The lower intensity observed for the basal reflection of sample PPE45 is attributed to a lower extent of pillaring. The XRD patterns also indicate that the higher the amount of Alp (see Table 2), the better ordered the pillared material. Significantly, the pillared acid-activated clays exhibit thermal stability comparable to that of the conventional pillared clay. After calcination in air at 500°C, the basal spacing of the pillared acid-activated clays reduces slightly to 19.3 Å with little effect on the intensity of the reflection. Interestingly, the basal spacing of the conventional pillared clay reduces, after calcination at 500°C, to 18.8 Å. However, on calcination at 600°C, the basal spacing of the pillared acid-activated clays reduces to 17.8 Å while that of the pillared clay reduces to 18.2 Å. The 0.4 Å difference may be attributed to the higher stability of the raw clay matrix compared to that of the acid-activated clays.

Figure 2 shows the nitrogen adsorption–desorption isotherms for the calcined (500°C in air) conventional pillared clay (PPE) and the pillared acid-activated clays (PPE25, PPE35, and PPE45). The sorption isotherm encountered for PPE is type I in the classification of Brunauer *et al.* (32) indicating the presence of micropores. The isotherms obtained for the pillared acid-activated clays are intermediate between type I and type II, indicating the presence of both microporosity and mesoporosity. The shift toward mesoporosity increases with increasing severity of acid treatment. The hysteresis loops encountered are of type B in the classification of de Boer or type H3 in the IUPAC classification. Among the materials that show this type of hysteresis are those which possess slit-shaped pores and plate-like particles with spaces between the parallel plates. The pillared acid-activated clays generally have higher surface area (with a lower contribution of micropore area) compared to PPE (see Table 3), although a gradual reduction in total surface area is observed with increasing severity of acid treatment. The pore volume increases significantly between PPE and PPE25 and continues to rise thereafter with increasing acid treatment. This may, in part, be due to the reduction in Alp leading to less interlayer space being occupied by the pillars. As expected, and in agreement with the shape of sorption isotherms, the micropore components of the surface area and pore volume reduce with increasing severity of acid treatment.

Pore size distribution (psd) curves are shown in Fig. 3. As expected, PPE exhibits a sharp (meso)pore size distribution characteristic of a conventional alumina-pillared clay. The (meso)pore size distribution of the pillared acid-activated clays indicate the presence of pores covering a wider range of sizes. A gradual broadening of the pore size range, with an increasing contribution of pores of diameter >35 Å is observed between PPE25 and PPE45. This is in agreement with the reduction in micropore area and volume (see Table 3) and changes in average pore diameter; the average pore diameter of PPE25 and PPE35 is ~25 Å (compared to 17 Å for PPE and 35 Å for PPE45). As the level of acid treatment increases the psd shifts to higher values to the extent that PPE60) has a bimodal psd, centered at 30 Å and 70 Å, similar to that of a nonpillared acid-activated clay.

Acidity of the Pillared Materials

Brønsted acidity. Table 2 gives values corresponding to the number of Brønsted acid sites obtained using cyclohexylamine as the probe molecule. The acid sites measured by this method are those that are accessible and strong enough to interact with the base. In computing the values given in Table 2, it is assumed that each molecule of the base interacts with one protonic (Brønsted) acid site (29). As indicated earlier, the values in Table 2 are expressed per weight of clay at 240°C so as to exclude any differences in the amount of physisorbed base or nonexchanged interlamellar water. The results clearly indicate that pillaring has a beneficial effect. It is likely that calcination of a nonpillared clay (raw or acid-activated) renders a proportion of acid sites on the clay sheets inaccessible to the base; pillaring props apart the clay structure thereby exposing the acid sites. It is also apparent that acid treatment prior to pillaring yields pillared materials with improved acidity. We propose that this is mainly as a consequence of the enhanced acidity of the clay sheets after acid treatment (24, 26). The Brønsted acidity of the pillared acid-activated clays peaks at a ReO value of between 23.5 and 28.7, indicating the existence of an optimum level of acid treatment.

