JOURNAL OF
Materials
CHEMISTRY

Al and Zr pillared acid-activated saponite clays: characterization and properties

Fathi Kooli and William Jones*

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW.
E-mail: WJ10@cam.ac.uk

An acid-activated saponite has been used in the preparation of Al and Zr pillared acid-activated clays. The properties of this new family of pillared clays (pillared acid-activated saponites, PAASs) have been compared to those of conventional pillared (non-activated) saponites (PILSs). It is found that the acid treated materials incorporate less Al or Zr than the parent saponite, with the most likely cause being the reduced cation exchange capacity of the matrix following acid-activation. Powder X-ray diffraction suggests that Al PAASs are thermally more stable than the corresponding Zr PAASs. The acidity of the pillared materials (as monitored by cyclohexylamine adsorption–desorption thermogravimetry studies) is related to the nature and to the amount of the metal oxides incorporated between the sheets of the host clays. Catalytic data for the Brønsted catalysed dehydration of pentan-1-ol is reported.

Introduction

The intercalation of smectite clays by hydroxy-metal polycations results, after calcination at approximately 500 °C, in the formation of so-called pillared clays (PILCs). When compared to parent non-pillared clays such PILCs have been demonstrated to possess improved thermal stability as well as increased surface area and surface acidity.[1] As a result interest has focused on PILCs as potential materials for a wide range of applications: for example, as catalysts and adsorbents.[2–6]

In the context of potential uses of pillared clays, it has been demonstrated that variation of the pillaring procedure[7,8] can affect the properties of the resulting pillared materials. Furthermore, it is known that the nature of the clay also plays a significant role in controlling, for example, the acidity of the PILC.[1,9,10] One approach to varying the nature of the matrix is by acid-activation—this treatment is known to result in materials with properties different to those of the parent clay, *e.g.* increased surface area and higher acidity values.[11–13] Furthermore, such acid-modified materials can be subsequently pillared and the resulting pillared acid-activated clays (PAACs) have improved chemical and physical properties compared to those of conventional PILCs, including higher pore volume and enhanced acidity.[14–16]

Several studies have focussed on the properties of pillared saponites—particularly with alumina pillars.[17–21] Recently, however, we have reported on the pillaring of saponite with zirconia[22] or titania.[23] The thermal stability and acidity of the pillared saponites which were obtained were shown to depend strongly on the nature of the metal oxide located between the layers.[22] To date, however, no data related to the preparation of pillared acid-activated saponites (PAASs) have been reported in the literature. In previous work,[24] we have fully characterized an acid-activated natural saponite (based on a saponite available from the Source Clay Repository, Columbia, USA). In this paper we examine the physico-chemical properties (*e.g.* structure, acidity and catalytic performance) of the products obtained after pillaring the acid-activated saponite with Al and Zr. We compare these properties with those of conventional pillared (non-activated) saponites.

Experimental section

Acid-activation of the saponite clay

The saponite clay was obtained from the Source Clay Repository, Columbia, USA, and was used in its as-received form. The clay contains tremolite as impurity. One purpose of the study was to develop methods for the large-scale synthesis of pillared materials and as a result no attempt was made to remove this impurity. The method of acid activation has been described in detail elsewhere.[24] In summary, the clay was slurried in a solution of distilled water and sulfuric acid at 90 °C for 16 h. Acid/clay (w/w) ratios between 0.1 and 0.4 were used (dry clay/98% H_2SO_4).[24] The resulting acid-activated clays were repeatedly washed with hot distilled water until SO_4^{2-} free and dried at 60 °C.

Exchange and pillaring of the acid-activated saponite

Al pillars. A constant solution/clay ratio of 50 ml g^{-1}(corresponding to an Al/clay ratio of 6 mmol g^{-1}) was used for the Al exchange. Precursor pillared clays were prepared by adding the acid-activated saponite to a stirred solution of the pillaring reagent, previously aged for 1 h at 80 °C. The pillaring agent was prepared using aluminium chlorhydrate solution (ACH) supplied by Albright and Wilson. The resulting mixture was maintained at 80 °C for a further 1 h and then cooled to room temperature by the addition of cold distilled water. The mixture was filtered and repeatedly washed with distilled water until free of Cl^- ions (as tested by $AgNO_3$). These precursor pillared materials were air-dried at room temperature. Samples were then calcined at 500 °C for 4 h in air to yield the final pillared material.

Zr pillars. A solution containing 9.66 g of zirconyl chloride octahydrate in 250 ml of distilled water was aged with stirring at 80 °C for 1 h. A suspension of clay (2% by weight) was then added (corresponding to 6 mmol of Zr per g of clay) and the mixture stirred for 1 h at 80 °C. The product was filtered and repeatedly washed with distilled water. Samples where then calcined at 500 °C for 4 h in air to yield the pillared material.

