Characterization and Catalytic Activity of Acid-Treated, Size-Fractionated Smectites

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Five layered silicates in which the octahedral sheet contained differing amounts of Al, Mg, Fe, and Li were acid leached using acid concentrations and treatment temperatures selected to produce materials in which the octahedral sheet was depopulated in a controlled, stepwise (yet comparable) manner. SAz-1 and JP are dioctahedral smectites with octahedral compositions rich in Mg and Al, respectively. SWa-1 is a ferruginous smectite and ST an iron-rich beidellite. The fifth mineral was a trioctahedral hectorite which contains almost exclusively octahedral Mg. The Brønsted acidity and catalytic activity of the resulting materials were highest for the samples prepared with the mildest acid treatments but decreased as the octahedral sheet became increasingly depleted. Only the hectorite exhibited no catalytic activity despite the proven existence of Brønsted acid sites. The elemental composition of the starting material did not appear to make a significant contribution to the catalytic activity for the chosen test reaction although it does play a key role in determining the severity of the activation conditions required for the optimization of catalytic activity. Fourier transform infrared (FTIR) spectroscopy was found to be as sensitive to structural acid attack as ²⁹Si magic angle spinning NMR and the octahedral depletion (measured using FTIR) correlated well with the acidity determined from thermal desorption of cyclohexylamine.

Introduction

The interest in acid-activated clays as sorbents and catalysts continues because they constitute a widely available, inexpensive solid source of protons which have proven effective in a number of novel and industrially significant reactions and processes. Until their replacement by zeolites in the 1960s acid-activated clays were employed as cracking catalysts¹ and are still currently used in industrial processes such as the alkylation of phenols² and the dimerization and polymerization of unsaturated hydrocarbons.³ Acid-activated clays have recently enjoyed renewed interest in their role as high surface area supports for environmentally benign catalysts in Friedel-Crafts alkylation and acylation reactions.^{4,5} Recent innovations in the use of these materials include the use of acid-treated clays pillared with oxyhydroxyaluminum species as both catalysts⁶ and as selective adsorbents for oil clarification7 and the use of TiIV-exchanged acid-leached clays as effective Diels-Alder catalysts.8

As a result of the considerable commercial utilization of acidtreated clays for decolorizing oils⁹ and in carbonless copying paper,¹⁰ the effect of acid attack on properties such as surface area and decolorizing ability has received considerable attention.^{9,11} Commercial products are normally treated with a fixed amount of acid which is sufficient to remove only that number of octahedral cations required to optimize the surface area and Brønsted acidity for a particular application. Consequently, a significant number of reports do not include a systematic appraisal of how the extent of acid decomposition of the parent structure contributes to the catalytic activity. This aspect has been rectified to some extent in recent accounts which show that the extent of acid attack requires optimization whether the clay is to be used as a support in Friedel–Crafts reactions¹² or as a catalyst in its own right.¹³ Even so there is still considerable disparity with regard to acid type and concentration, treatment times, and source clays studied. Another cause for major concern is that the chosen clays are often treated as received without regard for the number or type of mineral impurities present.^{12–16} Many impurities contain significant amounts of the elements present in the aluminosilicate under investigation, which means that the elemental compositions reported for acid-treated samples can only be used as a guide to the extent of structural attack.

Nonetheless, it is now widely accepted that smectites with high magnesium contents in the octahedral layer are leached more readily than those containing a higher proportion of aluminum.^{17–19} This has been underlined recently insofar as mild acid treatments at or near room temperature have proven sufficient to cause considerable degradation of the host layer in Mg-rich^{20a} and Fe-rich^{20b} saponites and hectorite,²¹ both minerals with high octahedral magnesium content. In addition to magnesium and aluminum the other ion which is regularly found in the octahedral sheet is iron. Surprisingly, little information is available concerning the influence that substantial quantities of octahedral iron have on the leaching rate or the subsequent catalytic activity,^{17,18,22,23} although the products formed from the acid activation of an Fe-rich saponite have received attention.^{20b}