If it is assumed that most of the Brønsted acid sites on

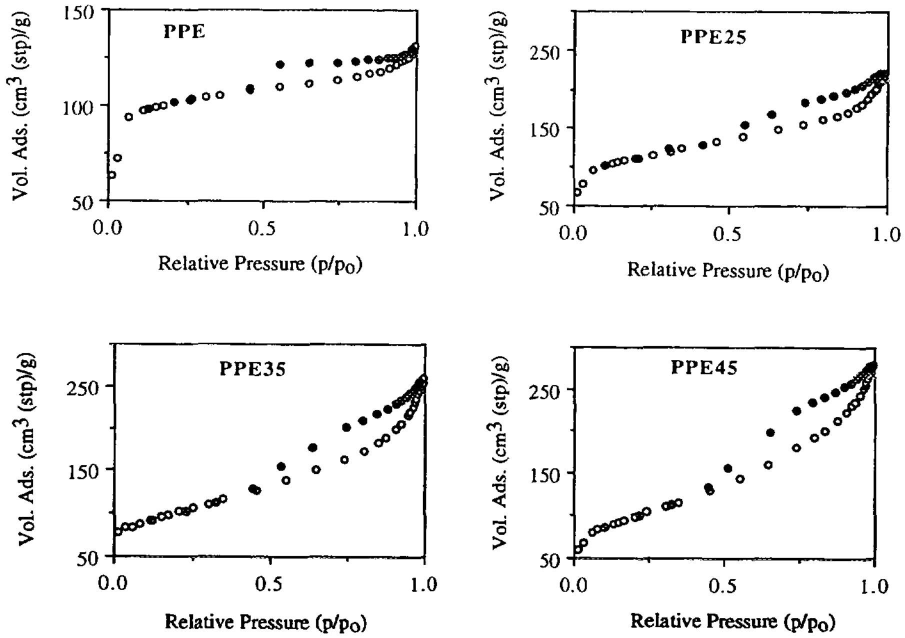

FIG. 2. Nitrogen adsorption–desorption isotherms of a pillared clay (PPE) and pillared acid-activated clays (PPE25, PPE35, and PPE45).

pillared clays are on the clay sheet (14), the significant amount of acidity observed for the conventional pillared clay (PPE) would imply that the sheets of the raw clay (PE) possess a considerable number of Brønsted acid sites. Furthermore, as the acidity of the calcined raw clay is almost nil while that of the calcined acid activated clays is much higher (0.29–0.38 mmol H^+/g clay at 240°C), it can be argued that most of the Brønsted acid sites on the raw clay are within the interlayer region and not on the external surface (that remains exposed after calcination), and that acid-treated clays possess Brønsted acid sites not necessarily associated with the interlayer region (26). This argument is consistent with the low surface area of calcined raw clays, i.e., ca. 20 m^2/g compared to ca. 250 m^2/g for calcined acid-activated clays. It appears, therefore, that accessible surface area is a significant factor in determining the acidity of these solid acids.

Brønsted and Lewis acidity. Figure 4 shows the infrared spectra, in the region 1800–1400 cm^{-1}, of various clay samples following exposure to pyridine vapour and subsequent thermal treatment at increasing temperatures. All the samples were calcined in air at 500°C for 3 h prior to exposure to pyridine. All the samples exhibit the expected bands which may be assigned to Lewis-bound pyridine (1450 and 1613 cm^{-1}, pyridine bound on Brønsted acid sites (1545 and 1640 cm^{-1}), and a band at 1490 cm^{-1} attributed to pyridine associated with both Lewis and Brønsted acid sites (33). The spectra indicate that the

TABLE 3

Surface Area and Pore Volume of Pillared Materials

Pillared clay	Surface area (m^2/g)	Micropore area (m^2/g)	Pore volume (cm^3/g)	Micropore volume (cm^3/g)
PPE	341	295(87)[a]	0.20	0.12(60)[b]
PPE25	387	207(54)	0.33	0.08(24)
PPE30	374	160(43)	0.34	0.06(18)
PPE35	364	135(37)	0.38	0.053(14)
PPE40	353	122(35)	0.39	0.048(12)
PPE45	350	110(31)	0.41	0.043(10)
PPE60	315	44(14)	0.48	0.02(4)

[a] Figures in parentheses are percentage micropore area.

