ABSTRACT: Four 15 g samples of an uncedimented Wyoming bentonite were treated with 200 cm$^3$ of 0.025, 0.050, 0.100 and 0.250 mol dm$^{-3}$ H$_2$SO$_4$ for 1 h at room temperature (samples I-IV, respectively). Three further 15 g samples were treated with 200 cm$^3$ of 50% (v/v) H$_2$SO$_4$ for 1 h at 20°C (sample V), and 1 and 2 h under reflux (samples VI and VII, respectively). X-ray fluorescence and diffraction studies revealed that only samples VI and VII suffered any substantial structural attack. The resulting acidity of the clays, determined by cyclohexylamine desorption, indicated that sample V contained the largest number of protons at 0.59 mmol H$^+$ (g clay)$^{-1}$. Sample V was also the most efficient catalyst for the dehydration and etherification of hexan-1-ol, giving a combined product yield of 17.0% after 2 h reflux in neat reactant. The parent bentonite and samples I and II showed no discernible catalytic activity despite measured acidities of 0.1, 0.24 and 0.34 mmol H$^+$ (g clay)$^{-1}$. In contrast samples III and IV gave combined product yields of 4.5 and 11.0%, respectively, which correlated well with the measured acidities of 0.38 and 0.48 mmol H$^+$ (g clay)$^{-1}$. Samples VI and VII, prepared by reflux in acid, contained 0.3 and 0.1 mmol H$^+$ (g clay)$^{-1}$, respectively, and gave combined product yields of 13.0 and 6.0%.

The use of proton-exchanged or acid-treated clays for use in catalysis is now well documented describing their use as cracking catalysts until the 1960s (Thomas et al., 1950), through their industrial use in processes such as the alkylation of phenols (Kaplan, 1966) and the dimerization and polymerization of unsaturated hydrocarbons (Hojabri, 1971), to their current role as both catalyst and comparison in novel and industrially-significant reactions catalysed by montmorillonites exchanged with Al$^{3+}$, Cr$^{3+}$ or similar highly polarizing cations (e.g. Atkins et al., 1983; Gregory et al., 1983; Ballantine, 1986; Adams, 1987). Moreover, acid-treated clays are commonly used commercially for decolourising oils and the effect of acid attack on properties such as surface area and decolourising ability have been widely studied (Morgan et al., 1985; Novak & Gregor, 1969). Another commercial usage of acid-treated clays is in colour formation with leuco-dyes in pressure sensitive recording paper (Hirokawa, 1980; Fahn & Fenderl, 1983).

Treatment of clays with cold, dilute acid has little effect on the elemental composition of the host layer and results in an essentially proton-exchanged clay, whereas activation with hot concentrated acid results in the removal of ions associated with the octahedral sheet and may not produce an exclusively proton-exchanged clay (Thomas et al., 1950). It is now accepted that the acid attack on the clay structure progresses inwards from the edge of the clay platelets leaching cations, particularly Mg if present, from the octahedral sheet. Acid activation causes little damage to the silicate layer and consequently the structure in the
centre of the platelet, at the limit of acid attack, remains intact (Hirokawa, 1980; Fahn & Fenderl, 1983; Morgan et al., 1985). The rate of dissolution of the octahedral sheet is a first-order process (Osthaus, 1956; Granquist & Gardner-Sumner, 1959) which increases not only with increasing concentration of acid, temperature and contact time, but also with increasing Mg content in the octahedral sheet (Mills et al., 1950; Novak & Gregor, 1969; Morgan et al., 1985).

