THERMOGRAVIMETRIC, INFRARED AND MASS SPECTROSCOPIC ANALYSIS OF THE DESORPTION OF TETRAHYDROPYRAN, TETRAHYDROFURAN AND 1,4-DIOXAN FROM MONTMORILLONITE

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(Received 26 October 1992; revised 26 April 1993)

ABSTRACT: The desorption of tetrahydropyran (THP), tetrahydrofuran (THF) and 1,4-dioxan (DIOX) from Na+, Ca2+, Al3+ and Cr3+-exchanged montmorillonite has been studied using variable temperature infrared spectroscopy and thermogravimetric analysis. The derivative thermograms for the desorption of each cyclic ether exhibited three maxima but there was little uniformity in the temperatures at which these maxima occurred. Nonetheless, the desorption of both THP and THF occurred at lower temperatures in the Cr3+-exchanged form than in the Al3+-form. The desorption of DIOX showed little cationic dependence. Mass spectroscopic analysis of the thermally evolved vapours indicated that no transformation products were desorbed at temperatures ≤ 230°C.

It is now well documented (Adams, 1987; Ballantine, 1986) that trivalent cation-exchanged montmorillonite is an effective catalyst for reactions in which a solid source of protons is required. The small highly-charged ions (such as Al3+, Cr3+ or Fe3+) cause considerable polarization of water in the primary coordination sphere which results in the generation of an acidic proton. Adams et al. (1982, 1983), in their extensive studies of the production of methyl tert-buty ether (MTBE) from methanol and isobutene using trivalent cation-exchanged montmorillonites as catalysts, have established that cyclic ether solvents give comparable yields of MTBE at temperatures = 30°C lower than if hydrocarbon solvents are used. Table 1 illustrates that the efficiency of the process, which depends on the cyclic ether employed, is optimized if 1,4-dioxan (DIOX) is used as solvent. However, the Cr3+- and Fe3+-exchanged forms also gave respectable yields with tetrahydrofuran (THP) and tetrahydrofuran (THF). Adams et al. (1983) suggested that DIOX was the optimal solvent because all the molecules participating in the reaction were miscible in it, thereby facilitating the rapid distribution of all the reactants and products between the clay interlayer and the external solution. Breen et al. (1987a) studied the rate at which these three cyclic ethers were adsorbed by the cation-exchanged forms under discussion and found that DIOX was sorbed almost six times slower than THP, THF, methanol and t-butanol. However, the diffusion coefficients for the cyclic ethers did not exhibit the increase with temperature expected of a thermally activated process nor did they conform to the 1/\sqrt{T} dependence for limiting Knudsen diffusion. Consequently, this study was initiated to ascertain whether the cyclic ethers underwent any transformation in the temperature region (18–105°C) of the diffusion experiment and was extended up to 800°C to conform with similar studies on alcohols (Breen et al., 1993), acetic acid (Al-Oswais et al., 1987) and nitrogen-containing bases such as cyclohexylamine (Ballantine et al., 1987), pyridine and

<table>
<thead>
<tr>
<th>Cation</th>
<th>Tetrahydrofuran</th>
<th>Tetrahydrofuran</th>
<th>1,4-Dioxan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al3+</td>
<td>4</td>
<td>0</td>
<td>61</td>
</tr>
<tr>
<td>Cr3+</td>
<td>42</td>
<td>28</td>
<td>63</td>
</tr>
<tr>
<td>Fe3+</td>
<td>35</td>
<td>32</td>
<td>65</td>
</tr>
</tbody>
</table>

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**EXPERIMENTAL**

Details of the montmorillonite used, the cation-exchange procedures, sample preparation and saturation with solvent are reported elsewhere (Breen et al., 1987b). Desorption thermograms were recorded using a Stanton Redcroft TG750 thermobalance equipped with a derivative accessory. Samples (=7 mg, <45 μm grain size) were transferred directly out of the ether vapour to the thermobalance and the desorption thermograms recorded at a heating rate of 20°C min⁻¹ under a flow of dry nitrogen purge gas of 25 cm³ min⁻¹. Identification of the species desorbed in the temperature range 25–230°C was achieved using a Perkin-Elmer ATD50 automatic thermal desorption system coupled to a Hewlett-Packard 5890 capillary gas chromatograph (GC) which was interfaced to a VG Trio-1 quadrupole mass spectrometer (MS). The cyclic ether saturated samples were subjected to a flow of helium gas, preheated to 230°C, for 15 min. The vapour phase products were collected in the cold trap and then swept into the GC-MS. This technique facilitates the separation and identification of the individual components desorbed from solvent-treated clay samples (Breen et al., 1993).