For both the Al and Zr samples a similar sample designation is used. For example, 01Sa90Zr indicates that the saponite was acid-activated at an acid/clay ratio of 0.1 at 90 °C and exchanged at 80 °C with Zr polycations followed by calcination at 500 °C.

To confirm the effect of acid activation on the properties of the pillared products, Al and Zr pillared saponite samples (*i.e.* without prior acid-activation of the clay) were also prepared using procedures similar to those for the acid-activated clays. These materials are designated SaCaAl and SaCaZr.

Characterization techniques

Elemental analysis was performed on a Camscan S4 scanning electron microscope operating at 20 kV. The data were processed through a ZAF4 program running on a Link 860 series 2 processor. Powder X-ray diffraction (PXRD) patterns were recorded on a Philips PW 1710 diffractometer, with Ni-filtered Cu-Kα radiation. Surface areas, pore volumes and pore size distributions were obtained using a Micromeritics ASAP 2000 porosimeter. The samples were out-gassed under vacuum (*ca.* 10^{-3} Torr) for 3 h at 200 °C prior to analysis.

Brønsted acidity (proton concentration) was determined using thermogravimetry (TG) and cyclohexylamine adsorption–desorption measurements.[25] TG was carried out under dry nitrogen ($25\ \mathrm{cm^3\ min^{-1}}$) at a heating rate of $10\ ^\circ\mathrm{C\ min^{-1}}$. The weight loss which was observed between 290 and 420 °C was used to compute the acidity in terms of mmol of cyclohexylamine desorbed. It was assumed that each molecule of the base interacts with one protonic acid site.

Pyridine was used as a probe molecule to distinguish between Brønsted and Lewis acid sites.[26] Fourier transform IR (FTIR) spectra of adsorbed pyridine were measured using a Nicolet 205 FTIR spectrometer. Approximately 40–50 mg of material that had been previously calcined in air for 4 h at 500 °C was pressed (for 2 min at 10 tonnes $\mathrm{cm^{-2}}$ pressure under approximately 10^{-2} Torr vacuum) into a self-supporting wafer of 13 mm diameter. The wafer was further calcined under vacuum (10^{-3} Torr) at 500 °C for 2 h and then exposed to pyridine vapour at ambient temperature. Whilst exposed to the pyridine atmosphere the sample was further heated at 100 °C for 1 h to allow the pyridine to permeate the sample. The wafer was cooled to ambient temperature and evacuated for 1 h at various temperatures between 100 and 500 °C. Spectra were then recorded at ambient temperature.

Catalytic activity was investigated using the dehydration of pentan-1-ol. Similar reaction conditions to those previously reported were chosen.[15,25] As an example, 0.3 g of pillared clay and 3 ml of pentan-1-ol were mixed in a stainless steel batch reactor which was sealed and heated (without stirring) at 200 °C for 4 h. The reaction was subsequently stopped by immersion of the reactors in ice. A Carlo Erba HRGC 5300 Mega series gas chromatograph was used to analyse the products.

Results and discussion

Chemical analysis

Fig. 1 indicates the amount of Al and Zr [expressed as mmol Al/Zr (g clay)$^{-1}$] exchanged into the raw and acid-activated clays. The parent saponite (*i.e.* without acid activation) contains the largest amount of intercalated Al or Zr. With increasing extent of acid activation the amount of Al or Zr incorporated decreases. It is likely that this decrease with increasing severity of treatment is connected to the decrease in cation exchange capacity of the clay during acid activation.[15] Fig. 1 indicates that the amount of Al incorporated into the acid-activated saponites is higher than that of Zr. One contributing factor to this difference may be the pH of the exchange solution—it is significantly lower for the Zr solution and may lead to a further acid activation and subsequently further decrease in exchange capacity. It will also depend on the exact nuclearity and charge of the exchanging polyoxocation.

Powder X-ray diffraction (PXRD)

Following exchange of the parent saponite with the Al polyoxocation an intense 001 reflection is observed at 19.30 Å. Similar spacings were also obtained for the acid-treated clays although the intensity of the reflection decreases with the degree of acid activation. Additional reflections due to the tremolite impurity are still present in the PXRD. Fig. 2 shows the PXRD patterns following calcination of the samples at 500 °C. The pillared materials still exhibit a sharp and intense 001 reflection, with a reduced d_{001} spacing of 18.20 Å. The slight decrease in spacing compared to the precursor materials (from 19.30 to 18.20 Å) results from the accompanying dehydroxylation of the hydroxy-Al polycations. Additional experiments confirmed that for the Al pillared materials the layered structure was preserved for calcination temperatures up to 700 °C.[27] Only for the most acid-activated matrix (04Sa90Al) is there no evidence for a reflection at 18.20 Å.

