The principles of chemical conversion of organic molecules using sheet silicate intercalates

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Abstract. Several recently identified commercially significant processes involving a range of organic reactants are catalyzed by certain cation-exchanged sheet silicates, which can be derived from a number of commonly available clay minerals. Methods of characterizing these catalysts, as well as techniques that throw light on the chemical nature and orientation of the intercalated reactants are discussed with the aid of specific examples utilizing various spectroscopic and diffraction methods. A unified mechanistic interpretation, based on the Brönsted acidity of the catalysts, accounting for the facile production of esters, ethers, certain dimers and polymeric hydrocarbons, is given.

Keywords. Catalysis; sheet silicates; smectites.

1. Introduction

Several distinct categories of organic reaction that proceed efficiently in the presence of cation-exchanged montmorillonites and hectorites have come to light since we first reported (Adams *et al* 1978, 1979) the facile production of di-(alk-2-yl) ethers from alk-l-enes three years ago. These include the production of esters from intercalated carboxylic acids (Ballantine *et al* 1981b); of di-(alk-l-yl) ethers by elimination of water from primary alcohols (Ballantine *et al* 1981a); of alkenes from secondary and tertiary alcohols (Ballantine *et al* 1981a); of dialkyl sulphides by elimination of H_2S from thiols (Ballantine *et al* 1981a); and of secondary amines by elimination of NH_3 from primary amines (Ballantine *et al* 1981b). In addition, many other types of organic reactions have been identified including dimerizations (Thomas *et al* 1977 and Adams *et al* 1977), low-temperature thermal decompositions of amines (Tricker *et al* 1975) and esters [Adams *et al* (in press)], intermolecular hydrogen transfer (Adams *et al* 1979a), lactonization Davies (1980) and polymerization (Ballantine *et al* 1981b) quite apart from the already substantial (Thomas 1982) list of reaction types which earlier workers such as Weiss (1969), Fripiat and Cruz-Cumplido (1974) Pinnavaia and Welty (1975) and others (Brindley 1970; Theng 1974; Barrer 1978) have uncovered. New classes

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of organic reaction involving sheet silicate intercalates continue to emerge, and it is now obvious (Thomas 1982) that considerable scope for controlled synthesis exists by judicious manipulation of the interlamellar regions of the expandable sheet silicates obtained from readily available clays of the montmorillonite type (also designated smectites).

During the course of our work we have paid increasing attention to two aspects of the behaviour of these so-called clay catalysts: the detailed characterization of the montmorillonite prior to use and under conditions that simulate those of the catalytic reactions, and the elucidation of reaction mechanisms.

In this paper we draw together the various threads of the arguments pertaining to the mode of preferred reaction exhibited by the intercalates, and in so doing focus attention on the characterization of the parent or ion-exchanged silicate with a view to emphasizing the key features of the catalysis. By highlighting the principal parameters that influence the catalytic properties of the sheet silicate, it permits a broader appreciation of the factors that may be manipulated to achieve a given catalytic end.

2. Structural considerations

Clay minerals are composed of two distinct types of layers containing SiO_4 tetrahedra and $M (O, OH)_6$ octahedra, with M being, in general, Al, Mg or Fe. The silicates of principal interest here result when one octahedral layer is sandwiched by two tetrahedral layers (see figure 1). If the ion M is divalent (*e.g.* Mg^{2+}), then all the possible octahedral sites within the structure are occupied and the silicate is of the trioctahedral
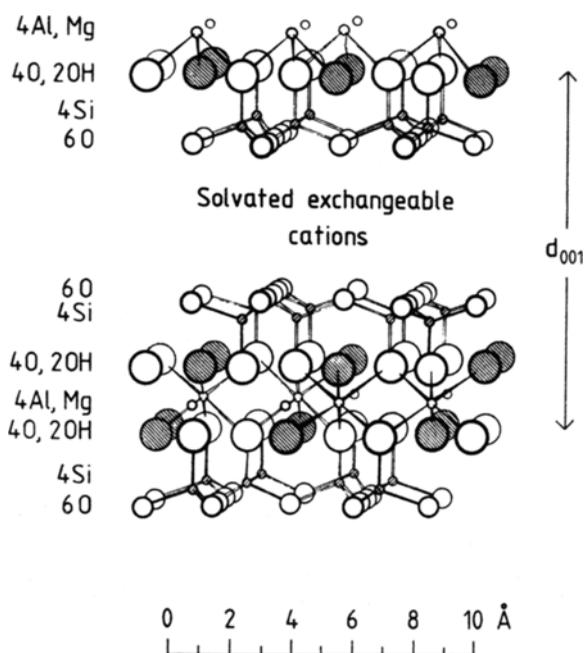

