Chem. Mater. **1997,** *9,* 2913−2920

Systematic Comparison of a Saponite Clay Pillared with Al and Zr Metal Oxides

Fathi Kooli and William Jones*

University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge CB2 1EW, UK

Received April 23, 1997. Revised Manuscript Received August 25, 1997[⊗]

Alumina and zirconia pillared Ballarat saponites have been prepared by cation exchange of the saponite in aluminum chlorhydrate and zirconyl chloride solutions, respectively. The nature of the pillaring species and the method of preparation have been varied in order to examine their effect on the amount of occluded oxide, as well as the thermal stability, surface area, and acidic properties of the resulting pillared clays. Higher reaction (cation exchange) temperature (80 °C) enhances the degree of polymerization, increases the mobility of the pillaring species, and results in greater incorporation between the sheets of the saponite. In general, it is observed that the alumina-pillared saponites have a higher thermal stability than their zirconia-pillared analogues and retain an ordered layered structure even after calcination at 700 °C. Infrared spectroscopy of adsorbed pyridine suggests the presence of Bronsted acid sites and two types of Lewis acid sites (of different strength) for the alumina-pillared materials. Only single types of Bronsted and Lewis acid sites, however, were detected for the zirconia-pillared saponites. The thermal desorption of cyclohexylamine and dehydration of pentan-1-ol were used as further probes to monitor the acidity of the different pillared saponites.

Introduction

There has been considerable interest in the intercalation of relatively large hydroxymetal polycations into the interlayer regions of smectite clays. Upon calcination at about 500 °C, these polycations are converted within the clay to stable metal oxide, thus keeping the silicate layers apart at an increased interlayer distance compared with the raw clay. A large variety of polycation species have been used to pillar smectites clays such as Al,[1−10] Zr,[11−13] Ti,[14−17] Cr,[18−20] and Fe.[21,22]

In general, pillared clays have a high specific surface area and increased pore volume compared to the parent clays, with a pore size distribution situated predominantly in the micropore range.[23] The clay sheets have weak acid sites found in the interlayer space at sites of cation exchange.[24] Therefore an improvement of surface acidity is expected for the pillared clays and thought to be partially due to the metal oxide pillars themselves.[25,26] The presence of pillars yield clay materials which possess both Lewis and Bronsted acid sites,[27] with at high temperatures (i.e., 400−500 °C) the acidity of pillared clays being predominantly of the Lewis type.[26,28]

Various applications of pillared clays as acid catalysts and adsorbents have been reported.[5,18,29−32] The identity of the pillaring species and/or the host clay and the preparation conditions have an important effect on the thermal stability, the texture and the acidic properties of the obtained pillared clay. It has, for example, been reported that alumina-pillared beidellite (a clay with tetrahedral lattice Al for Si substitution) is noticeably more active than alumina-pillared montmorillonite (with Mg for Al substitution in the octahedral layers) in certain catalytic reactions.[33,34] We have also recently reported that titania-pillared rectorite (TiRP) has a high

---

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1997.

(1) Kikuchi, E.; Matsuda, T.; Ueda, J.; Morita, Y. *Appl. Catal.* **1985**, *16*, 401.

(2) Brindley, G. W.; Sempels, R. E. *Clay Miner.* **1977**, *12*, 229.

(3) Ghosh, S.; Mukundan, P.; Warrier, K. G. K.; Damodaran, A. D. *J. Mater. Sci. Lett.* **1991**, *10*, 1193.

(4) Gutierrez, E.; Ruiz-Hitzky, E. In *Pillared Layered Structures: Current Trends and Applications*; Mitchell, I. V., Ed.; Elsevier Applied Sciences: London, 1990; pp 199−208.

(5) Jones, J. R.; Purnell, J. H. *Catal. Lett.* **1993**, *18*, 137.

(6) Mendioroz, S.; Gonzalez, F.; Pesquera, C.; Benito, I.; Blanco, C.; Poncelet, G. *Stud. Surf. Sci. Catal.* **1993**, *75*, 1637.

(7) Pesquera, C.; Gonzalez, F.; Benito, I.; Mendioroz, S.; Pajares, J. A. *Appl. Catal.* **1991**, *69*, 97.

(8) Pinnavaia, T. J.; Rainey, V.; Tzou, M. S.; White, J. W. *J. Mol. Catal.* **1984**, *27*, 213.

(9) Tichit, D.; Fajula, F.; Figueras, F.; Ducourant, B.; Mascherpa, G.; Gueguen, C.; Bousquet, J. *Clays Clay Miner.* **1988**, *36*, 369.

(10) Kooli, F.; Bovey, J.; Jones, W. *J. Mater. Chem.* **1997**, *7*, 153

(11) Burch, R.; Warburton, C. I. *J. Catal.* **1986**, *97*, 511.

(12) Burch, R.; Warburton, C. I. *J. Catal.* **1986**, *97*, 503.

(13) Yamanaka, S.; Brindley, G. W. *Clays Clay Miner.* **1979**, *27*, 119.

(14) Sterte, J. *Clays Clay Miner.* **1986**, *34*, 658.

(15) Baksh, M. S.; Kikkinides, E. S.; Yang, R. T. *Ind. Eng. Chem. Res.* **1992**, *31*, 2181.

(16) Bernier, A.; Admaiai, L. F.; Grange, P. *Appl. Catal.* **1991**, *77*, 269.

(17) Lin, J.-T.; Jong, S.-J.; Cheng, S. *Microporous Mater.* **1993**, *1*, 287.

(18) Bradley, S. M.; Kydd, R. A. *J. Catal.* **1993**, *142*, 448.

(19) Brindley, G. W.; Yamanaka, S. *Am. Mineral.* **1979**, *64*, 830.

(20) Pinnavaia, T. J.; Tzou, M. S.; Landau, S. D. *J. Am. Chem. Soc.* **1985**, *107*, 4783.

(21) Yamanaka, S.; Doi, T.; Sako, S.; Hattori, M. *Mater. Res. Bull.* **1984**, *19*, 161.

(22) Oades, J. M. *Clays Clay Miner.* **1984**, *32*, 49.

(23) Gil, A.; Montes, M. *Langmuir* **1994**, *10*, 291.

(24) Davitz, J. C. *J. Catal.* **1976**, *43*, 260.

