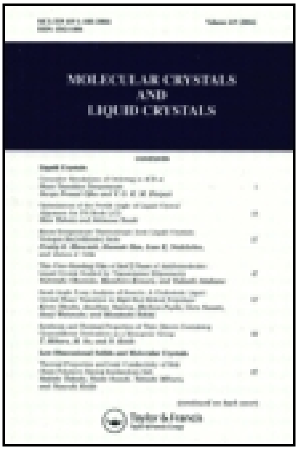

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Structural Characterisation of Catalytically Important Clay-Organic Intercalates

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STRUCTURAL CHARACTERISATION OF CATALYTICALLY IMPORTANT CLAY-ORGANIC INTERCALATES.

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Abstract: Several clay-organic systems of catalytic interest have been characterised by high temperature X-ray powder diffractometry and ^{13}C NMR spectroscopy.

INTRODUCTION

Several members of the clay mineral family of layer silicates are known to assimilate by intercalation a variety of organic compounds[1]. It is also known that certain cation-exchanged forms of the montmorillonite group of clay minerals act as efficient catalysts for a number of chemical conversions (such as the elimination of water from primary alcohols to yield di-(alk-1-yl) ethers, the low temperature thermal decomposition of amines and esters and the elimination of H_2S from thiols during the formation of dialkyl sulphides.)[2,3,4]. In the vast majority of examples so far discovered the inherent Bronsted acidity of the cation-exchanged clays is believed to be responsible for the observed activity. Furthermore, reaction is generally thought to occur primarily within the interlamellar region of the clay.

In any study aimed at the elucidation of the mechanism of clay catalysis it is necessary to establish both the arrangement between the sheets of the organic guest and the nature of the reaction site. However, unlike such minerals as vermiculite where intercalates are sometimes sufficiently ordered and crystalline for full three dimensional crystal structures to be obtained, the clay minerals that have catalytic activity tend, on the whole, to be both microcrystalline (with particle sizes less than 2 μm) and turbostratic. As a consequence single crystal analysis is generally impossible.

Because of these restrictions it is found that several different techniques are required in order to fully characterise such sheet silicate intercalates. In this paper we describe two of the many approaches we have adopted.

RESULTS AND DISCUSSION

(a) X-ray powder diffractometry

In general the measured d_{001} layer spacing may be used as a guide to ascertain whether intercalation has occured.

Under certain catalytic conditions and for certain intercalates however, unequivocal characterisation is difficult due to the rather small changes in spacing which are observed as well as the rather broad (001) peaks presented by some poorly crystalline clays. Thus, the so-called 1-layer, Al^{3+} ion exchanged bentonite (Al-bentonite)-water complex shows a d_{001} of 13.4 Å, whilst the corresponding pentanol complex obtained following the replacement of the water by pentanol has a d_{001} of 13.8 Å. In this case, X-ray diffraction studies carried out in a variable temperature, high pressure cell, have enabled us to use the thermal stability of the clay intercalate systems to distinguish between them. Thus, depending on the amount of interlayer water present, montmorillonites show three different d_{001} spacings and these are attributed to the one-, two- and three-layer water complexes respectively. Using a thin self-supporting film of Al^{3+} ion exchanged gelwhite (Al-gelwhite) saturated with water, in the high pressure X-ray diffraction cell, the d_{001} corresponding to the three-layer complex was observed at 19.6 Å. On heating the sample in an atmosphere saturated with water vapour, this peak was seen to broaden and at 44°C a peak corresponding to the two-layer complex appeared at 15.8 Å. Further dehydration at 51°C produced the one-layer complex