In recent studies, designed to compare the extent of leaching in minerals rich in octahedral magnesium or aluminum, we established that Fourier transform infrared (FTIR) spectroscopy, ²⁹Si magic angle spinning (MAS) NMR spectroscopy, and the catalytic test reaction used here were particularly sensitive to the small changes in the octahedral ion content which occurred in the early stages of acid attack.¹⁹ In this investigation we have extended these earlier studies into the effect of acid leaching on the nature and catalytic activity to include minerals of high octahedral iron contents and compare them with minerals

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 TABLE 1: Structural Formulas for the Fine Fractions of the Samples Used

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sample	M^{+a}	${\rm Si}^b$	Al^b	Al^c	Fe^{c}	Mg^c	Li ^c
$\begin{array}{c} {\rm SAz-1^{19}}\\ {\rm JP^{19}}\\ {\rm ST^{26}}\\ {\rm SWa-1^{30}}\\ {\rm HC^{21}} \end{array}$	1.11 0.91 0.95 0.81 0.89	8.00 7.71 7.22 7.33 7.99	0.00 0.29 0.78 0.67 0.01	2.67 3.00 1.96 0.91 0.01	0.15 0.38 1.60 2.86 0.01	1.20 0.63 0.58 0.28 4.76	$\begin{array}{c} 0.00 \\ 0.00 \\ 0.00 \\ 0.00 \\ 0.62 \end{array}$

^{*a*} interlayer cations. ^{*b*} tetrahedral cations. ^{*c*} octahedral cations.

of differing octahedral magnesium content. The five parent minerals, which were purified using standard procedures, were treated using different combinations of acid concentration, temperature, and time which allowed for the different dissolution rates associated with the differing octahedral compositions (Table 1). Using this protocol we were able to prepare samples in which the octahedral ion composition decreased in a controlled, stepwise manner thus allowing us to study the evolution of catalytic activity as the octahedral layer was progressively depopulated and relate this to information derived from a wide range of materials characterization techniques including X-ray diffraction analysis, X-ray fluorescence (XRF), ²⁹Si MAS NMR, FTIR, and thermal analysis.

Experimental Section

Materials. Four dioctahedral smectites were used in this study. Two were montmorillonites (SAz-1 and JP), the third was a ferruginous smectite (SWa-1) and the fourth (ST) was a beidellite. SAz-1 (Cheto, AZ), a magnesium rich montmorillonite, and SWa-1, a ferruginous smectite, were obtained from The Clay Mineral Repository of the Clay Minerals Society, Columbia, MO. JP is a hydrothermal, aluminum-rich montmorillonite from the Kremnica mountains in central Slovakia,^{24,25} and Stebno (ST) is an iron-rich beidellite from the Czech Republic, which contains about 21% of total iron bound in goethite.²⁶ The goethite is present as an admixture in the <2 μ m fraction and hence could not be removed. The fifth mineral used was a trioctahedral hectorite (HC) from Hector, CA, and was obtained from Ward's Natural Science Establishment, Inc. Coarse samples of JP, SAz-1, ST, SWa-1, and HC were suspended in deionized water, treated five times with 1.0 M aqueous calcium chloride, washed until free of chloride, and centrifuged, and the nominally $<2 \mu m$ sample was collected, dried at 60 °C, and ground to <0.2 mm prior to storage. The structural formulas of the purified smectites used are given in Table 1.

Equipment and Methods. 3g portions of the Ca form of each mineral were treated with 300 cm^3 of *x* M HCl for periods of *y* minutes. The HCl concentrations and treatment temperatures were 6 M and 95 °C for JP, 6 M and 80 °C for SAz-1, 6 M and 60 °C for ST, 1M and 95 °C for SWa-1, and 0.25 M and 30 °C for HC. After acid treatment, the samples were filtered, then washed with 1.5 dm³ deionized water, and centrifuged before being dried and ground to pass a 0.2 mm sieve. The treatment time is identified in the sample name. Thus, JP30 indicates that JP was treated in 6 M HCl for 30 min at 95 °C and ST120 means that ST was treated with 6 M HCl for 120 min at 60 °C.