The various methods which have been utilized for the determination of the acidity of these variously acid washed or treated clays have been described by Ballantine et al. (1987). Unfortunately, these approaches can be quite time consuming, particularly if the requirement is for a rapid evaluation of the acidity of the material produced. Recently, independent studies (Ballantine et al., 1987; Breen et al., 1987) have shown that thermogravimetric analysis of the desorption of bases such as butylamine, cyclohexylamine and pyridine can be used to evaluate rapidly the number and type of acid sites in clays. Cyclohexylamine is desorbed from Bronsted sites over a short temperature interval near 290°C resulting in sharp, easily distinguishable desorption maximum in the derivative thermogram, whereas the desorption of pyridine from these sites is more prolonged resulting in a broader maximum at 320°C. Conversely, the desorption of pyridine from the Lewis sites is rapid and results in a sharp maximum in the derivative thermogram, whilst cyclohexylamine does not distinguish Lewis sites quite so well. These differences in desorption characteristics, together with the different pK\textsubscript{b}s, allows not only a clear distinction between Lewis and Bronsted centres in the clay but also affords the potential to evaluate the number and type of site. A weak base such as pyridine (pK\textsubscript{b} = 8.8) will interact with strong acid sites whilst cyclohexylamine, due to its higher basicity (pK\textsubscript{b} = 3.3), will interact with both weak and strong acid sites (Tanabe, 1970).

In this paper, a Wyoming bentonite has been subjected to systematically harsher treatments from immersion in weak acid at room temperature to reflux in 50% H\textsubscript{2}SO\textsubscript{4}. The effect on the elemental composition, structure and the number and type of acid sites has been investigated using X-ray fluorescence (XRF) spectroscopy, X-ray diffraction (XRD) and thermogravimetry, whilst the catalytic activity of the acid-treated clay has been evaluated by studying the dehydration and etherification of hexan-1-ol.

**EXPERIMENTAL**

The Wyoming bentonite, donated by English China Clays, had a cation exchange capacity of 100 mEq/100 g and was used without purification. A sample of 15 g of bentonite was added to 200 cm\textsuperscript{3} of the acid mixture (Table 1) and kept in suspension by vigorous stirring at room temperature or by ebullition under reflux. Following acid treatment the clay was allowed to settle and the acid solution removed by decantation, prior to water washing and centrifugation until the supernatant reached a steady, high residual pH. The product was air-dried, ground and stored in glass containers to prevent ageing in solution (Vasil’ev & Ovcharenko, 1977). All analyses were performed on the fraction which passed through a <75 µm sieve. The base-saturated samples for both thermogravimetry and XRD were exposed to reagent grade pyridine or cyclohexylamine for periods in excess of 48 h. The acid-treated samples were back exchanged with Na\textsuperscript{+} ions by immersing 2 g of the clay in 40 cm\textsuperscript{3} of 0.5 mol dm\textsuperscript{-3} NaCl for 2 h followed by six washing and centrifugation steps. The resulting product was air-dried and ground to <75 µm.

Self-supporting clay films (=2 mg cm\textsuperscript{-2}) for infrared (IR) analysis were prepared by
Table 1. Preparation method, chemical analysis and XRD results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation method</th>
<th>SiO₂ (wt%)</th>
<th>Al₂O₃ (wt%)</th>
<th>Fe₂O₃ (wt%)</th>
<th>TiO₂ (wt%)</th>
<th>CaO (wt%)</th>
<th>MgO (wt%)</th>
<th>Na₂O (wt%)</th>
<th>K₂O (wt%)</th>
<th>LOI (wt%)</th>
<th>d_{001} (Å)</th>
<th>PXRD Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.025 mol dm⁻³ H₂SO₄, 1 h at 20°C</td>
<td>69.1</td>
<td>17.2</td>
<td>3.46</td>
<td>0.12</td>
<td>1.72</td>
<td>0.48</td>
<td>2.25</td>
<td>4.9</td>
<td>14.5</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>0.050 mol dm⁻³ H₂SO₄, 1 h at 20°C</td>
<td>66.8</td>
<td>17.9</td>
<td>3.41</td>
<td>0.10</td>
<td>1.42</td>
<td>0.34</td>
<td>2.12</td>
<td>5.6</td>
<td>14.5</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>0.100 mol dm⁻³ H₂SO₄, 1 h at 20°C</td>
<td>69.1</td>
<td>17.3</td>
<td>3.63</td>
<td>0.12</td>
<td>1.37</td>
<td>0.44</td>
<td>1.83</td>
<td>5.0</td>
<td>12.5</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>0.250 mol dm⁻³ H₂SO₄, 1 h at 20°C</td>
<td>68.6</td>
<td>17.4</td>
<td>3.53</td>
<td>0.13</td>
<td>1.24</td>
<td>0.40</td>
<td>1.87</td>
<td>5.0</td>
<td>12.5</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0.5% (v/v) HSO₄, 1 h at 20°C</td>
<td>68.7</td>
<td>17.1</td>
<td>3.42</td>
<td>0.14</td>
<td>0.64</td>
<td>0.44</td>
<td>1.87</td>
<td>5.0</td>
<td>12.5</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>1% (v/v) C₆H₅SO₃, 1 h reflux</td>
<td>82.5</td>
<td>10.1</td>
<td>1.63</td>
<td>0.11</td>
<td>0.55</td>
<td>0.50</td>
<td>0.69</td>
<td>3.2</td>
<td>11.9</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td>VII</td>
<td>0.5% (v/v) H₂SO₄, 1 h reflux</td>
<td>86.7</td>
<td>7.2</td>
<td>0.93</td>
<td>0.06</td>
<td>0.46</td>
<td>0.29</td>
<td>0.55</td>
<td>3.3</td>
<td>11.5</td>
<td>14.9</td>
<td></td>
</tr>
</tbody>
</table>