[b] Figures in parentheses are percentage micropore volume.

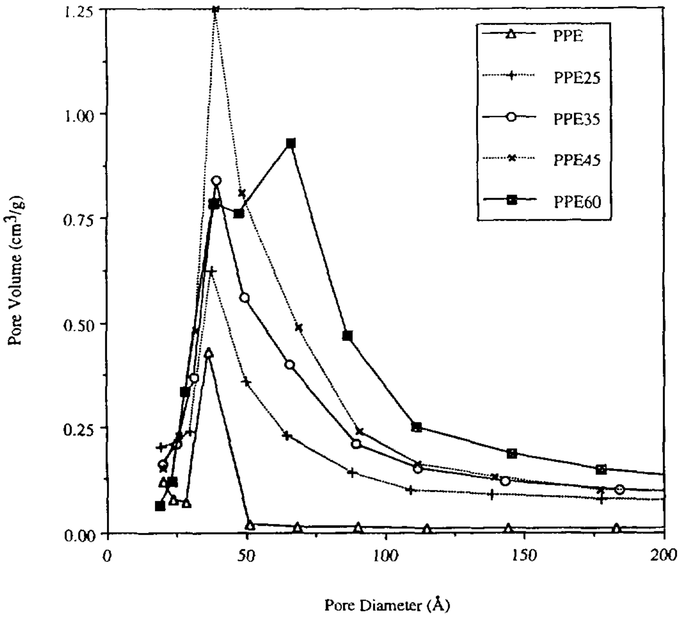

FIG. 3. Mesopore size distribution curves of a pillared clay (PPE) and pillared acid-activated clays (PPE25, PPE35, and PPE45).

pillared acid-activated clays (PAAC) have improved acidity compared to the conventional pillared clay (PPE) and the calcined acid-activated clays (CAAC) C-PE30 and C-PE40, and that the acidity generally increases in the order CAAC < PPE < PAAC. Further comparison shows that, compared to PPE, the improvement in the Brønsted acidity of the pillared acid-activated clays is greatest at 150°C, while compared to the calcined acid-activated clays (C-PE30 and C-PE40) the improvement is greatest at 350°C.

As expected (14, 15), the pillared acid-activated clays have higher Lewis acidity compared to the nonpillared acid activated clays (compare PPE30 with C-PE30 and PPE40 with C-PE40 in Fig. 5). This implies either or both of the following: (1) most of the Lewis acidity is associated with the pillars; and (2) collapse of the layer structure renders some Lewis acid sites, located on the clay sheet, inaccessible to the pyridine molecules. Furthermore, the Lewis acidity of the pillared materials increases with temperature of treatment while for the calcined acid-activated clays the Lewis acidity reduces between 250 and 350°C. Previous studies (14) have indicated a relationship between the Lewis acidity of pillared clays and the amount of pillars incorporated. In the present study, no such relationship is observed, probably due to the use of an Al/clay ratio (6 mmol/g) which is higher than the stoichiometric values. Indeed, an inverse relationship between the Lewis acidity and alumina incorporated (Alp) is observed.

The area of the absorption bands shown in Fig. 4 was obtained by integration and the peak areas were taken as a measure of the intensity of the bands. In order to obtain a normalised parameter which allows comparisons between the clay samples, the band area (corrected per gram of sample) was divided by the wafer density (g cm^{-2}) and multiplied by the infrared beam section (cm^2). The values obtained are shown in Fig. 5. The Brønsted acidity decreases with increasing temperature. Additionally, the large differences in Brønsted acidity of the samples at 150°C are much reduced at 350°C. The reverse is observed for the Lewis acidity; at 250 and 350°C the Lewis acidity of pillared acid-activated clays is spread over a wider range of values compared to the Brønsted acidity indicating that, while the Brønsted acidity remains more or less the same for all the pillared acid-activated clays, the Lewis acidity increases with increasing levels of acid treatment. This implies that acid treatment of a clay matrix followed by calcination generates Lewis acid sites with the number of sites generated increasing with the degree of acid treat-