Sample Characterization. X-ray diffraction profiles of pressed powder samples were obtained using a Philips PW1830 X-ray diffractometer using a copper tube ($\lambda = 1.5418$ Å) operating at 40 kV and 35 mA. Profiles were recorded at 2° (2 Θ) min⁻¹.

Samples for XRF analyzis were prepared using the $Li_2B_4O_7$ fusion method. The resulting beads were analyzed on a Philips

SCHEME 1



PW2400 XRF spectrometer using calibration graphs prepared from certified reference materials.

Thermogravimetric traces were obtained using a Mettler TG50 thermobalance equipped with a TC10A processor. Samples (7 mg) were exposed to cyclohexylamine vapor for 24 h and then transferred directly out of the vapor into the balance and heated from 35 to 800 °C at 20 °C min⁻¹ under a flow of 20 cm³ min⁻¹ of dry nitrogen carrier gas.

Infrared spectroscopy was performed using a Nicolet Magna 750 FTIR spectrometer. Each spectrum consisted of 256 scans at a resolution of 4 cm⁻¹. Samples were prepared as KBr disks using standard procedures.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) data were recorded using a Specac DRIFTS cell and a Mattson Polaris FTIR spectrometer at a resolution of 4 cm⁻¹. Samples were transferred directly out of the pyridine vapor and placed in the DRIFTS cell. The sample was then heated to 200 °C at 50 °C intervals.

High-resolution solid-state ²⁹Si MAS NMR spectra of acidtreated hectorite were recorded on a Bruker MSL 400 spectrometer at 79.49 MHz and at a sample spinning frequency in the range 3.5-4 kHz. A 30 s recycle delay between successive accumulations was used and 2000–3000 acquisitions were collected for each ²⁹Si spectrum. Reported chemical shifts for ²⁹Si are referenced to tetramethylsilane, and they correspond to peak maxima in the spectrum and are not corrected for quadrupolar shift contributions.

The catalytic activity was determined by reacting 2,3dihydropyran with methanol to yield the tetrahydropyranyl ether (Scheme 1).¹³

This reaction does not produce water as a byproduct thus making it more attractive than other ether-forming reactions where the water evolved may weaken or remove active Brønsted sites. Fifty milligrams of catalyst was activated at 120 °C in air for 2 h and then cooled to 0 °C before addition to a mixture of 0.01 mol of dihydropyran and 0.3 mol of methanol at 0 °C. The percentage conversion to the tetrahydropyranyl ether after a contact time of 30 min was determined using gas chromatography. The identity of the product was confirmed using gas chromatography—mass spectrometry.

Results and Discussion

The X-ray diffraction profiles (not shown) of the purified starting materials showed little evidence of any crystalline impurities. The strong characteristic 001 peak for the purified material became weaker and weaker as the treatments used became more severe, indicating that the samples became increasingly disordered. Moreover, a broad hump in the region $15-30^{\circ}$ (2 Θ), indicative of amorphus silica, grew as the severity of the treatment increased, as observed earlier in less extensive studies on SAz-1 and JP in which only three acid treatments were investigated.¹⁹

The elemental analyzes, determined using XRF (Table 2), are reported in full for the SAz-1 samples, whereas only selected values are presented for the other samples. The values were calculated on an ignited (0% H₂O) basis and confirmed that the chosen treatment times and conditions caused substantial changes in the clays. The almost complete reduction in the Ca content for all the acid-treated samples indicated that these cations, which originally occupied the exchange sites, were