1. LOI—loss on ignition at 1000°C
2. Sample exposed to cyclohexylene (CX) vapour for >48 h.
3. Sample exposed to pyridine (PYR) vapour for >48 h.

Desorption of bases from acid clay
evaporation of a dilute aqueous slurry on a polyethylene backing which was subsequently
removed. These air-dried (20°C, r.h. = 60%) films were exposed to reagent grade pyridine
as described above. IR spectra were recorded at room temperature and pressure and then
after 1 h at 50, 100, 150, 200 and 250°C using an evacuable variable temperature cell with a
maximum operating temperature of 250°C. The spectrometer used was a Perkin-Elmer 783
equipped with a PE3600 data station.

Thermogravimetric data were obtained on a Mettler TG50 thermobalance equipped with
a TC10A processor. Samples (= 7 mg, < 75 μm) were transferred directly out of the solvent
vapour to the thermobalance and the desorption traces were recorded at a heating rate of
20°C min⁻¹ under a flow of dry N₂ of 25 cm³ min⁻¹. Samples were generally conditioned in
the N₂ flow for 15 min to remove physisorbed base and hence accentuate the weight losses
associated with the Lewis and Bronsted acid centres. This facility was not available when
determining the basal spacing values.

XRD data were obtained from pressed powder samples presented to a Philips
PW1050 diffractometer operating at 40 kV and 20 mA using Ni filtered Cu-Kα radiation
(λ = 1.5418 Å). XRF data were obtained from fused glass beads presented to a Philips
PW1480 XRF spectrometer.

Typical catalytic studies involved the reflux of 0.5 g of clay catalyst in 10 cm³ of neat
reactant for 2 h. Identification of the reaction products was achieved using a Hewlett-
Packard 5890 capillary gas chromatograph coupled to a VG Trio-1 quadrupole mass
spectrometer. The capillary column was a 25 m SE30 column of 0.32 mm internal diameter.
The column temperature was increased from 50 to 150°C at 10°C min⁻¹ and was held at the
upper temperature for 10 min. The mass range of the spectra produced by electron impact
was scanned from 10 to 650. Quantitative analyses of the product mixture were performed
with a Perkin-Elmer 8310B fitted with a flame ionisation detector and coupled to a Perkin-
Elmer GP100 computing integrator. A 6' by ½” stainless steel column packed with 3% OV-1
on Chromosorb WHP (80–100 mesh) was used. The oven temperature was raised from 80 to
120°C at 10°C min⁻¹ and then held at the upper temperature for 5 min.

RESULTS AND DISCUSSION

Elemental analysis and XRD

Table 1 shows that there was little significant change in the proportion of Mg, Al, Si and
Fe until the samples were refluxed with 50% H₂SO₄ indicating that the less severe
conditions, including one hour’s treatment with 50% H₂SO₄ at room temperature, did not
attack the aluminosilicate layer, and when it did, it leached the octahedral cations in
preference to the tetrahedral Si atoms. The percentages of the octahedral sheet dissolved in
samples VI and VII are similar to the results of Mills et al. (1950) for a white Nevada
bentonite treated at 95°C for 8 h in 15–20% H₂SO₄. Clearly the reduced treatment time in
this study is compensated by the increase in acid concentration. Similar reductions in
octahedral ion composition in Mg-rich montmorillonites result from reflux in 11% H₂SO₄
(Yates, personal communication). XRD studies of samples I to VII confirm the results of
the elemental analysis in so far as a significant reduction in intensity and broadening of the
001, and to a lesser extent the 006, reflection was observed subsequent to reflux treatment.