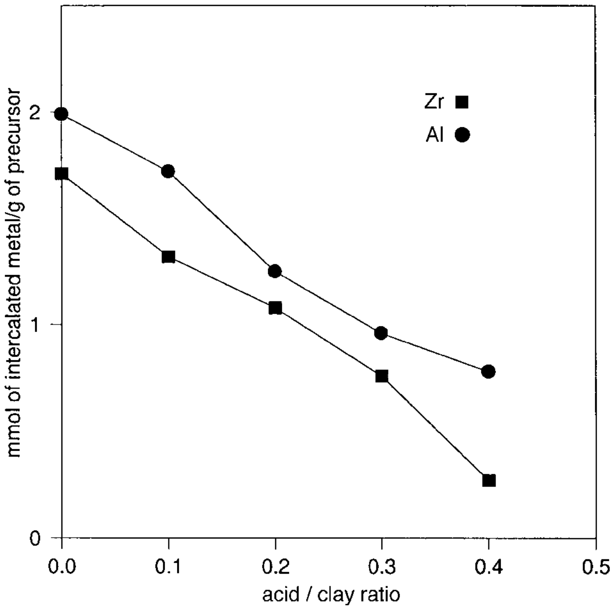

Fig. 1 Evolution of the amount of Al and Zr incorporated as a function of acid activation level

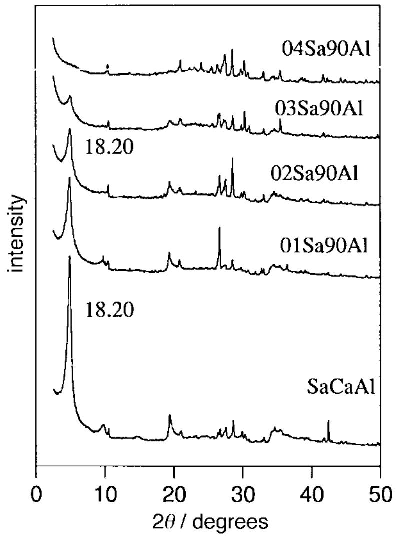

Fig. 2 PXRD patterns of the Al pillared acid-activated saponites after calcination at 500 °C

For the Zr exchanged samples, the intensity and the spacing of the 001 reflection were also related to the degree of acid activation of the saponite. As for Al the intensity of the 001 reflection decreased as the level of acid-activation increased. For clays acid activated at ratios 0.3 and 0.4 there is little evidence for a d_{001} reflection. For the other samples the d_{001} spacing decreases from 19.30 Å (for the non-activated clay) to 17.50 Å (for the sample activated at a ratio of 0.2). After calcination of the precursors at 500 °C (Fig. 3) X-ray diffraction confirmed that the layered structure for SaCaZr and 0.1Sa90Zr was still preserved. Again there was a small decrease in spacing

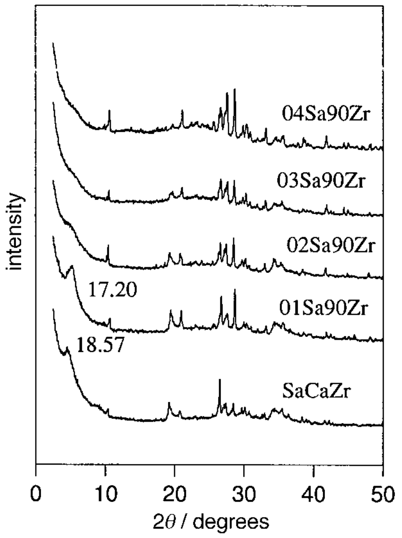

Fig. 3 PXRD patterns of the Zr pillared acid-activated saponites after calcination at 500 °C

after calcination. For 0.2SaZr90 the 001 reflection became very weak with most long-range structure lost and for 03Sa90Zr and 04Sa90Zr little structure close to 17 Å is seen in the pattern.

Previous studies have observed that the nature of the pillar influences the thermal stability of the product.[24,28] For Zr PAASs the structure appears stable up to 500 °C, whereas for Al PAASs the structure is maintained following calcination at 700 °C. In the case of Zr PAASs the d_{001} spacing decreases as less Zr is incorporated. This, apparently, is not the case for Al, where similar values are obtained irrespective of the amount of Al intercalated.

Microporosity and surface area

The shape of the isotherm for SaCaAl (Fig. 4) most closely follows that of type IV. The hysteresis loop is of type H3 in the IUPAC classification and corresponds to materials that possess slit-shaped pores between parallel layers.[29] For the Al pillared acid-activated saponites (the trace for 02Sa90Al is representative and is shown in Fig. 5) the isotherms also appears to be of type IV with a hysteresis loop similar to that of SaCaAl. The volume of nitrogen adsorbed at high pressures also increases for the pillared acid-activated matrix compared to the pillared non-activated material.