 TABLE 2:
 Elemental Composition, Acidity, and Catalytic

 Activity Data for Selected Samples

						mmol acid/	
	SiO ₂ , % w/w	Al ₂ O ₃ , % w/w	MgO, % w/w	Fe ₂ O ₃ , % w/w	CaO, % w/w	(g clay at 250 °C)	% yield THPE ^a
SA00	68.01	19.16	6.85	1.64	4.33		0
SA30	73.45	18.43	6.18	1.58	0.03	1.17	90
SA60	74.97	17.39	5.79	1.49	0.03	1.17	88
SA120	77.95	15.43	5.06	1.24	0.02	1.08	89
SA180	81.43	13.04	4.18	1.02	0.02	0.97	78
SA240	85.43	10.10	2.99	0.79	0.02	0.72	72
SA300	90.59	6.72	1.97	0.50	0.02	0.45	48
SA360	93.90	4.41	1.19	0.32	0.01	0.32	31
SA480	98.09	1.32	0.34	0.11	0.01	0.14	9
JP00	67.25	22.49	4.03	2.89	3.32		0
JP30	70.75	22.59	3.98	2.40	0.05	1.0	75
JP480	85.41	11.32	1.75	1.08	0.02	0.63	42
ST00	53.85	17.92	2.78	19.42	2.95		0
ST30	62.27	16.71	2.21	15.42	0.00	1.05	83
ST480	80.90	9.23	1.23	4.71	0.02	0.57	27
SW00	57.13	10.57	1.41	29.37	3.18		0
SW30	62.34	11.18	0.98	24.76	0.04	1.19	85
SW480	85.73	4.97	0.48	7.97	0.00	0.37	45
HC00	63.1	0.18	25.3	0.17	7.6		0
HC60	73.7	0.29	24.9	0.23	0.7	0.91	0
HC380	86.4	0.17	12.8	0.15	0.2	0.50	0

^{*a*} THPE = tetrahydropyranyl ether.

displaced by protons and/or polyvalent cations leached from the octahedral sheet. The marked decrease in the elements, Al, Mg, and Fe, which occupy positions in the octahedral sheet, together with the relative increase in silica content proved that the parent structures were substantially altered. Clearly, the range of acid treatments employed was successful in providing the required target materials in which the depletion of the octahedral sheet occurred in a controlled, stepwise manner. The relative ability of the samples to resist acid treatment is shown in the way that 50% of the octahedral ions were leached from SWa-1 after 6 h in 1 M HCl, whereas it required 8 h in 6 M HCl to achieve an equivalent extent of octahedral depletion in JP, yet SAz-1 required only 4 h in 6 M HCl. The hectorite was extremely susceptible to acid attack which is why a combination of 0.25 M HCl and only 30 °C was used. These data reinforce the considerable resistance to acid leaching, which octahedral sheets rich in aluminum exhibit. Consequently, the acid activation of layered silicates with different octahedral compositions must be optimized to maximize the catalytic activity. For example, treating SWa-1 with 6 M HCl would remove the catalytic activity after very short treatment times as is the case with the hectorite samples (vide infra). Indeed the same care needs to be taken with saponites which are also easily leached due to their octahedral composition which contains large amounts of magnesium and/or iron.20a,b

The acidity values given in Table 2 were derived from the weight loss curves associated with the maxima in the derivative thermograms for the desorption of cyclohexylamine near 306-340 °C in the acid-leached samples (Figure 1). The derivative thermograms for most samples contained only one desorption maximum as shown for selected samples of acid-treated SWa-1 (Figure 1a). In contrast, the desorption profiles for the hectorite samples (Figure 1b) suggested that cyclohexylamine was desorbed from more than one type of site in the 306-340 °C region. The variation in the amount of base desorbed over the temperature range 35-250 °C made direct comparison of the acidity values difficult. This problem was reduced by calculating the number of millimoles of cyclohexylamine desorbed from the Brønsted sites and normalizing these values to the weight of clay remaining at 250 °C. The results derived from this approach show that in general the acidity of the samples treated



Figure 1. Derivative thermograms for the desorption of cyclohexylamine from acid-treated samples of (a) SWa-1 and (b) hectorite. The numbers on the curves indicate the time of acid treatment in minutes.

for short periods reflected the different exchange capacities of the minerals while those for more extended treatment times decreased as the structural degradation progressed. The values quoted for the hectorite samples in Table 2 include the contribution from both desorption sites mentioned above and are thus less meaningful than for the other four minerals each of which displayed only one desorption maximum.