(25) Figueras, F. *Catal. Rev-Sci. Eng.* **1988**, *30*, 457.

(26) Ming-Yuan, H.; Zhonghui, L.; M, E. *Catal. Today* **1988**, *2*, 231.

(27) Occelli, M. L.; Tindwa, R. M. *Clays Clay Miner.* **1983**, *31*, 22.

(28) Bagshaw, S. A.; Cooney, R. P. *Chem. Mater.* **1993**, *5*, 1101.

(29) Molina, R.; Moreno, S.; Vieiracoelho, A.; Martens, J. A.; Jacobs, P. A.; Poncelet, G. *J. Catal.* **1994**, *148*, 304.

(30) Molina, R.; Schutz, A.; Poncelet, G. *J. Catal.* **1994**, *145*, 79.

(31) Burch, R.; Warburton, C. I. *Appl. Catal.* **1987**, *33*, 395.

(32) Occelli, M. L.; Hsu, J. T.; Galya, L. G. *J. Mol. Catal.* **1985**, *33*, 371.

(33) Molina, R.; Scutz, A.; Poncelet, G. *J. Catal.* **1994**, *145*, 79.

(34) Vieira-Coelho, A.; Poncelet, G. *Appl. Catal.* **1991**, *96*, 1991.

S0897-4756(97)00254-8 CCC: $14.00 Published 1997 by the American Chemical Society

thermal stability compared to titania-pillared montmorillonites (TiMP) and saponites (TiSP).[10] TiSP, however, has a higher acidity than TiMP and TiRP materials.

Alumina-pillared saponites (AlSP) have been recently prepared and well characterized by various authors.[35−45] However, little data concerning the titanium-pillared saponite[10] and no data concerning the zirconia-pillared saponite (ZrSP) have been reported. Here we examine the preparation and systematic characterization of a range of saponites pillared with alumina and zirconia. The acidity and catalytic activity of these materials are also reported.

Experimental Section

The saponite clay was obtained from the Source Clay Repository, of the Clay Minerals Society, and has a cation exchange capacity of 72 mequiv/100 g. It contains tremolite as impurity. We were particularly interested in studying the raw nonpurified clay because a long-term goal is to study pillaring with large amounts (e.g., kilogram) of clay. The saponite was, therefore, used as received.

Sample Preparation. *Aluminum Precursor-Pillared Clays (AlSP).* An aluminum chlorhydrate solution (Albright and Wilson) was used as the source of pillaring agent. A constant solution/clay ratio of 50 mL/g corresponding to an Al/clay ratio of 6 mmol/g was maintained throughout all the preparations. Precursor-intercalated clays were prepared by adding the raw air-dried saponite to the stirred pillaring reagent which had been previously aged for 1 h at 80 °C. The resulting reaction mixture was then maintained at 80 °C for a further 1 h with constant stirring to allow the intercalation reaction (by cation exchange) to take place. The resulting slurry was filtered and repeatedly washed with distilled water until free of Cl^- ions (as tested by $AgNO_3$). The sample was then air-dried to obtain the precursor aluminum-intercalated clays (AlSP80).

To study the effect of the temperature on the exchange of aluminum, the reaction was also performed at room temperature without prior aging of the aluminum solution. This precursor will be identified as AlSPRT.

Zirconium Precursor-Pillared Clays (ZrSP). Three methods were used to prepare the zirconium precursor-pillared clays.

(i) Aging method: A zirconyl chloride octahydrate solution of 120 mmol/L was aged at 80 °C for 1 h, corresponding to an Zr/clay ratio of 6 mmol/g. A suspension of clay (2 wt %) was added and maintained at 80 °C for 1 h with mechanical stirring. The resulting zirconium-precursor-pillared clay (ZrSP80) was cooled to room temperature and washed repeatedly with distilled water until free of chloride ions.

(ii) Room-temperature method: A zirconyl chloride octahydrate solution was used at room temperature without prior aging (ZrSPRT sample). Otherwise a similar procedure was followed to that described above.

(iii) Reflux method: A zirconyl chloride octahydrate solution was refluxed before exchange with the clay. A three-necked round-bottom flask containing 250 cm^3 of a solution of 30 or 60 mmol of zirconium was refluxed in a glycerol bath over a hot plate for 1 h and then cooled to 80 °C. A suspension of the clay (2 wt %) was added to the pillaring solution and the mixture held at 80 °C for 1 h with mechanical stirring. The precursor-pillared clays (ZrSPRF6 and ZrSPRF12, with Zr/clay ratio of 6 and 12 mmol/g, respectively) were separated by filtration and washed with distilled water until free of chloride ions.

The different precursor-pillared materials were calcined at temperatures between 500 and 850 °C for 4 h in air. The term “pillared” is used for materials obtained after calcination.

Characterization Techniques. A Philips PW 1710 diffractometer with Ni-filtered, Cu Kα radiation was used to record the powder X-ray diffraction (PXRD) patterns. Elemental composition (via EDX analysis) was obtained using a Camscan S4 scanning electron microscope at 20 kV. The data were processed through a ZAF4 program running on a Link 860 series 2 processor. Surface area, pore volume, and pore size distributions were obtained using a Micromeritics ASAP 2000 porosimeter. The samples were degassed under vacuum for 3 h at 200 °C prior to analysis.

The concentration of the Bronsted acid sites (proton concentration) was determined using thermogravimetric analysis (TG) of the pillared saponites following cyclohexylamine adsorption.[46] The thermogravimetric analysis was performed on a Polymer Laboratories TGA 1500. Dry nitrogen at a flow rate of 25 cm^3/min was used and a heating rate of 10 °C/min was employed. The weight loss between 290 and 420 °C was used to compute the acidity in terms of mmol of cyclohexylamine desorbed. This temperature range was chosen after examination of the profile of the TGA curve. 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 (Bronsted) acid site.

Fourier transform infrared (FTIR) spectra of adsorbed pyridine was used to differentiate between the Lewis and Bronsted acid centers. The FTIR spectra of chemisorbed pyridine were measured within a vacuum sell using a Nicolet 205 FTIR spectrometer. The pillared saponite (20−30 mg) was pressed (for 2 min at 10 tons/cm^2 pressure under vacuum) into a self-supporting wafer 13 mm in diameter. The wafer was subsequently calcined within the cell and under vacuum (10^{-3} Torr) at 500 °C for 2 h and then exposed to pyridine vapor at ambient temperature. The sample was then heated at 100 °C for 1 h (in the pyridine atmosphere) to allow the pyridine to permeate the sample. The wafer was again cooled to ambient temperature and held under vacuum for 1 h. The wafer was then heated under vacuum for 1 h at temperatures between 100 and 500 °C, with FTIR spectra subsequently recorded at ambient temperature.