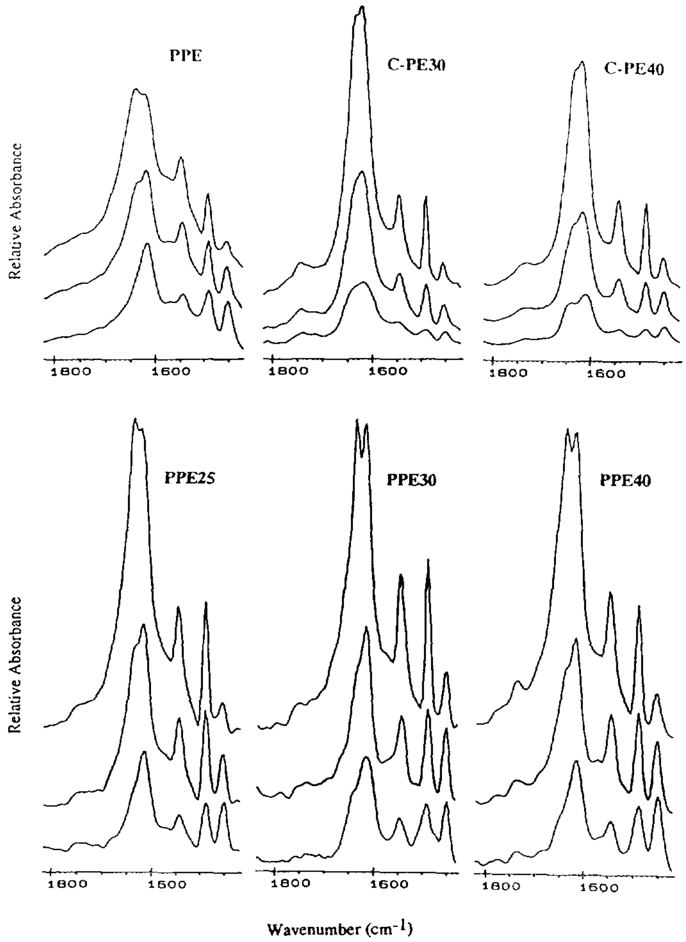

FIG. 4. IR spectra of pyridine adsorbed on a pillared clay (PPE), calcined acid-activated clays (C-PE30, and C-PE40), and pillared acid-activated clays (PPE25, PPE30, and PPE40) following thermal treatment at (top to bottom) 150, 250, and 350°C.