The results for the test reactions (Table 2) showed that the clays treated for short periods were capable of converting all the dihydropyran to the ether, but this ability diminished as the treatment time progressed and the octahedral cations were leached from the structure. Figure 2a-d summarizes the salient features of the data presented in Table 2. The normalized percentage yield of the tetrahydropyranyl ether is plotted against the acidity data (closed symbols) and the relative octahedral ion, O_h , content (open symbols) which have been normalized to the values for the mildest acid treatment used in this study and the initial octahedral ion content, respectively. This approach provides a unified method for presentation of the experimental data, obtained from a range of samples with differing octahedral populations, which aids assimilation and further discussion.



Figure 2. Plots of the normalized yield of tetrahydropyranyl ether (THPE) vs relative octahedral ion content (\Box) and acidity (\blacksquare) for acid-treated samples of (a) SAz-1, (b) JP, (c) ST, and (d) SWa-1.

Figure 2a shows that SAz-1 was leached systematically by the acid treatments used, and the Oh ion content varied from 1.00 to 0.06 which was the largest range achieved in this study. The mildest acid treatment used removed less than 5% of the O_h ion content of SAz-1 and JP (Figure 2b), but the data in Figure 2c,d suggest that it removed 14% of the octahedral population of ST30 and 11% of that for SW30. The reaction yield for each set of acid-treated samples followed the depopulation of the octahedral sheet and the concomitant fall-off in acidity. These are clearly linked because the protons balance the net negative charge on the layer which arises from isomorphous substitution in the octahedral sheet. Consequently, the number of protons was reduced as the octahedral ion content was depleted. It is interesting to note that the relative yield of the tetrahydropyranyl ether was reduced by 50% when the octahedral ion content of the catalytically active clays was 0.35-0.45 of the initial value. This suggests that the elemental composition of the starting material does not make a significant contribution to the catalytic efficiency for this particular reaction, although it does play a key role in determining the severity of the activation conditions required for the optimization of the catalytic activity.

FTIR is extremely sensitive to the small changes which occur in the octahedral ion population of SAz-1 and JP at the early stages of leaching.^{19b} This aspect of the study was extended here by increasing the number of samples investigated from three to eight and by including smectites with different elemental populations in the octahedral layer. The IR spectrum of untreated SAz-1 (Figure 3a) showed all the absorption bands expected for a Mg-rich montmorillonite with very low octahedral iron content.^{27,28} A weak band at 804 cm⁻¹ indicated the presence of amorphous silica in the sample.²⁹ The most intense band near 1032 cm⁻¹ was attributed to the Si–O stretching vibrations of the tetrahedral layer while the bands at 519 and 467 cm⁻¹ were due to Si–O bending vibrations. Two peaks were resolved in the hydroxyl bending region at 916 cm⁻¹ (Al₂OH) and 841 cm⁻¹ (AlMgOH).

No significant changes were observed in the IR spectrum of SA30 (Figure 3b). A clear decrease in the intensity of both OH bending vibrations at 916 and 841 cm⁻¹ along with that of the Si-O-Al bending band at 519 cm⁻¹ reflected the reduced content of the octahedral cations as treatment time progressed, which is in accord with the XRF results. Only slight inflexions near 840 and 917 cm⁻¹ were observed after 3 and 5 h of acid treatment, respectively (Figure 3e,g). The 519 cm⁻¹ band, which is the most sensitive indicator of the presence/absence of octahedral aluminum in acid-treated montmorillonites, was barely discernible after 6 h and disappeared after 8 h (Figure 3h,i).