Infrared (IR) spectra were recorded at room temperature, then after 1 h at 20, 50, 100 and 200°C, respectively, using an evacuable variable-temperature cell. The spectrometer used was a Perkin-Elmer model 983 equipped with pre-sample chopping and with a quoted accuracy of ±3 cm⁻¹.

**RESULTS**

In contrast to the transformations of the alcohols reported by Breen et al. (1993), the GC-MS analysis of the species desorbed from the cyclic ether treated clays studied here proved conclusively that only unmodified THF, THP and DIOX were desorbed at temperatures ≤230°C.

The d₀₀₁ spacings for air-dried samples in Table 2 indicate that the cyclic ethers were intercalated rather than being adsorbed on the external surface and within interparticulate voids. Figures 1a–c show the desorption profiles for THP, THF and DIOX, respectively, from a range of cation-exchanged forms. Breen et al. (1987b) have previously reported that the maximum in the desorption profile near 600°C can be attributed to loss of structural hydroxyl groups. In contrast to the desorption profiles for alcohols (Breen et al., 1993) and nitrogenous bases (Breen et al., 1987b, 1991a,b) there was little uniformity in the temperatures at which the maxima in the derivative thermograms for a particular ether, from the different cation-exchanged forms, were observed. Nonetheless, the temperatures at which the major predehydration events occurred (Table 3) showed some tentative trends. Desorption from Ca²⁺-montmorillonite always occurred in two distinct steps, the second of which was broad enough to encompass the two higher temperature maxima exhibited in the desorption profile of THP and DIOX from Na⁺-montmorillonite (Figs 1a,c). Desorption from the trivalent cation-exchanged forms occurred in three steps, the second of which generally occurred at higher temperatures in the Al³⁺-form, whereas the highest temperature desorption maxima were usually observed in the Cr³⁺-form.

Figure 2 shows the way in which the IR spectra of THF adsorbed on Al³⁺-exchanged montmorillonite changed as the sample was degassed and heated. The marked reduction in the characteristic IR absorption bands for water, near 3400 and 1650 cm⁻¹, is evident in Figure 2b, and Table 3 shows the way in which the temperature at which the principal desorption maxima appear in Fig. 1.

**Table 2. Basal spacings (Å) of M³⁺-montmorillonite/cyclic ether complexes.**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Cation</th>
<th>Tetrahydropyran</th>
<th>Tetrahydrofuran</th>
<th>1,4-Dioxan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al³⁺</td>
<td>15.0</td>
<td>14.5</td>
<td>15.6</td>
</tr>
<tr>
<td></td>
<td>Cr³⁺</td>
<td>15.0</td>
<td>14.3</td>
<td>15.8</td>
</tr>
</tbody>
</table>

**Table 3. Temperatures (°C) at which the principal desorption maxima appear in Fig. 1.**

<table>
<thead>
<tr>
<th>Cation</th>
<th>Tetrahydropyran</th>
<th>Tetrahydrofuran</th>
<th>1,4-Dioxan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30, 130, 275</td>
<td>20, 120, 220</td>
<td>30, 150, 240</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>30, 110, 300</td>
<td>20, 90, 180</td>
<td>30, 150, 270</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>30, 120, —</td>
<td>30, 145, —</td>
<td>10, 145, —</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>30, 110, 160</td>
<td>30, 130, —</td>
<td>10, 75, 115</td>
</tr>
</tbody>
</table>
Desorption of ethers from montmorillonite

Fig. 1. Desorption profiles for (a) tetrahydrofuran, (b) tetrahydropyran and (c) 1,4-dioxan from the cation-exchanged montmorillonites indicated.
1626 cm$^{-1}$, showed that degassing at room temperature for 1 h removed a considerable amount of water, whereas the affect on the absorption bands for THF, centred around 1400 cm$^{-1}$, was not so marked. Subsequent degassing for 1 h at 50, 100, 150 and 200°C further reduced the amount of sorbed ether and water. The