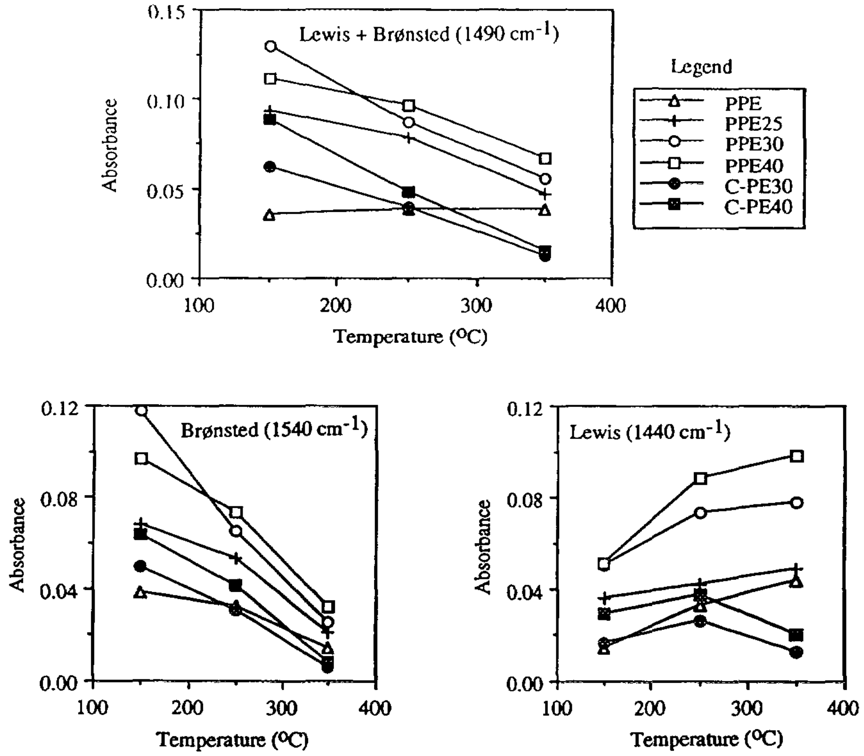

FIG. 5. Pyridine infrared absorbance for a pillared clay (PPE), calcined acid-activated clays (C-PE30, and C-PE40), and pillared acid-activated clays (PPE25, PPE30, and PPE40). Absorbance values used are absorbance per gram × ir beam cross section (cm^2) divided by wafer density (g cm^{-2}).

ment (up to a ReO value of 50 in the present study). This is supported by the higher Lewis acidity of C-PE40 (ReO = 28.7) compared to C-PE30 (ReO = 19.2). As the treatment temperature increases the area of the peak attributed to both Lewis and Brønsted acid sites reduces for all samples except PPE. It appears, therefore, that the reduction in the Brønsted acidity of the pillared acid-activated clays which accompanies increase in treatment temperature is greater than the expected increase in Lewis acidity, while for the conventional pillared clay, the increase in Lewis acidity compensates for the reduction in Brønsted acidity.

Catalytic Properties of the Pillared Materials

1-Butanol dehydration. Butanol dehydration studies were carried out for the conventional pillared clay (PPE), pillared acid-activated clays (PAAC), and calcined acid-activated clays (CAAC). The results presented in Table 4 reveal an order of conversion PAAC > PPE > CAAC. The values in Table 4 were determined after several pulses during which time the conversion stabilised. The main products of the reaction (i.e., 95–98%) are butenes. Trace amounts of dibutyl ether (DBE) are formed (CAAC ~ PPE > PAAC), which increase slightly with reaction temperature. Since the production of DBE is likely to require the occupation of two vicinal active sites by butanol molecules, the very low selectivity to DBE may be due to the use of a pulse microreactor which does not generate high butanol partial pressure in the reactant stream. As a result, the occupied active sites on the catalysts are distant from one another, thereby excluding the production of DBE. On the other hand, it is possible that the porosity and acidity of the clay catalysts favours the dehydration of butanol to butenes. This seems more likely and is in agreement with previous studies on butanol dehydration, over acid-washed clays, which reported similar product selectivity (96–100%) to butenes (34).

The order of conversion revealed in Table 4 correlates well with the acidity determined by the cyclohexylamine method (see Table 2), indicating that at 250°C Brønsted acid sites play an important role in the dehydration. A good agreement also exists between the catalytic activity and the acidity determined by FTIR spectroscopy of adsorbed pyridine. However, at 250°C, the catalytic activity of the CAAC is much lower than that of PPE despite comparable acidity, probably as a result of the lower surface area of the CAAC. What clearly emerges is the fact that the pillared acid-activated clays are better catalysts than the conventional pillared clay. In addition, the good activity of the pillared acid-activated clays at 450°C is an

TABLE 4

Butanol Dehydration Conversion over Various Clay Catalysts

Clay	Conversion (%)		
	250°C	350°C	450°C
PPE	19.5	57.5	82.0
PPE25	37.5	78.1	95.3
PPE30	40.1	80.2	96.4
PPE35	32.4	76.5	92.7
PPE40	31.7	77.2	92.3
PPE45	31.0	75.4	91.7
PPE60	29.7	75.0	89.0
C-PE30[a]	8.3	40.2	63.7
C-PE35[a]	9.0	44.8	69.0
C-PE40[a]	9.2	45.7	65.2

[a] Nonpillared acid-activated clays calcined at 500°C.

indication that these materials do not lose their catalytic activity at high temperatures. The variation in catalytic activity within the pillared acid-activated clays, although small, seems to indicate the attainment of a maximum for clay PPE30 corresponding to a ReO value of 19.2% and alumina incorporation of 1.32 mmol/g.