Changes in the Si environment with prolonged acid treatment were reflected in the position and shape of the complex Si–O stretching band in the $900-1200 \text{ cm}^{-1}$ region. The previous



Figure 3. Infrared spectra of acid-treated samples of SAz-1 treated for (a) 0, (b) 30, (c) 60, (d) 120, (e) 180, (f) 240, (g) 300, (h) 360, and (i) 480 min in 6 M HCl at 80 $^{\circ}$ C.

investigation^{19a,b} only considered IR spectra in which the parent structure of SAz-1 had been slightly (Si-O band near 1040 cm⁻¹) or drastically (Si–O band near 1100 cm⁻¹) altered. The treatment times and temperatures selected for this study enabled us to follow stepwise changes in the Si-O stretching region for a range of acid-treated materials. A slight shift of the 1032 cm⁻¹ band to higher wavenumbers, observed in spectra of SA30 and SA60, reflected a slight alteration of the structure. The IR spectra for SA180 and SA240 showed, in addition to the absorption near 1038 cm⁻¹, a pronounced band near 1085 cm⁻¹ assigned to Si-O vibrations of amorphous silica with a threedimensional framework,²⁹ formed during the course of acid treatment. Comparison of the intensities of both Si-O absorptions indicated that the extent of acid attack was less than 50%. The reverse situation was observed for the Si-O stretching band of the SA300 sample. The strong absorption band at 1090 cm^{-1} (with a shoulder near 1044 cm^{-1}) proved that amorphous SiO₂ was the dominant phase in this sample. The Si-O stretching band of the tetrahedral layer was absent from the spectra for SA360 and SA480 and only the band of free silica (cf. Table 2), near 1100 cm⁻¹, was observed for extensively leached SAz-1 (Figure 3h,i).

Further evidence for an increased amorphous SiO₂ content as acid dissolution progressed was also shown by the increase in intensity of the band near 800 cm⁻¹ (Figure 3). The broad band near 974 cm⁻¹ in the spectrum of SA480 (Figure 3i) is due to Si–O stretching of SiOH groups²⁹ which are present in the three-dimensional product formed as the octahedral sheet in the aluminosilicate layer becomes substantialy depleted.

Progressive changes in the absorption bands, similar to those observed for SAz-1, were observed for all acid-treated smectites as shown for selected samples of JP, ST, SWa-1, and HC in Figure 4. The Al₂OH (917 cm⁻¹), AlMgOH (844 cm⁻¹), and Si-O-Al (523 cm⁻¹) vibrations in JP decreased less rapidly than in SAz-1, despite the higher treatment temperature. The presence of an Si-O-Al band in the spectrum of JP treated for 12 h confirmed that complete dissolution of the octahedral

sheet of JP did not occur (Figure 4A). Slower dissolution of JP compared to SAz-1 is in accord with the lower substitution of Mg for Al in JP.^{17–19}

The IR spectra of untreated ST and SWa-1 (Figure 4B,C) exhibited absorption bands indicative of the higher iron contents in these samples. Two peaks were resolved in the hydroxyl bending region at 918 (Al₂OH) and 876 cm⁻¹ (AlFeOH) for ST and at 874 (AlFeOH) and 819 cm⁻¹ (FeFeOH) for SWa-1. The decrease in intensity of the OH bending bands for both smectites reflected diminishing amounts of octahedral cations as the leaching time increased. In contrast to the behavior observed for SAz-1, JP, ST, and HC, where only minor changes in the position of the Si-O stretching band were observed, the shortest acid treatment caused a pronounced shift from 1029 to 1037 cm^{-1} in the spectra of SWa-1. The Al₂O₃, MgO, and Fe₂O₃ values for ST480 and SW480 (Table 2) suggest that some of the octahedral sites remained populated after 8 h acid treatment. The IR data in Figure 4B.C support the existence of some undissolved layers. The Si-O band is complex and, in addition to the 1090 cm⁻¹ component attributed to threedimensional silica, there is a 1060 cm⁻¹ absorption attributed to a tetrahedral clay sheet. This together with the presence of a 530 cm⁻¹ band (Si-O-Al) in ST480 confirms the presence of some unaltered layers.