The catalytic activity of the different pillared saponites was investigated using as test reaction the dehydration of pentan-1-ol using the batch method. Pillared clay (0.3 g) and pentan-1-ol (3 mL) were mixed in stainless steel batch reactors, sealed and heated (without stirring) at 200 °C for 4 h.[47] The reaction was quenched by immersion of the reactors in ice. A Carlo Erba HRGC 5300 Mega series gas chromatograph was used to analyze the products.

Results and Discussion

Powder X-ray Diffraction. Figure 1 presents the PXRD patterns of the AlSP80 precursor-pillared saponite after calcination for 4 h at different temperatures. The pattern of the raw saponite is shown for comparison (Figure 1a).

---

(35) Bergaoui, L.; Lambert, J. F.; Suquet, H.; Che, M. *J. Phys. Chem.* **1995**, *99*, 2155.

(36) Bergaoui, L.; Lambert, J. F.; Franck, R.; Suquet, H.; Robert, J. L. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2229.

(37) Bergaoui, L.; Lambert, J. F.; Suquet, H.; Che, M. *J. Chim. Phys. Phys.-Chim. Biol.* **1995**, *92*, 1486.

(38) Bergaoui, L.; Lambert, J. F.; Vicente Rodriguez, M. A.; Michot, L. J.; Villieras, F. *Langmuir* **1995**, *11*, 2849.

(39) Chevalier, S.; Franck, R.; Lambert, J. F.; Barthomeuf, D.; Suquet, H. *Clay Miner.* **1992**, *27*, 245.

(40) Chevalier, S.; Suquet, H.; Franck, R.; Marcilly, C.; Barthomeuf, D. In *Expanded Clays and Other Microporous Solids*; Occelli, M. L., Robson, H. E., Eds.; Van Nostrand Reinhold: New York, 1992; pp 32−46.

(41) Chevalier, S.; Franck, R.; Lambert, J. F.; Barthomeuf, D.; Suquet, H. *Appl. Catal. A—General* **1994**, *110*, 153.

(42) Urabe, K.; Sakurai, H.; Izumi, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1074.

(43) Malla, P. B.; Komarneni, S. *Clays Clay Miner* **1993**, *41*, 472.

(44) Moreno, S.; Sun Kou, R.; Poncelet, G. *J. Catal.* **1996**, *162*, 198.

(45) Vicente, M. A.; Banares-Munoz, M. A.; Suaerz, M.; Pozas, J. M.; Lopez-Gonzalez, J. d. D.; Santamaria, J.; Jimenez-Lopez, A. *Langmuir* **1996**, *12*, 5143.

(46) Breen, C. *Clay Miner.* **1991**, *26*, 473.

(47) Bovey, J.; Jones, W. *J. Mater. Chem.* **1995**, *5*, 2027.

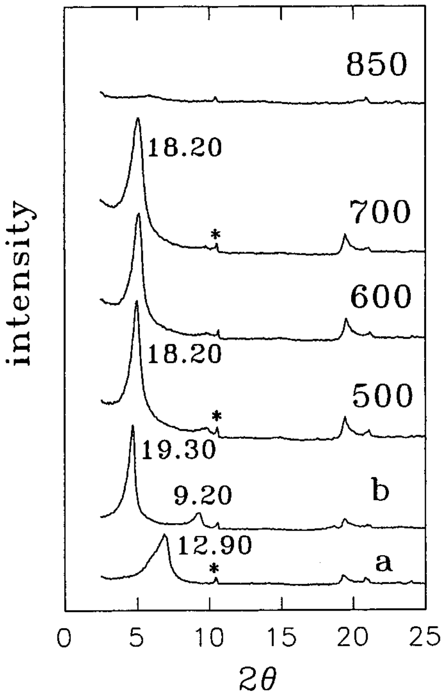

Figure 1. PXRD patterns of (a) the raw saponite and (b) after intercalation of aluminum at 80 °C; (c−f) correspond to precursor (b) calcined at 500, 600, 700, and 850 °C for 4 h, respectively. Asterisks indicate tremolite impurities.

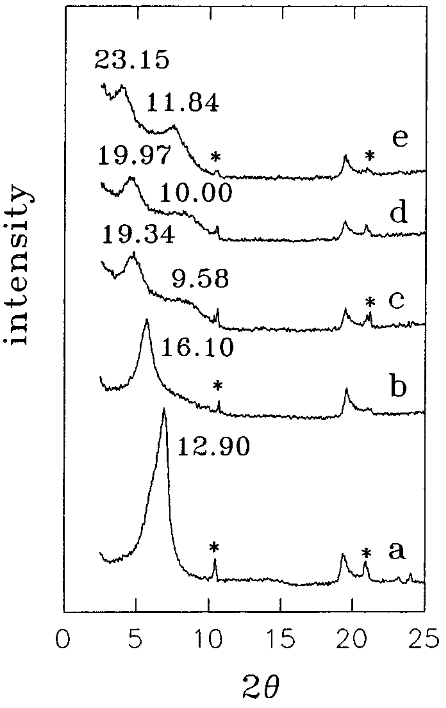

Figure 2. PXRD patterns of (a) the raw saponite and after intercalation of zirconium at different conditions: (b) at room temperature (RT); (c) after aging and exchange at 80 °C; (d, e) precursors prepared after refluxing the zirconium solution with different concentrations of 60 and 120 mmoles, respectively. Asterisks indicate tremolite impurities.