The extent of 1-butene (1B) isomerisation to 2-butene (2B) has previously been used to characterise the acidity of solid acid catalysts. Studying a range of silica-aluminas, Berteau *et al.* (28) found that isomerisation was associated with the presence of strong and very strong acid sites. Scokart *et al.* (35) have also shown that, on fluorinated aluminas, the isomerisation is related to the development of Brønsted acid sites. The ability of the clay catalysts, in the present study, to promote isomerisation was investigated by following the ratio of 2B to 1B at a reaction temperature of 250°C (corresponding to conversion in the range 8–40%). The results are given in Table 5 (2B/1B ratio at 350°C is given for clays with low conversion at 250°C) and show that all the catalysts exhibit significant isomerisation (78–88% selectivity to 2B). However, the extent of isomerisation on the PAAC (85–87% selectivity to 2B; 5.4–6.5 2B/1B ratio) is greater compared to PPE and the CAAC (78–80% selectivity to 2B; 3.5–3.9 2B/1B ratio). The results obtained are in some ways similar to those obtained for silica-aluminas by Berteau *et al.* (28). They found that for silica-aluminas with an alumina content of <60% the selectivity to 2B and 1B was 70% and 20%, respectively, corresponding to a 2B/1B ratio of 3.5. This similarity is to be expected because on silica-aluminas, as with clays, some Brønstead and Lewis acid sites originate from the isomorphous substitution of trivalent aluminum for tetravalent silicon in the silicate lattice (for silica-aluminas) or the tetrahedral manifold for montmorillonite clays. Furthermore, the production by the clay catalysts of trace amounts of DBE is similar to the behaviour of pure silica (28). This is also to be expected as both silica and clay matrices (especially acid-treated matrices) possess hydroxyl groups which are in fact intrinsic Brønsted acid sites. We suggest, therefore, that the acidity developed by the clay catalysts studied here is comparable to that possessed by pure silica and silica-aluminas with alumina content <60% and that the extent of isomerisation indicates the presence of a significant number of strong and very strong acid sites. The greater isomerisation for PAAC suggests that, at the reaction temperature (250°C) used in the investigation, these materials possess stronger (Brønsted) acid sites compared to PPE or the CAAC.

Cumene Cracking/Dehydrogenation

Cumene conversation was carried out over four different sets of clays: (1) the conventional pillared clay (PPE), (2) the pillared acid-activated clays (PAAC), (3) calcined acid-activated clays (CAAC), and (4) calcined raw clay (C-PE). The results are summarised in Table 6. The values shown are those determined after several pulses during which the conversion stabilised. It emerges that the nonpillared clays have lower activity compared to the pillared clays with C-PE exhibiting the lowest activity. This is to be expected as montmorillonite clays treated at high temperatures are known to possess low surface area and acidity (15). The highest activity is shown by the pillared acid-activated clays with a maximum for clays PPE30 and PPE40 (corresponding to ReO values of 19.2 and 28.7). As with the butanol dehydration reaction, the order of

TABLE 5

Selectivity of Butanol Conversion at 250°C

Clay	Product selectivity (μmol)		
	2-Butene	1-Butene	2-Butene/1-Butene
PPE	8.3	2.2	3.8(3.9)[b]
PPE25	17.2	3.2	5.4
PPE30	18.4	3.4	5.9
PPE35	15.0	2.7	5.6
PPE40	14.8	2.5	5.4
PPE45	14.2	2.4	5.9
PPE60	13.7	2.1	6.5
C-PE30[a]	3.5	0.9	3.9(2.7)
C-PE35[a]	3.8	1.0	3.8(2.8)
C-PE40[a]	3.9	1.1	3.5(2.6)

[a] Nonpillared acid-activated clays calcined at 500°C.

[b] Figures in parentheses are 2B/1B ratio at reaction temperature of 350°C.