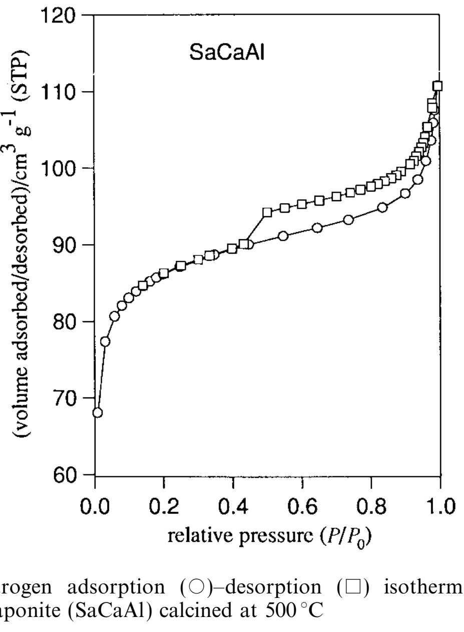

Fig. 4 Nitrogen adsorption (○)–desorption (□) isotherms of Al-pillared saponite (SaCaAl) calcined at 500 °C

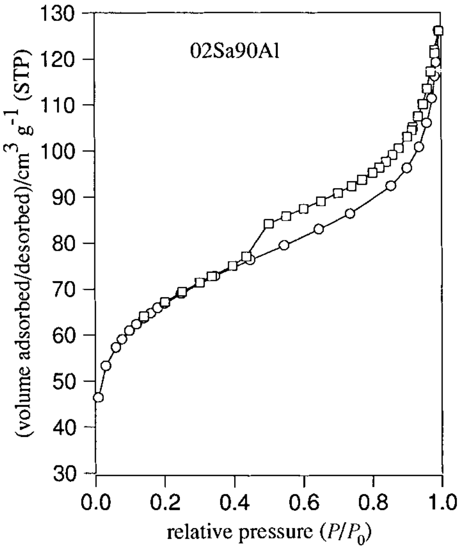

Fig. 5 Nitrogen adsorption (○)–desorption (□) isotherms of Al-pillared acid-activated saponite (02Sa90Al) calcined at 500 °C

Table 1 shows the total BET and micropore specific surface areas and pore volumes as well as the average pore diameters for the various Al containing samples—see ref. 30 for a full discussion of the procedure. The surface areas are (except for the 03Sa90Al and 04Sa90Al samples) higher than those of the starting non-pillared clays. The surface area arising from the presence of micropores decreases as the degree of acid activation increases such that the highest total and micropore surface areas are obtained for SaCaAl (a trend which is noticeably opposite to that for the clays prior to pillaring). The average pore diameters for the samples vary between approximately 20 and 30 Å. Similar behaviour has been reported for Al pillared acid-activated montmorillonites.[15,30]

Similar trends are seen in the case of Zr pillared materials. The adsorption isotherm is comparable to the alumina case (compare Fig. 5 and 6) although the desorption branch does not close at low relative pressures. Similar observations have been noted for a titanium pillared saponite.[23] The specific surface areas of the Zr pillared materials, like their Al counterparts, generally increase, compared to the non-pillared matrix, as a result of pillaring (Table 1). The non-activated sample SaCaZr material has the lowest specific surface area, with the specific surface area and the specific micropore and pore volume increasing with increasing acid treatment. The trends differ, therefore, from the case with Al pillars and again may reflect the effect of the lower pH of the exchange solution for Zr, resulting in increased amounts of silica being present for the Zr case. Comparable average pore diameter values to those for Al are obtained.

Acidity characterisation

Brønsted acidity. Table 2 gives the numbers of Brønsted acid sites for the Al and Zr pillared materials as measured using cyclohexylamine as the probe molecule. The values are expressed per weight of clay at 290 °C so as to exclude any differences in the amount of physisorbed base or interlamellar water. The acid sites measured by this method are those accessible and strong enough to interact with the base, and it is assumed that each molecule of the base interacts with one protonic (Brønsted) acid site.[25,31] The number of acid sites in Al pillared clays is higher than that of the corresponding non-pillared clays confirming that pillaring increases acidity. SaCaAl has the highest number of Brønsted sites (0.60 mmol H^+ per g of clay at 290 °C): the numbers of Bronsted acid sites then decreases for the pillared acid-activated materials. The acidity of 04Sa90Al is relatively high compared to the