The IR spectra for untreated hectorite contained bands attributed to OH bending at 659 cm⁻¹, Si-O stretching at 1015 cm⁻¹, Si-O out-of-plane bending at 703 cm⁻¹, and Si-O inplane bending at 468 cm⁻¹ (Figure 4D). In addition, there were weak bands at 1432 (not shown) and 875 cm⁻¹, attributed to a small amount of calcite admixture which was removed by short acid treatments. There was also a contribution from amorphus silica at 803 cm⁻¹. These impurity bands underline the difficulties associated with purifying large quantities of these naturally occurring minerals. The changes in the IR spectra of HC due to acid dissolution are similar to those observed for dioctahedral smectites. Unfortunately, the characteristic 659 cm⁻¹ OH band was not sufficiently intense, and Si-O-Mg bending vibration (460–450 cm⁻¹ region) was overshadowed by the Si-O-Si bending, thus it was not possible to correlate changes in these bands with the acid dissolution as in montmorillonites. Changes in the Si-O stretching region are more distinct and thus more useful for monitoring the dissolution of hectorite. As acid treatment progressed, the Si-O stretching band at 1015 cm⁻¹ diminished and the intensity of the Si-O band for amorphus SiO_2 near 1100 cm⁻¹ increased. The presence of a shoulder near 1020 cm⁻¹ in the spectrum of HC480 suggests the continued presence of Si in a layered structure, and this aspect was confirmed by ²⁹Si MAS NMR (vide infra) which showed that the transformation from a twoto a three-dimensional silica network was incomplete after 8 h in acid.

The data for each series of samples in Figure 2 indicated that the acidity values followed the depopulation of the octahedral sheet as determined from the elemental analysis data. This is anticipated because the protons are sorbed to compensate for the net negative charge on the aluminosilicate layer which arises from isomorphous substitution in the octahedral sheet. Consequently, the acidity should decline as the octahedral site population decreases. Given that the absorbance of the band near 520 cm⁻¹ is a sensitive indicator of octahedral aluminum content during acid attack,^{19a} this should correlate with the acidity values measured by cyclohexylamine desorption. Figure 5 shows that this is clearly the case for SAz-1 and JP which exhibit a measurable Si-O-Al absorption.

The ²⁹Si MAS NMR spectrum of untreated hectorite was virtually identical to that shown for HC30 (Figure 6). Both



Figure 4. Infrared spectra of (A) JP treated for (a) 0, (b) 30, (c) 360, (d) 480, and (e) 720 min; (B) ST treated for (a) 0, (b) 30, (c) 240, (d) 360, and (e) 480 min; (C) SWa-1 treated for (a) 0, (b) 30, (c) 240, (d) 360, and (e) 480 min; (D) HC treated for (a) 0, (b) 30, (c) 180, (d) 360, and (e) 480 min. See text for details.



Figure 5. Correlation of acidity with IR absorbance of the 522 cm⁻¹ (Si-O-AI) band for JP (\Box) and SAz-1 (\blacksquare).

spectra contained a strong ²⁹Si Q³(0 Al) signal centred at -95.5 ppm, which agrees well with literature values for Si in low Alsubstituted smectites,^{31–34} and a weak, broad Q⁴ peak at -112 ppm which indicates the presence of a small amount of amorphus SiO₂ as suggested by the IR band at 803 cm⁻¹. As the acid-treatment increased, an additional peak at -102 ppm, attributed to Si(OSi)₃(OH) (Q³(1 OH)) sites, grew in intensity as did the Q⁴ peak at -112 ppm at the expense of the peak at -95.5 ppm. It is interesting to note that the correlation between the FTIR spectra and the MAS NMR results for the hectorite samples is as satisfying as that which we previously observed with mildly acid-treated^{19a} and extensively acid-leached mont-morillonites.^{19b}