The d-spacings in Table 1 for the pyridine and cyclohexylamine saturated samples were
remarkably consistent at 14.9 and 14.5 Å. This probably indicates that there was some
Desorption of bases from acid clay

Physisorbed or hydrogen bonded base present in so far as pyridinium-exchanged montmorillonite exhibits a basal spacing of 12.5 Å (Farmer & Mortland, 1966). The intensities of the 001 peaks in the base-saturated, acid-refluxed samples were stronger than the 001 peaks of their air-dried counterparts but were weak in comparison to the base-saturated samples obtained by acid-treatment at room temperature. However, this enhanced intensity coupled with the observation of two or three orders of reflection in the base-saturated, acid-refluxed samples illustrates that intercalation of pyridine and cyclohexylamine into the aluminosilicate layers remaining after acid treatment increases the degree of orientation of those layers with respect to the c-axis. Fahn & Fenderl (1983) observed this behaviour when treating acid activated clays with crystal violet lactone and N-benzoyl leuco methylene blue.

**Thermogravimetric studies**

Fig. 1a presents the derivative thermograms for the desorption of water from the acid-treated clays, which in general exhibit desorption maxima near 60 and 600°C which can be attributed to the desorption of physically adsorbed water, and the dehydroxylation of the aluminosilicate layer, respectively (Breen et al., 1987). An additional desorption maximum near 100°C was observed for samples I, II and III which could not be removed by washing with water but was removed following back exchange with Na⁺ ions (Fig. 1b). The origin of this peak is not fully understood but probably results from the desorption of water from a divalent or trivalent ion, possibly mobilised by acid attack of a surface oxyhydroxy species, and exchanged into the interlayer space. In addition, Banin & Shaked (1969) have shown that H⁺-montmorillonite is unstable and partially converts to Al³⁺-montmorillonite which

![Fig. 1. Profiles for the thermal desorption of water from (a) the acid-treated samples described in Table 1, (b) as in (a) following back exchange with Na⁺ ions. WB is untreated Wyoming bentonite.](image-url)
may also explain this additional desorption peak. The hatched areas in Fig. 1a show the effect of acid treatment on the dehydroxylation of the samples investigated. In samples I to IV the temperature of the desorption maximum was little affected but the dehydroxylation peak became increasingly asymmetric on the low-temperature side. In samples V to VII the dehydroxylation maximum shifted to lower temperatures and became significantly more asymmetric on the low-temperature side indicating a large number of different hydroxyl sites. These observations are in general agreement with the differential thermal analysis traces presented by Granquist & Gardner-Sumner (1959) for a Texas bentonite refluxed with excess HCl for periods up to 6 h. However, cognisant that dehydroxylation may be affected by the exchange cation (Horvath & Galikova, 1979; El-Akkad et al., 1982), the acid-treated samples were back exchanged with Na\(^{+}\) ions and the resulting desorption thermograms are presented in Fig. 1b. This procedure had little effect on the dehydroxylation region of the samples but did remove the 100°C peak from the thermograms for samples I, II and III.

Figs. 2a and 2b present the derivative thermograms for the desorption of cyclohexylamine from the acid-treated clays prior and subsequent to Na\(^{+}\)-back exchange, respectively. Ballantine et al. (1987) have shown, from their studies on Al\(^{3+}\)-exchanged montmorillonite, that the desorption maximum near 290°C, which also occurs in cyclohexylammonium exchanged montmorillonite, can be used for the determination of Bronsted acidity. Corroborative IR investigations by Breen et al. (1987) have shown that desorption of pyridine from Bronsted sites occurs in this temperature region. The desorption thermogram for cyclohexylamine from the untreated Wyoming bentonite (sample WB, Fig. 2a) exhibited three desorption maxima, prior to the dehydroxylation