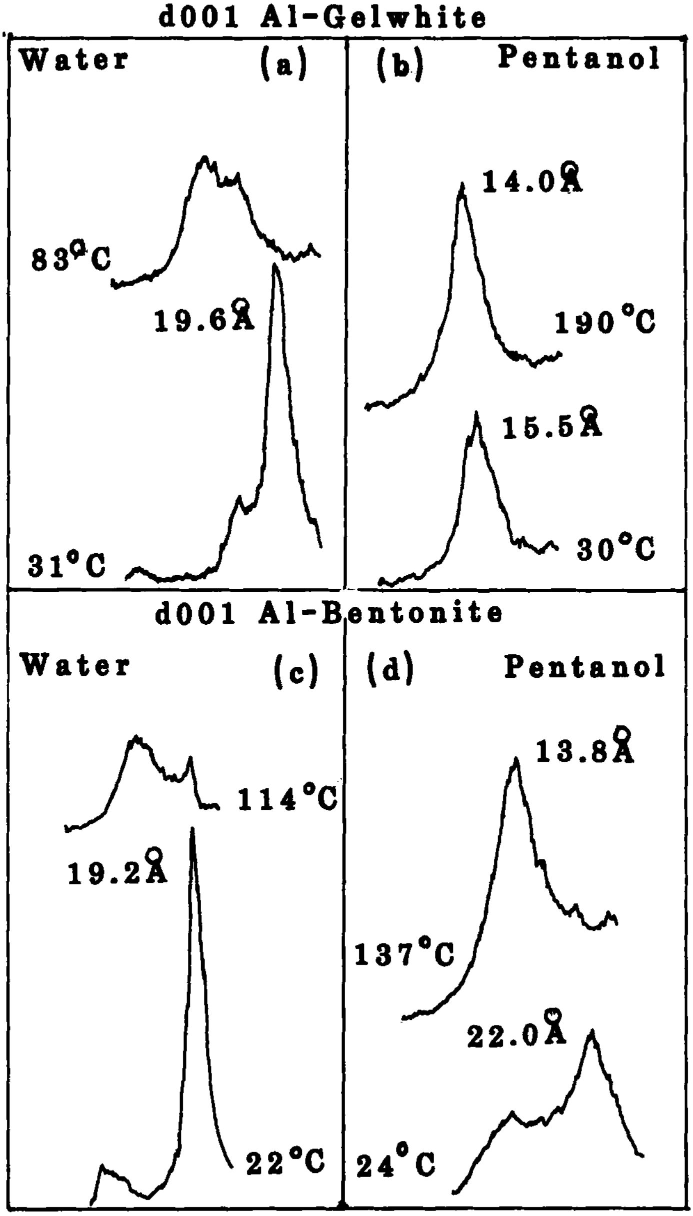
d001 Al-Gelwhite
Water
(a)
(b)
Pentanol
83°C
19.6Å
31°C
14.0Å
190°C
15.5Å
30°C
d001 Al-Bentonite
Water
(c)
(d)
Pentanol
114°C
19.2Å
22°C
13.8Å
137°C
22.0Å
24°C

Figure 1

with a d_{001} of 13.4 Å and above 83°C complete collapse of peak was observed. Fig. 1a shows the d_{001} observed at 31°C and 83°C. For the corresponding pentanol system (Fig. 1b), the highest spacing observed was at 15.5 Å and this may be likened to the two-layer water complex. Dehydration at 93°C produces the one-layer type with a d_{001} of 14.0 Å. This clay-pentanol complex showed much greater thermal stability than the water complex and persisted to temperatures in excess of 190°C.

Thus, by monitoring the thermal stability of the one-layer complex the differences in the behaviour of the clay-water and clay-pentanol systems can be clearly distinguished. Similar studies with Al-bentonite, a clay with a cation exchange capacity similar to that of gelwhite, showed certain differences, (Fig. 1c and 1d). Whilst the behaviour of the Al-bentonite-water system closely paralleled that of Al-gelwhite, showing the three, two and one layer complexes at 19.2 Å, 15.8 Å and 13.4 Å respectively, the three-layer pentanol complex was also observed at 22 Å. Thus it appears that Al-bentonite shows greater affinity than Al-gelwhite, for the intercalation of pentanol. The thermal stability of the Al-bentonite-pentanol system was however, lower than that of the Al-gelwhite system, complete collapse being observed above 150°C. Thus, it is