The lack of catalytic activity shown by the hectorite samples was unexpected particularly in view of the reasonably high acidity values. It is known that the desorption of cyclohexylamine does not distinguish between Brønsted and Lewis acid sites³⁵ and that the conversion of dihydropyran to the tetrahydropyranyl ether is not catalyzed by Lewis acids. In an attempt to reconcile this dilema, HC30 was saturated with pyridine vapor and then heated at 50 °C intervals in an environmentally controlled DRIFTS cell. The spectrum obtained for pyridinesaturated hectorite heated at 50 °C exhibited strong bands at 1442 and 1489 cm^{-1} together with a very weak band at 1540 cm^{-1} and a shoulder near 1435 cm^{-1} . The 1442 and 1435 cm^{-1} bands diminished as the treatment temperature was increased while the 1540 cm^{-1} band grew in intensity. The 1489 cm^{-1} band remained largely unchanged. This behavior has been observed before in acid-activated14 and cation-exchanged bentonites.³⁶ The removal of physisorbed pyridine (1435cm⁻¹) and pyridine hydrogen-bonded to the pyridinium cation (1442 cm^{-1}) results in an increase in the diagnostic band for Brønsted-bound pyridine at 1540 cm⁻¹. The presence of a weak band near 1442



Figure 6. 29 Si MAS NMR spectra for hectorite samples treated in 0.25 M HCl at 30 °C for (a) 30, (b) 240, and (c) 480 min.



Figure 7. DRIFTS spectra of pyridine-saturated HC30 after heating for 30 min at temperatures of 50, 100, 150, and 200 °C.

 cm^{-1} at elevated temperatures suggests the presence of pyridine bound to a small number of Lewis acid sites. The 1489 cm^{-1} band is present in the IR spectrum of both Lewis and Brønsted bound pyridine but is generally more intense for protonated pyridine. The intensity of the band at 1540 cm^{-1} in the resulting DRIFTS spectra (Figure 7) confirmed the presence of a considerable number of Brønsted acid sites in the heated samples, while the weak 1442 cm^{-1} band indicates a small number of Lewis acid sites. The disparity between results from the test reactions on the one hand and those from the derivative thermograms and the DRIFTS spectra on the other must be attributed to the ability of the different molecules to interact with the available protons. Cyclohexylamine and pyridine are much stronger bases than DHP and will thus be able to interact

with acid sites which are not strong enough to protonate DHP. Our current interpretation is that a significant number of the Mg²⁺ ions leached from the octahedral sheet of hectorite reside on the exchange sites in the interlamellar region. The water molecules in the primary coordination sphere of Mg^{2+} will be sufficiently polarized to protonate the nitrogen-containing bases but not DHP. It has been previously noted that the desorption of cyclohexylamine from acid-treated clays back-exchanged with Ca²⁺ indicated a high concentration of protons which was not reflected in an ability to convert DHP to the tetrahydropyranyl ether.^{19b} The derivative thermograms for the desorption of cyclohexylamine from the hectorite samples all show the presence of two unresolved maxima, which provides further evidence for this interpretation since we have shown that the maximum in the derivative thermogram for the desorption of cyclohexylamine from acid-treated clays occurs at 306 °C while that from the catalytically inactive Ca²⁺ clay occurs at 330 °C.

Conclusions

Five layered silicates of varying elemental composition were acid leached using acid concentrations and treatment temperatures selected to produce materials in which the octahedral sheet was depopulated in a controlled, stepwise (yet comparable) manner. The Brønsted acidity and catalytic activity of the resulting materials decreased as the octahedral sheet became increasingly depleted, except for the hectorite which exhibited no catalytic activity despite the proven existence of Brønsted acid sites. The elemental composition of the starting material did not appear to make a significant contribution to the catalytic activity for the chosen test reaction although it does play a key role in determining the severity of the activation conditions. FTIR spectroscopy was found to be as sensitive to structural acid attack as ²⁹Si MAS NMR, and the octahedral depletion (measured using FTIR) correlated well with the acidity determined from thermal desorption of cyclohexylamine.

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