![Graph](image1.png)

**Fig. 2.** Profiles for the thermal desorption of cyclohexylamine from (a) the acid-treated samples described in Table 1, (b) as in (a) following back exchange with Na\(^{+}\) ions. WB is untreated Wyoming bentonite.
Desorption of bases from acid clay

peak, at 60, 120 and 300°C. The 300°C peak only just exceeded the limit of detection but was present in all repetitions and agrees with IR observations reported for cyclohexylamine saturated Na⁺-montmorillonite (Yariv & Heller, 1970). Acid treatment at room temperature resulted in what appeared to be a slight enhancement of this 300°C maximum together with the appearance of a desorption maximum at 290°C which increased in intensity with increasing severity of acid attack. Reflux in 50% H₂SO₄ (samples VI and VII, Fig. 2a) resulted in a more complex group of peaks in the 280-330°C region, perhaps indicating a range of acid sites of slightly differing adsorption strengths.

There are two further points to note concerning the desorption profiles in Fig. 2a. The intensity of the 120°C maximum decreased as the strength of the acid treatment was increased and another less prominent peak appeared as a shoulder at 130°C, a temperature reminiscent of that reported by Ballantine et al. (1987) for the desorption of strongly hydrogen-bonded or Lewis-bound cyclohexylamine. Secondly, the desorption in the dehydroxylation region, for samples I to VII, moves progressively to temperatures below those recorded for the samples which were not saturated with cyclohexylamine. This could reflect the onset of dehydroxylation at a lower temperature due to the cyclohexylammonium ions propping the layers apart, similar to the effect observed by Loeppert et al. (1979) when the exchange cation was Fe(1,10-phenanthroline)₃²⁺. Alternatively, it could be the loss of the polymeric species formed on cyclohexylamine saturated clay reported by Ballantine et al. (1987). However, the associated weight loss does not exceed that required for dehydroxylation and the same temperature offsets are recorded for pyridine saturated samples (Fig. 4a) on which these polymers do not form.

The desorption of cyclohexylamine from the acid-treated samples back exchanged with Na⁺ ions (Fig. 2b) results in a constant, small, but significant desorption, near 300°C, which does not reflect the differing acid treatments and can be attributed to desorption from Bronsted sites which were present in the untreated clay (Sample WB, Fig. 2a) thus agreeing with the work of Yariv & Heller (1970). Consideration of the desorption maximum near 120°C shows that, subsequent to reflux in acid, there were some Lewis sites, characterized by a desorption maximum at 130°C, which were unaffected by back exchange (cf. samples VI and VII, Fig. 2a). This latter observation is not difficult to reconcile when the probable presence of coordinately unsaturated Al ions either at the limit of acid attack of the layers or which have moved between the remaining sheets is considered.

In an attempt to determine the visual effect on the desorption thermogram of different numbers of acid sites, physical mixtures of sample V and the untreated Wyoming bentonite were prepared and exposed to cyclohexylamine vapour. The resulting derivative thermograms are collected in Fig. 3. This approach showed quite clearly that there was a significant increase in the intensity of the desorption maximum at 290°C. The desorption of pyridine from the Bronsted sites in samples of the same physical mixtures followed a similar pattern but the intensity change did not occur until the acid clay content was near 70%. This serves to amplify the point that the desorption of pyridine does not accentuate Bronsted sites.

Figs. 4a and 4b present the derivative thermograms for the desorption of pyridine from the acid-treated clays prior and subsequent to Na⁺ back exchange, respectively. Parallel IR and thermal desorption studies (Breen et al., 1987) have shown that the desorption maximum near 320°C, present in pyridinium montmorillonite, can be attributed to the desorption of pyridine from Bronsted sites, whilst that near 160°C reflects desorption of pyridine from Lewis sites. As expected, the desorption associated with protonated pyridine
was not observed until the acid treatment had become quite severe, because the desorption of pyridine occurs gradually and thus does not accentuate Bronsted sites in the way that the rapid desorption of cyclohexylamine does. Conversely, the peak at 160°C, attributed to the desorption of pyridine from Lewis acid centres, was in evidence after milder acid treatments than the corresponding desorption from the cyclohexylamine treated samples. Moreover, this peak at 160°C was clearly evident alongside the 120°C maximum associated with pyridine desorbing from the parent bentonite. This shows that samples II, III and IV contain some regions which resemble the parent Na⁺-exchanged bentonite and others which are more acidic. Surprisingly, the pyridine desorption thermograms exhibited little evidence of the Lewis sites remaining after back exchange with Na⁺, which had been identified by cyclohexylamine desorption (Fig. 2b). This may indicate that these sites were not strong enough to interact with pyridine.