Table 1 Specific surface areas and pore volumes of pillared materials after calcination at 500 °C

sample	surface area/m^2 g^{-1}	micropore area/m^2 g^{-1}	pore volume/ ml g^{-1}	micropore volume/ ml g^{-1}	average pore diameter/Å
SaCaAl	329(8)	262(1)	0.163(0.027)	0.103(—)	20
01Sa90Al	254(112)	142(23)	0.162(0.125)	0.060(0.01)	25
02Sa90Al	243(216)	106(81)	0.180(0.196)	0.042(0.034)	29
03Sa90Al	171(321)	85(137)	0.121(0.261)	0.035(0.048)	30
04Sa90Al	241(332)	60(137)	0.185(0.231)	0.026(0.057)	31
SaCaZr	190(8)	56(1)	0.120(0.027)	0.067(—)	25
01Sa90Zr	225(112)	73(23)	0.148(0.125)	0.087(0.01)	26
02Sa90Zr	236(216)	100(81)	0.173(0.196)	0.112(0.034)	28
03Sa90Zr	277(321)	139(137)	0.216(0.206)	0.163(0.048)	32
04Sa90Zr	338(332)	161(137)	0.234(0.231)	0.170(0.057)	29

Values in parentheses are the values of the starting acid-activated saponites calcined at 500 °C for 4 h. (—) Negligible.

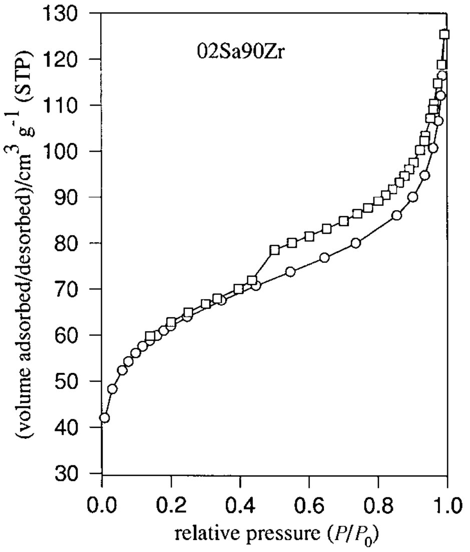

Fig. 6 Nitrogen adsorption (○)–desorption (□) isotherms of Zr pillared saponite (02Sa90Zr) calcined at 500 °C

Table 2 Acidity values and catalytic activity for pentan-1-ol dehydration

samples	mmol H^+ per g of pillared clays[a]	pentanol conversion, non-pillared[b]	pentanol conversion, pillared[c]
SaCaAl	0.60(0.20)	0	85(0.57)
01Sa90Al	0.51(0.45)	23	48(0.45)
02Sa90Al	0.57(0.46)	26	71(0.67)
03Sa90Al	0.43(0.35)	11	56(1.54)
04Sa90Al	0.32(0.09)	—	12(9)
SaCaZr	0.58(0.20)	0	39(0.78)
01Sa90Zr	0.49(0.45)	23	25(0.68)
02Sa90Zr	0.42(0.46)	26	23(1.01)
03Sa90Zr	0.36(0.36)	11	10(1.59)
04Sa90Zr	0.16(0.09)	—	3.5(5.2)

[a] Values in parentheses correspond to acidity values of the starting acid-activated saponites. [b] After calcination at 500 °C for 4 h. [c] Values in parentheses correspond to selectivity expressed as the molar ratio of pentene : ethers. (—) Negligible.

clay matrix and may be related to Al adsorbed on the surface of the amorphous silica phase. In the case of Zr pillared materials, the presence of Zr increases the concentration of protons for SaCaZr and 01Sa90Zr materials. The acidity then decreases compared to the starting matrix. SaCaZr has the highest concentration of protons (0.58 mmol H^+ per g) in the series. This decline in apparent acidity for acid-activated saponites may be related to the inaccessibility of the probe molecule to the acidic sites—Fig. 2 confirms that the layered structure is collapsed for an acid/clay ratio higher than 0.2.

The Al pillared acid-activated saponites show higher acidity compared to the Zr analogues, possibly as a result of the better crystallinity of the Al materials. It has been previously reported that in the case of montmorillonite clays acid activation can result in an increase in the acidity of the resulting pillared materials.[15,32] In the case of saponite clays, however, acid activation prior to pillaring decreases the acidity of the resulting pillared clays.

Brønsted and Lewis acidity. The adsorption–desorption of pyridine at different temperatures has been used to further investigate the nature and strength of the acid sites present on the pillared acid-activated saponites.

The FTIR of pyridine adsorbed on SaCaAl has been previously reported.[22] For SaCaAl a single Brønsted (B) acid site (bands at 1547 and 1640 cm^{-1}) and two Lewis acid sites (L1 at 1449 and 1612 cm^{-1} and L2 at 1456 and 1621 cm^{-1}) were identified. We have suggested elsewhere[22] that the two Lewis sites may be due to adsorption on the clay sheets and the interlayer pillars. These two sites responded differently to thermal treatment. At 300 °C or higher temperature, pyridine bound to Bronsted sites has desorbed, and only the L2 sites remained.