The precursor-pillared AlSP80 pattern (Figure 1b) shows that the basal d_{001} spacing increases from 12.90 to 19.30 Å upon intercalation of the aluminum polycationic species. Similar values have been previously reported for clays exchanged with aluminum polyhydroxy cations.[39,43,44,47] The PXRD pattern exhibits a sharp and intense basal reflection, suggesting that the precursor is well ordered. Upon calcination at 500 °C, the PXRD pattern (Figure 1c) shows that the intense 001 reflection shifts from 19.30 to 18.20 Å. This slight contraction is due to the dehydroxylation of the aluminum pillaring species. Figure 1 also shows that the layered structure of AlSP80 is stable even after calcination at 700 °C. At 850 °C, however, the structure is destroyed, with no significant reflections at low angles. At this high temperature, dehydroxylation of the silicate sheet has occurred.[48]

The PXRD pattern (not shown) of aluminum precursor-pillared saponite prepared at room temperature (AlPSRT) is similar to that prepared at 80 °C (AlSP80), with an intense and sharp reflection at 19.30 Å, suggesting that similar materials are obtained regardless of the exchange temperature.

In the case of zirconium, however, the nature of the PXRD pattern obtained is strongly related to the preparation conditions of the precursors. Figure 2a corresponds to the starting clay, and Figure 2b corresponds to PXRD pattern of the ZrSPRT precursor. The 001 reflection is shifted from 12.90 to 16.10 Å. This value is lower than that obtained (19.34 Å) when the exchange is carried out at 80 °C (Figure 2c). The sharpness and the intensity of the 001 reflection are also different for both precursors, suggesting that the long-range order is better following exchange at room temperature than at 80 °C. It has been reported that the reduction of the intensity of the 001 reflection during acid activation of montmorillonite[47,49] and saponite[50] clays is due to the degradation of the layered structure as a result of acid attack of the silicate sheets. In the present case, during the aging process at 80 °C, the zirconium solution becomes progressively more acidic and the silicate layers of the raw saponite may be degraded. If this were the case, less zirconium is expected to be intercalated, as a result of the decrease in CEC during acid degradation. From the chemical analysis data, however, the content of zirconium in ZrSP80 is higher than that of ZrSPRT. An explanation may be that different types of Zr species are being inserted at room temperature and at 80 °C. Such differences would clearly affect the composition and also influence the nature of the corresponding X-ray powder patterns.

When the zirconium solution (with a ratio of 6 mmol of Zr/g of clay) is refluxed prior to exchange (ZrSPRF6), the basal spacing increases slightly and the intensity of the 001 reflection decreases (Figure 2d). When the ratio of mmoles of zirconium in the solution is doubled prior to reflux, the PXRD pattern obtained (ZrSPRF12, Figure 2e) indicates that the basal spacing increases further to ca. 23.15 Å, and the layered structure is better ordered with a 002 reflection clearly observed at ca. 11.84 Å.

Clearly, the nature of the hydroxyzirconium cations intercalated between the clay sheets is related to the concentration of zirconium and temperature of aging of the exchange solution. When the solution of zirconium

---

(48) Mackenzie, R. C. *Simple phyllosilicates based on gibbsite and brucite-like sheets*; Academic Press: London, 1970; Vol. I, p 497.

(49) Mokaya, R.; Jones, W. *J. Chem. Soc., Chem. Commun.* **1994**, 929.

(50) Kooli, F.; Jones, W. *Clay Minerals* **1997**, *32*, 633.

Table 1. Chemical Analysis of Precursor-Pillared Saponites with Aluminum and Zirconium Prepared under Various Conditions[a]

sample	SiO_2	Al_2O_3	MgO	Fe_2O_3	TiO_2	ZrO_2	Na_2O	CaO	m^{*b}
saponite	62.46	4.44	23.30	1.49	0.38	0.63	4.75	2.53	
AlSPRT	61.34	14.04	20.47	1.22	0.42	0.21		1.63	1.93
AlSP80	60.38	15.14	20.55	1.26	0.41	0.14		1.44	2.20
ZrSPRT	55.15	4.00	22.04	1.37	0.19	15.24		1.33	1.10
ZrSP80	44.71	3.50	18.98	1.03	0.25	29.27		1.57	1.76
ZrSPRF12	42.90	3.07	18.65	0.98	0.33	31.95		1.63	1.86

[a] Weight % oxide. [b] m^* corresponds to the amount of the aluminum or zirconium intercalated (mmol/g of clay).

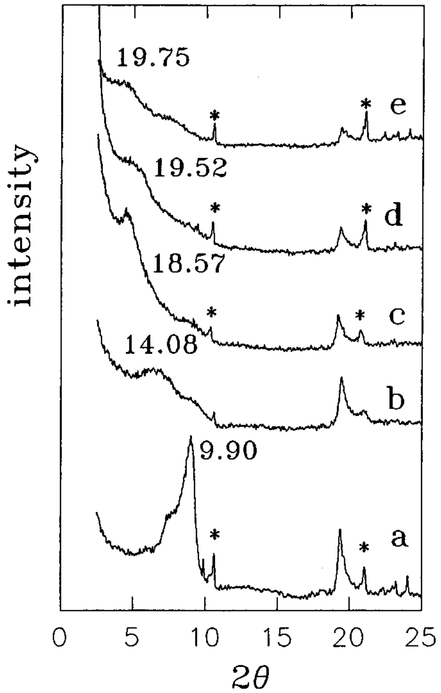

Figure 3. PXRD patterns of (a) the raw saponite and precursors obtained after intercalation of zirconium at different conditions and calcined at 500 °C for 4 h (legends see Figure 2). Asterisks indicate tremolite impurities.

is refluxed, polymerization to three-dimensional clusters based upon the tetramers occurs,[51] which leads to a more expanded product compared to that obtained after aging at 80 °C. Similar results have been obtained with a synthetic sodium fluoride tetrasilicic mica silicate clay.[52]

The PXRD patterns of raw saponite and zirconium-pillared precursors, following calcination at 500 °C, are presented in Figure 3. A complex 001 reflection of low intensity is observed at 14.08 Å for the ZrSPRT (Figure 3b). This value is higher than the 001 reflection of calcined raw saponite (9.9 Å, Figure 3a), confirming the presence of zirconium species between the layers. In the case of ZrSP80 (Figure 3c), a reflection at 18.57 Å is observed with lower intensity compared to the non-calcined precursor. The PXRD patterns of ZrSPRF6 and ZrSPRF12 (Figure 3d,e, respectively) exhibits a 001 reflection at about 19.52–19.75 Å with a fairly ordered layered structure preserved for the calcined ZrSPRF12. When the precursor pillared saponite (ZrPS80) is calcined at higher temperatures between 600 and 700 °C, the intensity of the 001 reflection declines and becomes broad (PXRD patterns not shown). At 850 °C, destruction of the lattice structure occurs.