![Fig. 2. Effect of outgassing temperature on the 1200-4000 cm$^{-1}$ region of the IR spectra of Al$^{3+}$-montmorillonite/tetrahydrotetruran intercalates. Spectra from bottom to top were recorded at 20°C and then after degassing for 1 h at 20, 50, 100 and 200°C, respectively.](image1)

![Fig. 3. Effect of outgassing temperature on the IR spectra of Al$^{3+}$-montmorillonite saturated with (a) tetrahydrofuran, (b) tetrahydrofuran and (c) 1,4-dioxan. Spectra from bottom to top were recorded after degassing for 1 h at 20, 50, 100 and 200°C, respectively.](image2)

changes in both intensity and position of the bands in the 3200 to 3500 cm$^{-1}$ region reflect the general trend for all the samples studied, although there were some subtle differences in detail. In general, the IR spectra of all the samples studied illustrated that the air-dried films were not substantially dehydrated by exposure to ether vapour, but the co-adsorbed water was less resistant to the room temperature degassing procedure.

Figures 3a–c show the changes in the 1300 to
1800 cm$^{-1}$ region of the IR spectrum caused by outgassing the ether-treated Al$^{3+}$-montmorillonite at progressively higher temperatures. These changes are also representative of the desorption from the Cr$^{3+}$-form except that THF desorbed from this form at lower temperatures. For clarity, the spectra recorded at elevated temperatures are presented with similar intensities although, as Fig. 2 shows, the actual intensities of the bands decreased with increasing treatment temperature. The bottom spectrum in Fig. 3a, obtained after degassing THP saturated Al$^{3+}$-montmorillonite at room temperature, showed that the major absorption bands attributed to THP occurred at 1450, 1440, 1385 and 1303 cm$^{-1}$, together with bands at 1275 and 1258 cm$^{-1}$ which are not illustrated. As the temperature was increased through 50 to 100$^\circ$C the bands near 1440 and 1365 cm$^{-1}$ increased in intensity and then replaced the bands at 1450 and 1385 cm$^{-1}$. Furthermore, a band near 1487 cm$^{-1}$ appeared and grew in intensity but subsequently disappeared upon heating at 150$^\circ$C although the other bands were unaffected. The top spectrum in Fig. 3a shows that the bands remaining at 200$^\circ$C were centred near 1595, 1463, 1373 and 1309 cm$^{-1}$.

The bottom spectrum in Fig. 3b, obtained after degassing at room temperature, shows the two absorption bands for THF at 1458 and 1365 cm$^{-1}$. Heating at 50$^\circ$C for 1 h resulted in the appearance of further bands at 1522, 1415 and 1403 cm$^{-1}$. After 1 h at 100$^\circ$C the sharp band, characteristic of THF, near 1365 cm$^{-1}$ was much reduced in intensity whilst the bands at 1522 and 1403 cm$^{-1}$ were unaffected. The 1403 cm$^{-1}$ band was still evident after degassing at 150$^\circ$C but a band at 1456 cm$^{-1}$ dominated the spectrum subsequent to heating at 200$^\circ$C (top spectrum, Fig. 3b). Interestingly, in contrast to the corresponding spectrum in Fig. 3a, the band at 1626 cm$^{-1}$, normally attributed to water in these systems, survived.

The IR spectrum of DIOX adsorbed on Al$^{3+}$-montmorillonite subsequent to degassing at room temperature (bottom spectrum, Fig. 3c) exhibited bands near 1449, 1373 and 1293 cm$^{-1}$, together with a band at 1256 cm$^{-1}$ which is not illustrated. The positions of these bands were unchanged as the temperature was increased up to 100$^\circ$C. The 1373 cm$^{-1}$ band was removed on heating at 150$^\circ$C and replaced by a broad, unresolved absorption near 1350 cm$^{-1}$ and was similar to the top spectrum in Fig. 3c obtained at 200$^\circ$C.

**DISCUSSION**

The IR evidence in Fig. 2 confirms that the cyclic ethers were more strongly held than was water on the various cation-exchanged forms. Moreover, since all the maxima below 50$^\circ$C in the thermal desorption profiles (Fig. 1) were removed by a prolonged flow of dry nitrogen it is clear that these low temperature events can be attributed to the desorption of physically adsorbed ether and water. The higher temperature at which the maxima occurred in the desorption of cyclic ethers from the Al$^{3+}$-form indicates that THP and THF were more strongly bound on this exchange form than on the Cr$^{3+}$-form. In contrast, DIOX desorbed from both exchange forms over the same temperature range.