Fig. 5 shows how the IR spectrum of sample IV which was saturated with pyridine varied with increasing temperature. The sample fresh from pyridine exhibited peaks at 1435, 1442,
Desorption of bases from acid clay

Fig. 4. Profiles for the thermal desorption of pyridine from (a) the acid-treated samples described in Table 1, (b) as in (a) following back exchange with Na⁺ ions. WB is untreated Wyoming bentonite.

Degassing at the beam temperature of 35°C reduced the intensity of the 1435 and 1578 cm⁻¹ bands, whilst the 1592 cm⁻¹ band shifted to 1595 cm⁻¹ and became weaker and perceptibly broader. Outgassing at 50°C (Fig. 5, bottom spectrum) resulted in further reduction of the 1435, 1578 and 1595 cm⁻¹ bands, together with the appearance of a shoulder at 1607 cm⁻¹. After degassing at 100°C the bands associated with physisorbed and/or hydrogen-bonded pyridine (1435, 1578 and 1595 cm⁻¹) had been removed. Of the bands remaining at this temperature, only the 1442 cm⁻¹ band, its contribution to that at 1490 cm⁻¹, cannot be attributed to Bronsted-bound pyridine. These bands which are diagnostic of Lewis-bound pyridine (Ward, 1968) were completely removed at 200°C, leaving only those associated with the pyridinium ion at 1490, 1540, 1607 and 1630 cm⁻¹. Thus there can be no question that the maximum in the desorption thermogram for pyridine at 320°C was due to pyridinium ion, and that physisorbed and hydrogen-bonded pyridine were removed by 150°C. The 1607 cm⁻¹ band is generally attributed to Lewis-bound pyridine when observed together with a strong band near 1450 cm⁻¹. However, the 1607 cm⁻¹ band has been observed in the absence of a 1450 cm⁻¹ band in Al³⁺- and Fe³⁺-exchanged montmorillonite (Breen et al., 1987) and in pyridinium hydrochloride in chloroform (Parry, 1963). Ni²⁺-montmorillonite exhibits only Lewis-bound pyridine, at 200°C, characterized by strong absorptions at 1450 and 1607 cm⁻¹, of comparable intensity, together with a 1490 cm⁻¹ band which is much weaker than that observed here (Breen, 1991). Cr³⁺-montmorillonite, which has a mixture of Lewis and Bronsted bands at 200°C, exhibits strong bands near 1450, 1490, 1540 and 1607 cm⁻¹ (Breen et al., 1987). It appears that the 1607 cm⁻¹ band can be attributed to both Lewis and Bronsted sites and its assignment relies on the presence or absence of a band near 1450 cm⁻¹.
Fig. 5. The effect of evacuation temperature on the IR spectrum of pyridine sorbed on sample (IV) (see Table 1). Temperatures from bottom to top are 50°, 100°, 150°, 200° and 250°C.
The variation in contributions from physisorbed and Lewis bound (30–240°C) base prior to the desorption of base from Bronsted sites (240–360°C) made direct comparison of the number of acid sites, based on the initial sample mass, difficult. This problem was minimised by calculating the number of mmol of pyridine or cyclohexylamine desorbed from the Bronsted sites and normalising these values to the weight of clay remaining at 240°C. The acid concentrations calculated from cyclohexylamine desorption, expressed in mmol (g at 240°C)^{-1}, are given in Table 2. The values derived from the desorption of pyridine closely parallel these values suggesting that both the pyridine and cyclohexylamine interact with all the available protons and therefore do not, in this instance, distinguish between weak and strong acid sites. This close agreement is not observed when comparing the desorption of pyridine and cyclohexylamine from montmorillonite fully exchanged with Al^{3+} and Cr^{3+} ions, perhaps due to the difficulties associated with separating the desorption of Lewis-bound from protonated pyridine. Similar calculations were performed for the desorption of cyclohexylamine from the physical mixtures and are presented in Fig. 6a together with the data for the acid-treated samples.