Table 2. Specific Surface Areas and Pore Volumes of the Different Pillared Saponites after Calcination at 500 °C

sample	specific surface area (m^2/g)	micropore area (m^2/g)	pore vol (cm^3/g)	micropore vol (cm^3/g)	av pore diam (Å)
saponite	8	1	0.027		130
AlSPRT	245	189	0.127	0.075	21
AlSP80	329	262	0.163	0.103	20
ZrSPRT	57	47	0.071	0.061	49
ZrSP80	190	57	0.120	0.067	25
ZrSPRF12	219	149	0.125	0.058	23

The stability of the pillared clays at higher temperatures is due to the presence of the metal oxide pillars themselves. It appears that the stability is affected by the nature of the pillaring cation and the pillar density.[53,54] It has previously been reported that zirconia-pillared montmorillonites are more stable than the equivalent alumina-pillared clays.[12] However, in our case, it seems that the Al-pillared saponites are more stable compared to Zr-pillared clays with a very ordered material obtained for Al-pillared saponites.

Chemical Analysis. Table 1 presents the results of elemental analysis of the saponite after exchange of aluminum and zirconium under the various preparation conditions.

Comparing AlSPRT and AlSP80, the amount of aluminum intercalated increases slightly when the aluminum solution is aged at 80 °C. A similar trend is observed for the ZrSPRT and ZrSP80 precursors; the amount of zirconium in ZrSPRT is lower than that in the ZrSP80 sample. When the zirconium exchange solution is refluxed, a further slight increase of the zirconium content is observed compared to that obtained at 80 °C. The content of intercalated aluminum is higher compared to that of zirconium, irrespective of the experimental conditions. We observe also that the ratios of mmol of Al or Zr/g of clay after exchange are always lower compared to the starting solutions.

Calcium is not completely removed during the cation exchange reaction (Table 1), with residual amounts due to the tremolite impurity in the starting clay.

Textural Properties. PXRD data as a function of temperature provides information about the well-ordered regions of the sample and high surface areas may be obtained form apparently poorly ordered samples. To correlate the stability of the pores with temperature, we have measured N_2 adsorption data after calcination of the samples at different temperatures. The average pore diameters, total BET, and micropore specific surface areas and total and micropore volumes of the different pillared saponites are given in Table 2 for materials calcined at 500 °C in air for 4 h. We note

---

(51) Fryer, J. R.; Hutchison, J. L.; Paterson, R. *J. Colloid Interface Sci.* **1970**, *34*, 238.

(52) Ohtsuka, K.; Hayashi, Y.; Suda, M. *Chem. Mater.* **1993**, *5*, 1823.

(53) Bovey, J. Ph.D. Thesis, Cambridge, 1992.

(54) Tichit, D.; Fajula, F.; Figueras, F.; Bousquet, J.; Gueguen, C. *Stud. Surf. Sci. Catal.* **1985**, *20 (Catal. Acids Bases)*, 351.

that a well-pillared sample is likely to give a high micropore content and that any mesoporosity is likely to be due to stacking disorder and/or platelet stacking effects.

The nitrogen isotherms (not shown) of the alumina-pillared saponites (AlSPRT and AlSP80) are of Langmuir type I for low relative pressures (p/p_0), indicating the presence of micropores. For high values of p/p_0 a type IV isotherm is observed, corresponding to mesoporous solids.[55] The hysteresis loops are of type H3 in the IUPAC classification, attributed to adsorbents having slit-shaped pores between parallel layers. Similar shapes of isotherms are obtained for the zirconia-pillared materials, with a decrease of the adsorbed volume (cm^3/g) of nitrogen.

The specific surface areas of the pillared samples are much higher than those of the raw saponite itself, although the value obtained varies with the exchange reaction conditions and with the nature of the pillars between the clay sheets. AlSPRT has a lower specific surface area and pore volume compared to AlSP80, i.e., the micropore area and volume are enhanced when the temperature of intercalation is approximately 80 °C. Only a slight difference is observed for the average pore diameters which are intermediate between microporous and mesoporous materials.

In the case of zirconia-pillared saponites, the values of the specific surface area and pore volumes are always lower than those of corresponding the alumina-pillared materials (Table 2). The highest value of specific surface area and pore volume is obtained for ZrSPRF12. The ZrSPRT has the lowest value of specific surface area and pore volume. The average pore diameter increases as the amount of zirconia in the pillared materials decreases, i.e., larger pores are formed as the interpillar distance increases. The values of the average pore diameters indicate that zirconia-pillared saponites have more mesoporous character than the alumina-pillared saponites.

We note that the specific surface area and pore volume of the alumina-pillared saponites (AlSP80) reduce rapidly upon calcination at temperatures between 600 and 700 °C, although the PXRD patterns obtained for samples calcined at 500, 600, and 700 °C are similar.[56] Similar data have been reported for alumina-pillared montmorillonites.[53] The reduction in specific surface area and pore volume may be due to the collapse of a fraction of the micropores. Alternatively, a number of micropores may become inaccessible to nitrogen molecules as a result of some structural rearrangement upon exposure to high temperature. At higher temperatures (about 850 °C), a sharp reduction of the specific surface area occurs to ca. 2 m^2/g. In this case complete dehydroxylation of the host lattice occurs and no ordered layered structure is obtained. Similar results are observed for the zirconia-pillared saponite (ZrSP80). The surface area is strongly related to the temperature of calcination and the nature of the pillars between the clay sheets.

Acidity Characterization. *Bronsted Acidity.* The acidity values obtained by temperature-programmed desorption of cyclohexylamine for the raw and pillared saponites calcined at 500 °C are given in Table 3. The values are expressed in mmol of protons per weight of pillared clay at 290 °C.

Table 3. Proton Concentration and Conversion of Pentan-1-ol of Raw and Pillared Saponites

sample	mmol of H$^+$ g^{-1}	pentan-1-ol conversion
saponite	0.20	[a]
AlSPRT	0.60	60 (0.60)[b]
AlSP80	0.62	85 (0.57)
ZrSPRT	0.55	49 (0.82)
ZrSP80	0.58	39 (0.78)
ZrSPRF12	0.48	[c]

[a] Negligible. [b] Indicates the molar ratio of pentene to ethers. [c] Not determined.