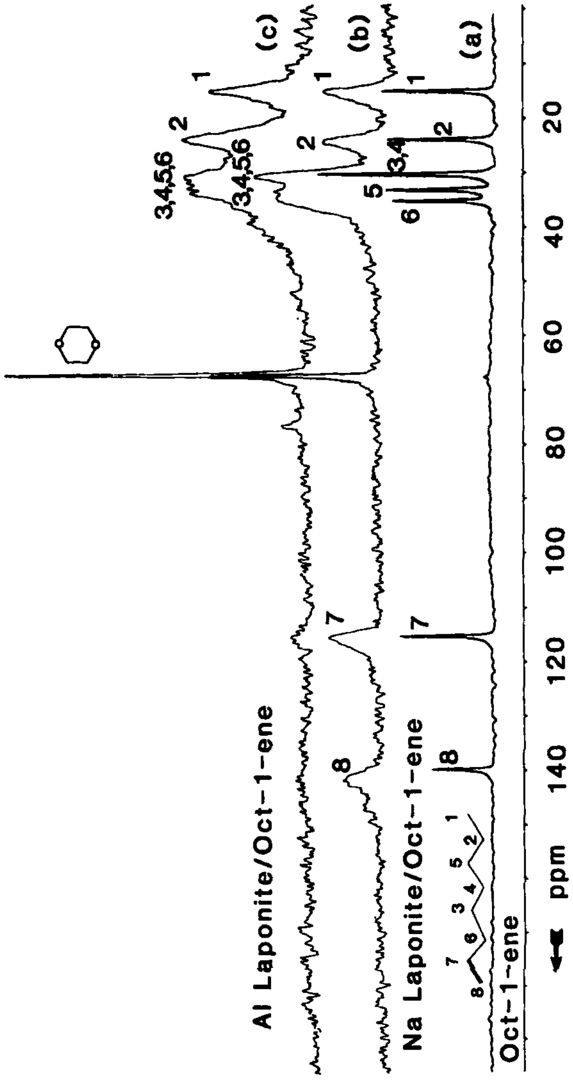
Al Laponite/Oct-1-ene
(c)
1
2
3,4,5,6
Na Laponite/Oct-1-ene
(b)
1
2
3,4,5,6
7
8
Oct-1-ene
(a)
1
2
3,4
5
6
7
8
8 7 6 3 4 5 2 1
ppm
20
40
60
80
100
120
140

Figure 2

seen that for the two clays, whilst the Al-bentonite shows greater affinity for the intercalation of pentanol, of the one-layer pentanol complexes that of Al-gelwhite has the greater thermal stability. These X-ray diffraction studies therefore show, that significant differences in the clay-organic interactions exist even for closely related clays

(b) ^{13}C NMR Studies

To explore further the possibility of using conventional ^{13}C NMR spectroscopy to characterise clay-organic systems[6], a model clay, laponite XLG a synthetic hectorite, exposed to oct-1-ene vapour was studied.

Fig. 2 shows the ^{13}C NMR spectra of (a) oct-1-ene, (b) laponite XLG and (c) Al^{3+} ion exchanged laponite XLG, exposed to oct-1-ene vapour. It is seen that in the first instance, the peaks observed for the clay systems are broad, indicating reduced mobility of the organic guest. In the laponite XLG-oct-1-ene system, the peaks corresponding to the olefinic carbons 1 and 2 at 141 ppm and 115 ppm respectively are clearly seen. In the Al-laponite XLG-oct-1-ene system these absorptions are absent whilst the remainder of the spectrum is similar to that of the laponite XLG-oct-1-ene system. This loss of olefinic absorptions may be due to either the chemical transformation of the double bond or to the immobilisation of the double bond at some site on the clay such that the other carbons remain relatively free. Since no new absorptions are seen, the latter explanation seems to be more likely. As the only difference between the clays is the nature of the exchangable cation, it appears that the olefinic carbons are closely associated with Al^{3+} species whilst the rest of the chain is free to move. This behaviour has also been observed with hex-1-ene and may well be general to all straight chain alkenes.

EXPERIMENTAL:

The X-ray powder diffraction data were obtained using a variable temperature high pressure cell in conjunction with a Phillips APD10 powder diffractometer employing Cu Kα radiation. During the variable temperature studies, a fixed pressure of the vapour of the guest material was maintained in the cell by injection of the relevant liquid.

^{13}C NMR spectra were recorded using a Bruker 250 MHz spectrometer employing D_2O as lock material and dioxane as external reference.

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