For the acid-activated clays prior to pillaring two types of Lewis acid sites exist as the acid/clay ratio increases.[24] (Fig. 7 illustrates the case for an acid:clay ratio of 0.2.) Above 300 °C

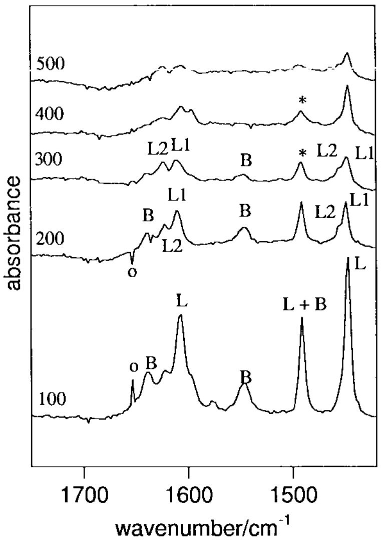

Fig. 7 FTIR spectra of pyridine adsorbed on an acid-activated saponite (0.2Sa90 sample) followed by outgassing at different temperatures (°C). (B) and (L1, L2) correspond to pyridine bound to Bronsted and two different types of Lewis site. (B + L) corresponds to pyridine bound to both types of acid sites (*). Peaks marked (○) result from poor subtraction of the background spectra.

pyridine bound on Brønsted sites is lost and pyridine remains only on the L1 sites. After pillaring with Al polycations the Brønsted acidity is not greatly modified, although there is an apparent increase in the Lewis acid content, and especially that associated with L2 sites. This is clearly the case above 300 °C. (Fig. 8 illustrates the behaviour for the 02Sa90Al sample.) FTIR of pyridine adsorbed on Zr pillared saponite suggests similar Brønsted acidity to the non-pillared acid-treated clay as well as the Al pillared variant. For the Zr pillared acid-activated clays, however, only one type of Lewis site is evident (Fig. 9).[22]

The concentration of Brønsted and Lewis acid sites referenced to unit weight of sample (q_H/μmol g^{-1}) has been obtained according to the equation:[33]

$$q_H = (A_I \pi R^2)/w\varepsilon_I \quad (1)$$

where R (cm) is the radius of the wafer and w (g) is the weight of the sample. Integrated absorbance values, A_I, were obtained from the spectra after baseline optimisation at 1547 and 1456–1443 cm^{-1}; q_H values were then determined using eqn. (1) from A_I data obtained at different temperatures, and ε_I values relative to Brønsted and Lewis sites are 1.67 and 2.22 cm mmol^{-1}.[34] The data for the different pillared clays are presented in Table 3 and are based on measurements for samples after outgassing at 200 °C (the temperature at which catalytic testing was performed).

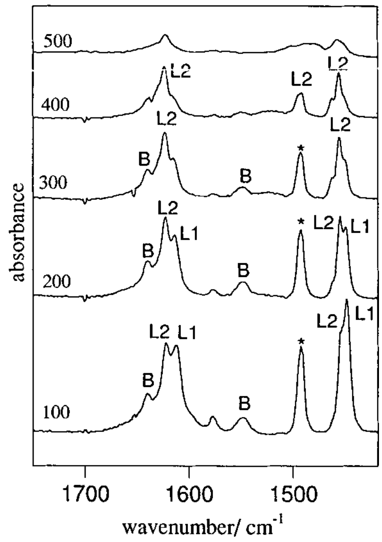

Fig. 8 FTIR spectra of pyridine adsorbed on Al-pillared acid-activated saponite (0.2Sa90Al material) following by outgassing at different temperatures (°C). Two different types of Lewis sites are present. (*) see legend to Fig. 7.

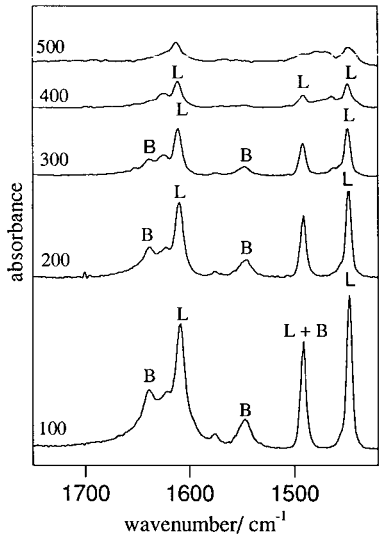

Fig. 9 FTIR spectra of pyridine on Zr pillared acid-activated saponite (0.2Sa90Zr) followed by outgassing at different temperatures (°C). Only one type of Lewis acid site is detected.