The results indicate that the pillaring process increases the acidity of the pillared clays compared to that of raw saponite. The number of acid sites in the pillared samples depends on the nature of the pillars and on the synthesis conditions. The alumina-pillared saponites have higher acidity compared to those pillared with zirconia. We observe that the acidity of the pillared clays prepared at 80 °C is slightly higher compared to that of materials prepared at room temperature, probably as a result of different amounts of intercalated aluminum or zirconium. For the ZrSPRF12, the acidity (0.48 mmol of H$^+$ g^{-1}) is lower than that prepared at 80 °C (0.58 mmol of H$^+$ g^{-1}), although a higher amount of intercalated zirconium and a larger surface area are obtained for this material. This could be an anomaly or could indicate that some sites in the interlayer region of sheets are blocked by the zirconium species.

Bronsted and Lewis Acidity. FTIR spectroscopy of pyridine was used to further probe the nature and the strength of the acid sites of the pillared saponites.

Previous studies of the raw saponite indicated that few Lewis acid sites are detected on the clay.[50,57] Depending on the nature of the pillar, different trends are observed for the pillared clays. For the AlSP80 material, the FTIR spectra obtained in the region 1750–1420 cm^{-1} following exposure to pyridine vapor and thermal treatment at increasing temperatures under vacuum are shown in Figure 4. The FTIR spectra are different compared to that of raw saponite. After desorption of pyridine at 100 °C, new bands at 1640, 1612, 1547, 1492, and 1449 cm^{-1} are observed with a shoulder at 1621 cm^{-1} also recorded. The bands at 1547 and 1640 cm^{-1} are assigned to pyridine bound on Bronsted acid sites (B).[58,59] The bands at 1612 and 1449 cm^{-1} are attributed to pyridine bound to Lewis acid sites (L1).[58,59] The band at 1492 cm^{-1} may be attributed to pyridine associated with both Lewis and Bronsted acid sites (L1+B).[58,59] At 200 °C, the intensity of the bands corresponding to L1 (1449 and 1612 cm^{-1}) decreases, and we observe a splitting of the band in the region 1460–1440 cm^{-1}, indicating that pyridine is bound to two different Lewis acid sites (the additional band at 1621 cm^{-1} may be associated to pyridine bound to Lewis acid sites (L2)). The Bronsted band (B) is also present. When the temperature of desorption increases (300 °C), the L1 bands decrease compared to those of L2. The

---

(55) Gregg, S. J.; Sing, W. *Adsorption, Surface Area and Porosity*; Academic Press: London, 1982.

(56) Kooli, F.; Jones, W., unpublished data.

(57) Chevalier, S.; Franck, R.; Suquet, H.; Lambert, J. F.; Barthomeuf, D. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 667.

(58) Parry, E. P. *J. Catal.* **1963**, *2*, 371.

(59) Lefrancois, M.; Malbois, G. *J. Catal.* **1971**, *20*, 350.

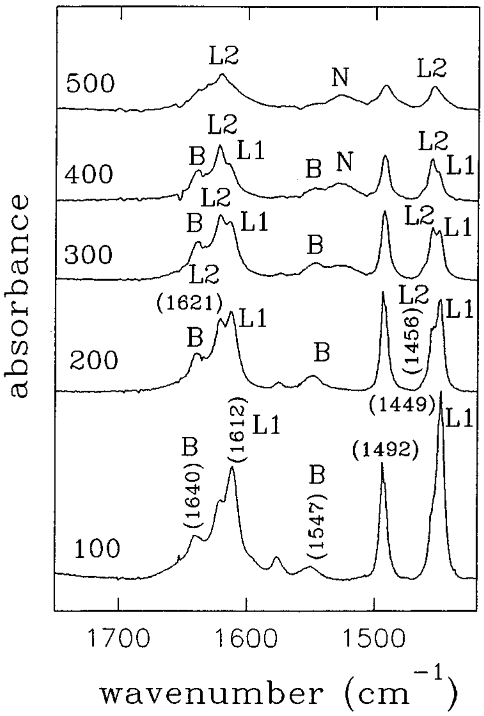

Figure 4. FTIR spectra of adsorbed pyridine on alumina-pillared saponite prepared at 80 °C (AlSP80), followed by outgassing at different temperatures (in °C). B = Bronsted, L1 and L2 = Lewis bands, N = new band due to the decomposition of pyridine (see text and ref 60).

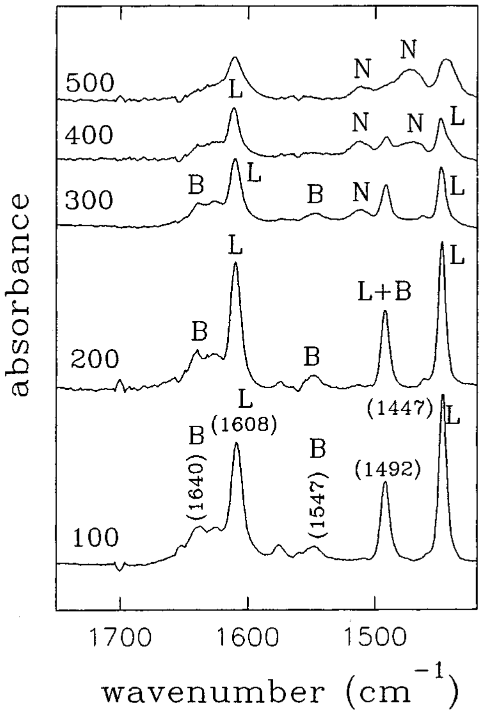

Figure 5. FTIR spectra of adsorbed pyridine on zirconia-pillared saponite prepared at 80 °C (ZrSP80), followed by outgassing at different temperatures (in °C). B = Bronsted band, L = Lewis band and N = new band due to the decomposition of pyridine (see text).

absorption bands for pyridine bound to Bronsted acid sites at 1640 and 1547 cm^{-1} have reduced but are still observed. At 400 and 500 °C, bands for Bronsted acid sites are completely absent, and only bands of pyridine bound to strong Lewis acid sites (mainly L2) are observed. A band (N) is also seen at the higher temperatures and is likely to result from decomposed pyridine.[60]

In case of ZrSP80, the FTIR spectra after desorption of pyridine are presented in Figure 5. At 100 °C, the spectrum is similar to that of AlSP80 with bands at 1640 and 1547 cm^{-1} corresponding to Bronsted (B) acid sites and bands attributed to Lewis (L1) acid sites at 1447 and 1608 cm^{-1}. When the temperature of outgassing is 300 °C, the intensity of all the bands is markedly reduced, and a new (N) band at 1510 cm $^{-1}$ is observed, possibly the result of decomposition of the pyridine.[60] No splitting of the Lewis band, however, is observed, indicating that only one type of Lewis (L1) acid sites is present. At 400 °C, the bands for Bronsted sites disappear while the bands related to pyridine bound on Lewis (L1) acid sites are still observed, indicating that Lewis acid sites are the main acid centers in the ZrSP80 clay.