Figure 1. Schematic illustration of the structure of montmorillonite (after Brindley and MacEwan 1953).

type. For trivalent ions (*e.g.* Al^{3+}) only two-thirds of the available sites are occupied leading to a dioctahedral silicate. In addition the tetrahedral and octahedral layers may be partially substituted by ions of lower valency. This produces a negative charge on the layers which is balanced by interlamellar exchangeable cations, which are often Na^+ or Ca^{2+} in naturally occurring clays. The ideal formulae of some smectites are shown in table 1.

With regard to the intercalated organic molecules, figure 2 shows three of the possible ways in which an organic molecule with a hydrocarbon chain may be accommodated in the interlamellar space. Information on the actual orientation adopted may be obtained from x-ray diffraction studies of oriented films of the intercalate (Thomas *et al* 1977; Adams *et al* 1977; Kanamaru and Vand 1970; Adams *et al* 1977a; Williamson *et al* (unpublished)). For smaller molecules information pertaining to orientation is a little less reliable, but we do know some of the broad details of the disposition adopted by butyrolactone and related molecules (Adams *et al* 1977a; Williamson *et al* (unpublished)).

Table 1. Idealised formulae for some selected clay minerals.

Montmorillonite	(½Ca, Na)$_x$ (Si$_8$) (Al$_{4-x}$Mg$_x$)	O$_{20}$(OH)$_4$.nH$_2$O
Beidellite	(½Ca, Na)$_x$ (Si$_{8-x}$Al$_x$) (Al$_4$)	O$_{20}$(OH)$_4$.nH$_2$O
Hectorite	(½Ca, Na)$_x$ (Si$_8$) (Mg$_{6-x}$Li$_x$)	O$_{20}$(OH)$_4$.nH$_2$O
Saponite	(½Ca, Na)$_x$ (Si$_{8-x}$Al$_x$) (Mg$_6$)	O$_{20}$(OH)$_4$.nH$_2$O

$x = 0.66 - 1.0$

(Mg$_6$) O$_{20}$(OH)$_4$.nH$_2$O

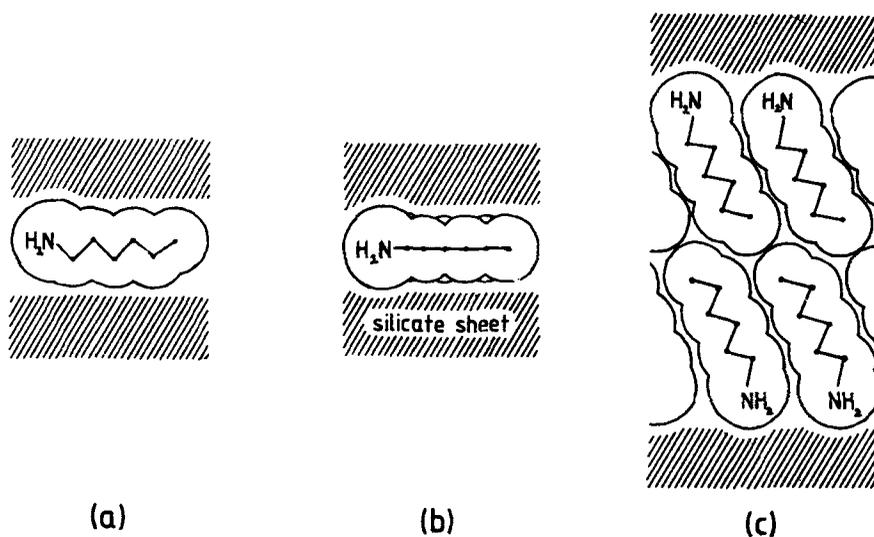(a)   (b)   (c)

Figure 2. Schematic diagram showing three possible orientations of the intercalated *n*-hexylamine molecule: (a) the α_I-configuration, with chain parallel to sheets. (b) the α_{II}-configuration, also with chain parallel to sheets, (but rotated by $\pi/2$ with respect to (a) and (c) the β-configuration, with chain inclined to sheets Nomenclature after Brindley and Hoffman (1962)

3. Chemical composition of montmorillonites

In practice the distinction between the different silicates described above is rarely clear-cut and in particular many clays have substitutions both in the octahedral and in the tetrahedral sites. In addition to the types substitution listed above and in table 1, other elements, particularly iron, are frequently found. Some idea of the variety in composition that exists can be gained from table 2, which lists some structural formulae of several clays taken from the literature.