After pillaring with Al or Zr (Table 3), the Brønsted concentration increases for the pillared material prepared from the non-activated saponite. However, for the clays pillared using the acid-activated saponites, the Brønsted concentration does not differ significantly from the starting materials. The number of Lewis acid sites is improved, however, after pillaring. The highest Lewis concentration is obtained with SaCaAl. The general trend would appear to follow the amount of either Al or Zr introduced during pillaring. The relative proportion of Brønsted to Lewis acidity is also presented in Table 3. The ratio [B]/[L] is lower for the pillared clays compared to the starting clays further indicating that the presence of alumina or zirconia improves Lewis acidity compared with Brønsted acidity.

Dehydration of pentan-1-ol

In the presence of acid sites pentan-1-ol is dehydrated to form a mixture of products, with the major constituents being pentene, 1,1-diethyl ether and 1,2-diethyl ether.[35] Table 2 indicates the percentage of pentan-1-ol conversion for the various pillared clays. Values for the parent clay and acid-activated clays without pillaring are also shown. The product selectivity values are expressed as the molar ratio of pentene : ethers. The presence of alumina in the pillared saponites improves the pentan-1-ol conversion compared to the non-pillared variants (Table 2), with SaCaAl being the most active. For the pillared acid-activated saponites, dehydration reaches a maximum at an acid/clay ratio of about 0.2, then decreases at an acid/clay ratio of 0.4. These data are in good agreement with the concentration of protons evaluated from the cyclohexylamine desorption measurements except for the 04Sa90Al sample which gave a relatively low conversion. The dehydration of pentan-1-ol to ethers has been reported to be related to the strength of the Brønsted acid sites on the surface of the catalyst. The selectivity data in Table 2 indicate that SaCaAl has the highest Brønsted acidity with low selectivity to pentene formation.

In the case of Zr pillared clays Table 2 indicates that the conversion of pentan-1-ol decreases as the acid activation level of the clay increases. For the pillared acid-activated saponites, however, the conversion is quite similar to the starting non-pillared materials, and might suggest that some acid sites are not accessible to pentan-1-ol, in agreement with the PXRD data indicating collapse for 02Sa90Zr and 03Sa90Zr (Fig. 3). The SaCaZr sample shows high selectivity to ethers, indicating that the Brønsted acid sites are strong compared to those of pillared acid-activated saponites. These data are in good agreement with the acidity values calculated from the adsorption–desorption of cyclohexylamine.

Overall the conversion by Al pillared acid-activated

Table 3 Concentration of Brønsted (q_B) and Lewis (q_L) acid sites (μmol g^{-1}) of pillared clays after outgassing under vacuum at 200 °C

sample	q_B	q_L	[B]/[L]
SaCaAl	15(00)	122(—)	0.12(—)
0.1Sa90Al	15(16)	80(32)	0.19(0.50)
0.2Sa90Al	14(18)	83(50)	0.17(0.36)
0.3Sa90Al	12(12)	70(41)	0.17(0.29)
SaCaZr	19(00)	100(—)	0.19(—)
0.1Sa90Zr	17(16)	70(32)	0.24(0.50)
0.2Sa90Zr	20(18)	55(50)	0.36(0.36)
0.3Sa90Zr	15(12)	40(41)	0.38(0.29)

Values in parentheses correspond to the starting clays. (—) Neglible.

saponites is higher than for the Zr materials suggesting that the Al pillared materials are more acidic than the Zr samples.[22] The higher crystallinity of the Al pillared materials is also likely to improve the accessibility of the pentan-1-ol molecules to the acid sites. No apparent trends in selectivity are observed.

Concluding remarks

It is known that the removal of some charge sites along with the dissolution of the clay during acid activation decreases the cation exchange capacity of a clay. This is reflected in the fact that the amount of Al or Zr incorporated is lower in the acid-activated saponites than for the parent saponite clay (Fig. 1). The layered structure of Al pillared acid-activated saponites is stable to about 700 °C whereas for Zr samples loss of structure (as monitored by PXRD) occurs at 500 °C. Reasonably ordered structures are obtained from mildly acid-activated saponites with calcination temperatures below 500 °C.

The microtextural properties of the Al pillared acid-activated saponites are different to those of the non-activated derivatives. The specific area decreases with increasing levels of acid activation, although pore volumes increase, reflecting the mesoporous character of the pillared material obtained from the acid-activated clays. The specific surface areas and pore volumes of the Zr pillared materials, however, generally increase with the level of acid activation of the clays.