The creation of new Bronsted acid sites after intercalation of aluminum has been proposed by Bagshaw and Cooney[28] to be associated with pillar-to-layer bonding sites between Al from the pillaring species and the tetrahedral layer. The splitting of the Lewis bands in the case of AlSP80 suggests that the pyridine is adsorbed on two different types of acid sites, with different strengths and different behavior as a function of temperature. Similar splitting of this band has been previously observed, e.g., for pyridine adsorbed on silica−alumina,[61,62] alkali-doped MoO_3/TiO_2[63] oxides, and zeolites.[64] The presence of two types of Lewis acid sites has previously been attributed to the adsorption of pyridine on different aluminum sites in the case of acid-activated saponites.[50] Chevalier et al.[57] have reported that for the alumina-pillared saponites the splitting of the Lewis bands is due to pyridine coordinately bonded to acid sites of the clay layers and to the pillars in the interlayer region. In the case of zirconia-pillared saponite (ZrSP80), Bronsted acid sites are detected and only one type of Lewis acid is formed. The splitting of the Lewis band does not occur. The presence of Bronsted acid sites has been reported to be due to the clay-layer hydroxyls or to the pillar-layer bonding sites.[28]

The concentration of Bronsted and Lewis acid sites are presented in Table 4, referenced to unit weight of pillared clay [q_H(μequiv g^{-1})]; it has been obtained according to the equation[65]

$$q_H = (A_I \pi R^2)/w\epsilon_I \qquad (1)$$

where R (cm) is the radius of the wafer and w (g) is the weight of the sample. A_I values (integrated absorbance values, in arbitrary units) were evaluated from the spectra after baseline optimization at 1545 and 1456−

---

(60) Connerton, J.; Joyner, R. W.; Padley, M. B. *J. Chem. Soc., Faraday Trans.* **1995**, 91, 1841.

(61) Ballivet, D.; Barthomeuf, D.; Pichat, P. *J. Chem. Soc., Faraday Trans. I* **1972**, *68*, 1712.

(62) Bourne, K. H.; Cannings, F. R.; Pitkethly, R. C. *J. Phys. Chem.* **1970**, *74*, 2197.

(63) Martin, C.; Martin, I.; del Moral, C.; Rives, V. *J. Catal.* **1994**, *146*, 415.

(64) Jiang, M.; Karge, H. G. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 59.

(65) Barzetti, T.; Selli, E.; Moscotti, D.; Forni, L. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1401.

Table 4. Concentration of Bronsted (q_B) and Lewis (q_L) Acid Sites of Pillared Clay (μequiv g^{-1}) Prepared in Different Conditions, after Outgassing of Pyridine at 100 °C

sample	q_B	q_L	[B]/[L][b]
saponite	0	[a]	0
AlSPRT	18	157	0.11
AlSP80	19	185	0.10
ZrSPRT	14	40	0.35
ZrSP80	22	112	0.19

[a] Negligible. [b] Relative proportion of Bronsted to Lewis acid sites.

1443 cm^{-1}; q_H values were then determined via eq 1 from A_I data obtained at different temperatures, and ϵ_I are extinction coefficients relative to Bronsted and Lewis sites with values of 1.67 and 2.22 cm μmol^{-1}, respectively.[66] This method may be considered as yielding a "quantitative estimation" of surface acidity with an error that, although not negligible, is acceptable.[65]

The data presented in Table 4 indicate that the concentration of Bronsted acid sites is only slightly affected by the nature of the pillars and the preparation conditions, whereas the concentration of Lewis acid sites depends strongly on the nature and amount of the pillars between the layers. Indeed when the aluminum/zirconium solution is aged at 80 °C (AlSP80 and ZrSP80), the concentration of Lewis acid sites is improved compared to a sample prepared at room temperature (AlSPRT and ZrSPRT). However, it is lower in the case of zirconia-pillared saponites compared to those of alumina-pillared clays. In both cases, the relative proportion of the Bronsted to Lewis acid sites indicates that the Lewis acidity dominates the surface of the pillared clays. The concentration of the Bronsted and Lewis acid sites in the case of AlSP80 is higher compared to those reported for an iron containing saponite (Griffithite) pillared with alumina.[45] The number of Bronsted sites detected by pyridine (19 μmol g^{-1}) is lower than that obtained by the adsorption of cyclohexylamine (0.62 mmol g^{-1}) due to the fact that pyridine is adsorbed only on strong acid sites.

Figures 6 and 7 present the variation of the normalized area N_B and N_L as a function of temperature (N_H is the ratio between the Bronsted or Lewis absorption band area, measured after pyridine adsorption followed by outgassing at temperature T, and the area of the same band measured after evacuation at 100 °C) for AlSP80 and ZrSP80, respectively.[60] It is to be noted that since the samples had been previously calcined to 500 °C, it is unlikely that any change in absorption will be due to sintering and surface area decrease in the samples. The curve shows that evacuation at 200 °C resulted in a significant reduction in intensity of bands due to both Lewis and Bronsted bound pyridine to around 80 and 60%, respectively, for AlSP80. At 300 °C, N_B and N_L are still decreasing. At 500 for AlSP80 and 400 for ZrSP80 300 °C Bronsted acid sites are not observed and principally Lewis centers are detected on the surface of the pillared clays. Similar trends are found for the AlSPRT and ZrSPRT materials.