Surprisingly, despite the large excesses of H^+ ion offered, the proton concentration did not reach the complete exchange value of 1 mmol g^{-1}. Ballantine et al. (1987) reported that the proton concentration of a fully Al^{3+}-exchanged montmorillonite, determined using the desorption of cyclohexylamine, was 0.38 mmol g^{-1}. Perhaps the values reported here do not reach 1 mmol g^{-1} because the acid treatment releases small amounts of Al^{3+} from either the octahedral sheet or an oxyhydroxy overlayer which is immediately adsorbed on the exchange sites. This would have little effect on the total percentage of Al (Table 1) but would reduce the number of available protons and would also explain why the midly acid-treated clays, which should only exhibit Bronsted acidity, show evidence of Lewis sites.

Reflux of hexan-1-ol in the presence of Al^{3+}-exchanged montmorillonite results in the production of both hexenes and dialkylethers formed from the attack of an unprotonated alcohol molecule on a protonated alcohol molecule. With reference to Adams et al. (1979),

| Table 2. Acidity values and percentage yields for acid-treated samples. |
|-----------------|-------|--------|--------|--------|
| Sample          | \([H^+]^{1}\) /mmol g^{-1} | % yield alkene^{2} | % yield 1,1-ether^{3} | % yield total^{4} |
| Wyoming          |      |        |        |        |
| bentonite       |      |        |        |        |
| I               | 0.24 | 0.0    | 0.0    | 0.0    |
| II              | 0.34 | 0.0    | 0.0    | 0.0    |
| III             | 0.38 | 1.0    | 2.5(1.0) | 4.5    |
| IV              | 0.48 | 3.0    | 6.5(1.5) | 11.0   |
| V               | 0.59 | 3.0    | 11.0(3.0) | 17.0   |
| VI              | 0.30 | 3.0    | 7.0(3.0) | 13.0   |
| VII             | 0.10 | 1.0    | 4.0(1.0) | 6.0    |

1. mmol H^+ calculated per gram of clay at 240°C to allow for differing amounts of physisorbed cyclohexylamine.
2. combined yield of hex-2-ene and hex-3-ene.
3. 1,1-ether is 1,1'-dihexylether, combined yield of 1,2'- and 1,3'-dihexylether given in brackets.
4. Combined yield of the two alkenes and the three ethers.
in which the possible products from the ether forming reaction and their respective fragmentation patterns were explained in some detail, and Ballantine et al. (1984), it was possible to identify the products of the catalytic studies undertaken in this work as hex-2-ene, hex-3-ene, 1,1′-dihexylether, 1,2′-dihexylether and 1,3′-dihexylether. The percentage yields of the products, given in Table 2, show that the 1,1′-dihexylether generally constitutes the major product, which is in accord with the results of Ballantine et al. (1984). The variation of the alkene, ether and total product yield with the measured proton concentration is shown in Fig. 6b. It is evident that clay exhibits little catalytic activity before ≈30% of the exchange sites are taken up by protons. Purnell et al. (1989) have observed a very similar threshold value for the dehydration of pentan-1-ol using a mixed Na⁺/Al³⁺-montmorillonite.

CONCLUSIONS

The Wyoming bentonite resists observable structural damage and impairment of swelling ability until refluxed in 50% H₂SO₄. Milder acid treatments result in progressively higher interlayer proton content and corresponding catalytic activity for the dehydration and etherification of hexan-1-ol. The most potent catalyst produced in this study was prepared by treatment at room temperature with 50% H₂SO₄. Moreover, the minimal effect of mild acid treatments obviates the concern that treatment with solutions of trivalent cations (e.g., Al³⁺, Cr³⁺), which are moderately acidic due to water hydrolysis, causes some structural damage or imparts considerable catalytic activity.
ACKNOWLEDGMENTS

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REFERENCES