The acidity calculated from the adsorption–desorption of cyclohexylamine and pyridine indicates that pillared saponite (SaCaAl or SaCaZr) is more acidic compared to the Al or Zr pillared acid-activated saponites, with Al samples more acidic compared to Zr analogues. In general, the pillared clays obtained from acid-activated saponites show different properties than those obtained from pillared non-acid-activated saponites. Overall, there is, however, little improvement in terms of microtexture and acidity for pillared acid-activated saponites. This is to be compared with pillared acid-activated montmorillonites, where the pillared acid-activated clays have higher surface areas and are more acidic than the non-activated variants.

The authors are grateful to EC for funding this work (BE Contract BRE2-CT94-0629). We are particularly grateful to Laporte Industries Ltd, and Dr. G. Elwell and colleagues, for the determination of surface area and porosity data. Useful discussions with Dr. R. Mokaya are gratefully acknowledged.

References

1 K. Ohtsuka, *Chem. Mater.*, 1997, **9**, 2039.
2 M. L. Occelli, J. T. Hsu and L. G. Galya, *J. Mol. Catal.*, 1985, **33**, 371.
3 R. Burch and C. I. Warburton, *Appl. Catal.*, 1987, **33**, 395.
4 J. R. Jones and J. H. Purnell, *Catal. Lett.*, 1993, **18**, 137.
5 R. Molina, A. Schutz and G. Poncelet, *J. Catal.*, 1994, **145**, 79.
6 E. Gutierrez and E. Ruiz-Hitzky, in *Pillared Layered Structures: Current Trends and Applications*, ed. I. V. Mitchell, Elsevier Applied Sciences, London, 1990, pp.199–208.
7 K. Takahana, M. Yokoyama, S. Hirao, S. Yamanaka and M. Hattori, *J. Mater. Sci.*, 1992, **27**, 1297.
8 K. Ohtsuka, Y. Hayashi and M. Suda, *Chem. Mater.*, 1993, **5**, 1823.
9 K. Urabe, N. Kouno, H. Sakurai and Y. Izumi, *Adv. Mater.*, 1991, **3**, 558.
10 A. Vieira-Coelho and G. Poncelet, *Appl. Catal.*, 1991, **96**, 1991.
11 I. Zyla and M. Olzar, *Mineral. Pol.*, 1984, **15**, 67.
12 S. Mendioroz, J. A. Pajares, C. Pesquera, F. Gonzalez and C. Blanco, *Langmuir*, 1987, **3**, 676.
13 C. N. Rhodes and D. R. Brown, *Catal. Lett.*, 1994, **24**, 285.
14 R. Mokaya and W. Jones, *J. Chem. Soc., Chem. Commun.*, 1994, 929.
15 J. Bovey and W. Jones, *J. Mater. Chem.*, 1995, **5**, 2027.
16 T. Mishra and K. Parida, *J. Mater. Chem.*, 1997, **7**, 147.
17 K. Urabe, H. Sakurai and Y. Izumi, *J. Chem. Soc., Chem. Commun.*, 1986, 1074.
18 P. B. Malla and S. Komarneni, *Clays Clay Miner.*, 1993, **41**, 472.
19 L. Bergaoui, J. F. Lambert, R. Franck, H. Suquet and J. L. Robert, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 2229.
20 L. Bergaoui, J. F. Lambert, H. Suquet and M. Che, *J. Phys. Chem.*, 1995, **99**, 2155.
21 S. Moreno, R. Sun Kou and G. Poncelet, *J. Catal.*, 1996, **162**, 198.
22 F. Kooli and W. Jones, *Chem. Mater.*, 1997, **9**, 2913.
23 F. Kooli, J. Bovey and W. Jones, *J. Mater. Chem.*, 1997, **7**, 153.
24 F. Kooli and W. Jones, *Clay Miner.*, 1997, **32**, 633.
25 C. Breen, *Clay Miner.*, 1991, **26**, 473.
26 E. R. Parry, *J. Catal.*, 1963, **2**, 371.
27 F. Kooli and W. Jones, unpublished data.
28 R. Burch and C. I. Warburton, *J. Catal.*, 1986, **97**, 503.
29 S. J. Gregg and K. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 1982.
30 R. Mokaya and W. Jones, *J. Porous Mater.*, 1995, **1**, 99.
31 J. A. Ballantine, J. H. Purnell and J. M. Thomas, *Clay Miner.*, 1983, **18**, 347.
32 R. Mokaya and W. Jones, *J. Catal.*, 1995, **153**, 76.
33 T. Barzetti, E. Selli, D. Moscotti and L. Forni, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 1401.
34 C. A. Emeis, *J. Catal.*, 1993, **141**, 347.
35 J. A. Ballantilline, M. Davies, I. Patel, J. H. Purnell, M. Rayanakorn, K. J. Williams and J. M. Thomas, *J. Mol. Catal.*, 1984, **26**, 37.

Paper 8/04101F; *Received* 1st *June*, 1998