Dehydration of Pentan-1-ol. The ability of the pillared saponites to act as acid catalysts was investigated using

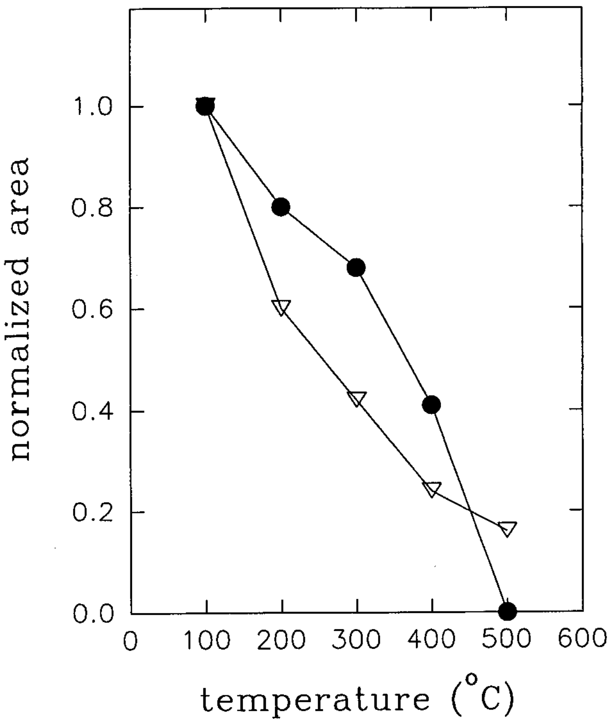

Figure 6. Normalized area (see text) relative to (●) Bronsted and (▽) Lewis sites after outgassing at different temperatures for the alumina-pillared saponite (AlSP80).

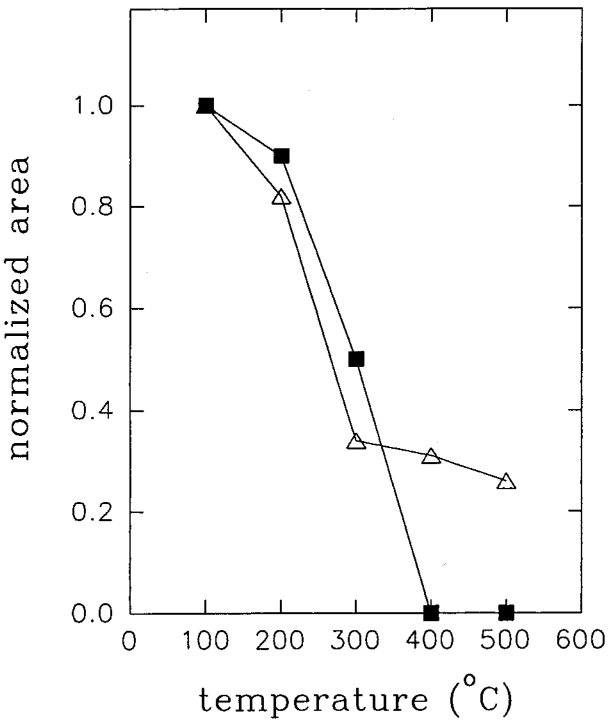

Figure 7. Normalized area (see text) relative to (■) Bronsted and (△) Lewis sites after outgassing at different temperatures for the zirconia-pillared saponite (ZrSP80).

the dehydration of pentan-1-ol. In the presence of Bronsted acid sites pentanol is dehydrated to form a mixture of products, the major constituents being pentene, 1,1-diethyl ether, and 1,2-diethyl ether.[67]

Table 3 shows the percentage of pentanol conversion by the pillared clays and the raw saponite. The product

---

(66) Emeis, C. A. *J. Catal.* **1993**, *141*, 347.

(67) Ballantine, J. A.; Davies, M.; Patel, I.; Purnell, J. H.; Rayanakorn, M.; Williams, K. J.; Thomas, J. M. *J. Mol. Catal.* **1984**, *26*, 37.

selectivity are shown and expressed as the molar ratio of pentene/ethers.

The raw saponite has very low catalytic activity. The conversion is, however, significantly improved with the pillared saponites. The dehydration of pentan-1-ol is related to the synthesis conditions of the pillared clays. AlSP80 has a high conversion of pentan-1-ol (85%) compared to AlSPRT. However, in the case of zirconia-pillared saponites, it seems that a higher catalytic activity is obtained for ZrSPRT compared to ZrSP80. The percentages of converted pentan-1-ol on the pillared clays (Table 3) are in agreement with the acidity values calculated from the desorption of cyclohexylamine, except for ZrSP80. A similar situation has been reported previously for pillared-acid-activated montmorillonite.[47] The dehydration of pentanol to ethers has been reported to be related to the strength of the Bronsted acid sites on the surface of the catalyst with stronger sites yielding more ethers than pentene.[67] The selectivity data in Table 3 shows that the alumina-pillared saponites have lower selectivity to pentene formation, indicating that Bronsted acid sites are stronger compared to those detected on the zirconia-pillared saponites. Again, the nature of the acid sites are closely related to the nature of the metal oxide pillars intercalated between the sheets of the clay.

Concluding Remarks

The pillaring of Ballarat saponite is reported using two different polyhydroxycations (aluminum and zirconium). The amount of intercalated species depends strongly on the exchange reaction conditions. An increase in exchange is obtained when the pillaring solution is aged at 80 °C. Different species of zirconium are intercalated depending upon the treatment of the zirconium solution prior to the reaction with saponite. Alumina saponite exhibits a higher thermal stability (with an ordered layered structure stable until 700 °C) compared to zirconia-pillared clays. The specific surface area and pore volume and acidic properties are also related to the nature of the pillaring species between the layers; while a microporous material is obtained for an alumina-pillared clay, the zirconia-pillared saponites have mesoporous character. The adsorption−desorption of pyridine molecules indicates that Bronsted (B) sites are detected for both the alumina- and zirconia-pillared saponites. Two different types of Lewis (L1 and L2) acid sites with different strength are, however, detected on the alumina-pillared saponites, while only one type of Lewis (L) acid sites is observed on the zirconia-pillared saponites. The pentan-1-ol dehydration test indicates that the alumina-pillared saponites are more acidic and active compared to the zirconia-pillared ones.

Acknowledgment. The authors are grateful to the EC for funding this work (Contract BRE2-CT94-0629) and Laporte Industries Ltd. for the use of facilities for the determination of surface area and porosity data. We thank Dr. Robert Mokaya and Mr. Steve Newman for their help and suggestions during the preparation of the manuscript.

CM970254S