In the mass spectroscopic identification of the desorption products, the cyclic ether treated samples were subjected to a flow of helium pretreated to 230$^\circ$C prior to the vapours being condensed and injected into the GC-MS. This technique proved conclusively that the cyclic ethers were desorbed unchanged in this temperature interval and compared well with the IR evidence for the desorption of DIOX from both Al$^{3+}$- and Cr$^{3+}$-exchanged montmorillonite in which no changes in peak position nor the appearance of new peaks occurred. However, the IR spectra for THP, and to a lesser extent THF, did exhibit new bands and shifts in peak positions which may arise from a change in molecular geometry in the confines of the interlamellar region or an acid-catalysed transformation.

Subsequent to degassing at 100$^\circ$C the IR spectrum of THP-treated Al$^{3+}$-montmorillonite underwent noticeable changes (Fig. 3a). In particular the appearance of a band at 1487 cm$^{-1}$, which together with the appearance of bands at 1595, 1463 and 1373 cm$^{-1}$, following degassing at temperatures up to 200$^\circ$C, may have suggested some form of transformation. For example, the formation of diols from THP is not unlikely insofar as the acid-catalysed ring-opening of THP and THF over HY zeolites has been observed (Fujita et al., 1974; Ono et al., 1976). A similar mechanism has been invoked to explain the formation of polymers from THF, via the diol, over acid treated clays (Mueller et al., 1979, 1981).

Subsequent acid-catalysed dehydration of such a diol, formed from THP in the mechanism shown
in Fig. 4, could yield alkenes which could then undergo oligomerization. This is suggested as a tentative explanation for the presence of the maximum near 300°C in the derivative thermograms (Fig. 1) insofar as it could indicate the desorption of this oligomeric species or a component thereof. However, since the temperatures employed in the catalytic (Adams et al., 1982, 1983) and diffusion (Breen et al., 1987) studies were much lower than 300°C, the complete identification of this species was considered unnecessary.

The desorption of DIOX from Al³⁺-montmorillonite was uneventful by comparison. Neither shifts in peak positions nor the appearance of new bands in the IR spectra were recorded (Fig. 3c) suggesting that most of the DIOX was desorbed, as the mass spectral data confirmed, without modification. These observations thus show that the major desorption, at 150°C, in the derivative thermograms (Fig. 1c) is due to the desorption of unchanged DIOX from the Ca²⁺-, Cr³⁺- and Al³⁺-exchanged forms.

It is interesting to find, once again, that DIOX behaves in a different manner to the other two cyclic ethers. Adams et al. (1983) reported that DIOX was the optimum solvent for the formation of methyl t-butyl ether. In their studies of the sorption of methanol (MeOH) from binary solution with DIOX, THF and THP, Breen & Deane (1987) found that although the amount of DIOX adsorbed exceeded that of THF and THF, the ratio of DIOX:MeOH was lower than that of THF:MeOH. This means that the solvent, DIOX, allows more of the reactant, MeOH, into the interlamellar space which contains the active acidic site. Furthermore, in their studies of the sorption of THF, THP and DIOX onto AP⁺⁺- and Cr³⁺-montmorillonite Breen et al. (1987a) found that the rate of uptake of DIOX was considerably slower than that of the alcohols MeOH, propan-2-ol and 2-methylpropan-2-ol (Breen et al., 1987c) and that of the cyclic ethers THF and THF. Therefore, in both a dynamic and an equilibrium sense, DIOX allows more of a reactant molecule, such as an alcohol, to approach the active sites.

CONCLUSIONS

The cyclic ethers, THP, THF and DIOX are held more strongly than water in all the exchange forms studied. The desorption of DIOX appears to be cation-independent, whereas the desorption of both THP and THF show some cation-dependence. Mass spectroscopic analysis of the gases evolved during the desorption process indicates that all the cyclic ethers are desorbed unchanged up to temperatures of 230°C.

REFERENCES


Vapour phase sorption kinetics for methanol, propan-2-ol and 2-methylpropan-2-ol on Al\textsuperscript{3+}, Cr\textsuperscript{3+} and Fe\textsuperscript{3+-} montmorillonite. *Clays Clay Miner.* 35, 336-342.