TABLE 6

Cumene Hydrocracking Results over Various Clays

Clay	Conversion (%) 300°C	 400°C	 500°C
PPE	3.2(7.1)	33.0(18.0)	50.1(7.7)
PPE30	14.2(36.0)	42.0(31.8)	60.3(7.9)
PPE40	13.3(44.0)	46.2(29.1)	61.3(7.6)
PPE45	10.0(34.8)	40.7(28.2)	57.8(7.8)
PPE60	7.3(37.5)	35.6(31.4)	53.2(11.0)
C-PE30[a]	1.2(2.4)	9.4(2.6)	31.4(1.8)
C-PE45[a]	2.2(0.9)	7.1(1.2)	35.6(1.2)
C-PE[b]		3.1(0.35)	24.4(0.25)

Note. (Figures in parentheses are the ratio of benzene yield to α-methylstyrene yield).

[a] Nonpillared acid-activated clays calcined at 500°C.

[b] Raw clay calcined at 500°C.

activity revealed in Table 6 correlates well with the acidity of the clays after thermal treatment at 350°C (see Figs. 4 and 5).

The calcined raw clay (C-PE) exhibits mainly dehydrogenation activity with the cracking/dehydrogenation ratio (given as the benzene/α-methylstyrene ratio in Table 6) remaining more or less constant at 400 and 500°C despite a large difference in total conversion. We may, therefore, conclude that most of the acid sites on this clay are of the Lewis type. CAAC, on the other hand, exhibits both cracking and dehydrogenation with a slightly higher proportion of cracking. The pillared materials are significantly different, exhibiting mainly cracking with a very small amount of dehydrogenation. The improvement in the activity of the pillared materials (both PPE and the PAAC) over the nonpillared clays is primarily due to increase in benzene production. It would appear, therefore, that exposed silicate (clay sheet) Brønsted acid sites are responsible. This contention is supported by the higher cracking/dehydrogenation ratio (at 300 and 400°C) of the PAAC compared to PPE which can only be explained by the higher silicate Brønsted acidity of the PAAC (generated by acid treatment prior to pillaring). As with the butanol dehydration reaction, the product selectivity of cumene conversion over the pillared materials is similar to that reported for silica-aluminas (35), i.e., mainly cracking to benzene and propene. Studying silica-aluminas, Parera *et al.* (36) found that cumene cracking activity was proportional to Brønsted acidity stronger in equivalence than 72% H_2SO_4. It therefore seems likely that in the temperature range 250 to 400°C pillared acid-activated clays exhibit acidity similar to that of silica-aluminas and that a large proportion of the acid sites are strong Brønsted acid sites. It is, however, surprising that the high Lewis acidity noted at 350°C (see Figs. 4 and 5) in the pyridine IR studies does not lead to higher levels of dehydrogenation. Nonetheless, the results obtained are a good indication of the variation, with temperature, of the Brønsted/Lewis acidity ratio for the clays studied.

CONCLUSIONS

Pillared acid-activated clays (PAAC), suitable as solid acid catalysts, may be prepared by the exchange of polymeric cations into the interlayer region of suitably acid-activated clays. It is necessary to select the level of acid treatment carefully in order to optimise the surface area, pore volume, surface acidity, and thermal stability of the final pillared clay. For the clay used in the present study, the optimum level of acid treatment is that which removes between 19 and 35% of the metal ions from the octahedral manifold of the clay matrix. Due to the varying nature of montmorillonite clays, these values are expected to change from clay to clay. The PAAC have basal spacings, surface areas, and thermal stability comparable to conventional pillared clays but possess significantly higher pore volume and acidity. Additionally the (meso)pore size distribution of the PAAC is broader and shifted toward higher values with the extent of the shift dependent on the level of acid treatment of the host matrix. The higher acidity of the PAAC over conventional pillared clays is mainly due to an increase in intrinsic Brønsted acid sites on the clay matrix brought about by acid treatment prior to pillaring. The higher acidity of the pillared acid-activated clays is reflected by better catalytic activity for the acid-catalysed reactions studied. Based on observations from both test reactions, we conclude that the additional matrix Brønsted acid sites are similar to those on silica-aluminas and are strongest in the temperature range 250 to 400°C.

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