The unambiguous determination of such structural formulae presents a number of difficulties. Firstly, the clays are often found in deposits containing such impurities as quartz, micas and iron oxides. If these are not removed by sedimentation or other methods, the results of a bulk chemical analysis may be misleading.

Secondly, conversion of the analytical results into a structural formula involves several assumption concerning the allocation of the different elements to the sites available. For example, it is usually assumed that all silicon is present in tetrahedral sites, and that any remaining tetrahedral sites are filled by Al^{3+} and Fe^{3+} ions. Until

Table 2. Typical compositions of some clays.

	Tetrahedral layer	Octahedral layer	CEC*
Montmorillonite[a] "Gelwhite L"	$Si_{7.65}Al_{0.35}$	$Al_{3.20}Fe^{III}_{0.09}Mg_{0.74}$	100
Montmorillonite[b] Chambers, Arizona (Cheto)	$Si_{7.7}Al_{0.3}$	$Al_{2.67}Fe_{0.44}Mg_{0.90}$	150
Montmorillonite[b] Belle Fourche, South Dakota	$Si_{7.86}Al_{0.14}$	$Al_{3.03}Fe_{0.43}Mg_{0.45}$	110
Montmorillonite[c] Camp Berteau Morocco	$Si_{7.75}Ti_{0.06}(Al,Fe^{III})_{0.22}$	$(Al,Fe^{III})_{3.22}Mg_{0.69}$	115
Montmorillonite[d] Wyoming ("Volclay")	$Si_{7.84}Al_{0.16}$	$Al_{3.10}Fe^{III}_{0.38}Mg_{0.52}$	87
Beidellite[c] Black Jack mine	$Si_{6.92}Al_{1.08}$	$Al_{3.92}Fe^{III}_{0.08}$	142
Beidellite[c] Rupsroth	$Si_{7.35}Ti_{0.06}(Al,Fe^{III})_{0.64}$	$(Al,Fe^{III})_{3.54}Mg_{0.45}$	148
Hectorite[c]	$Si_{8.0}$	$Mg_{5.45}Li_{0.55}$	92
Kozakov[c] saponite	$Si_{6.6}Al_{1.36}Fe_{0.04}$	$Mg_{5.0}Fe^{III}_{0.48}Fe^{II}_{0.52}$	120

* The cation exchange capacities are expressed in units of milliequivalents per 100 g. (1 electron/unit cell is *ca.* 140 meq/100 g).
[a] Georgia Kaolin Co., New Jersey.
[b] Cicel and Machajdik (1981).
[c] Chourabi and Fripiat (1981).
[d] Tsunashima *et al* (1981).

other methods are developed for confirming the resulting formula, this approach, which is widely used, should be viewed with some scepticism. Possible confirmatory techniques might include infra-red spectroscopy to determine the location of the negative charge within the sheets (Chourabi and Fripiat 1981), and Mössbauer spectroscopy to determine the oxidation state and location of any iron present (Goodman 1980).

Due to very small particle size of montmorillonites ($<2\mu$m diameter) the information that can be obtained concerning their structure and that of their intercalates is generally limited to that available from x-ray powder diffraction or selected area electron diffraction. Several workers have, however, successfully grown organic intercalates of a closely-related solid, vermiculite (a clay mineral not generally so active catalytically), which does form single crystals, and information obtained concerning the arrangements and contacts within these intercalates may also be relevant to those of the montmorillonites.

4. Techniques and results of characterization

Alongside the determination by chemical analysis the *cation exchange capacity* (CEC) is determined. Several methods are available. The one used by us involves measuring the decrease in concentration of ammonium ions (using an ammonium ion selective electrode) in a solution of ammonium chloride when a known weight of clay is added. Typical values for a range of montmorillonites are given in table 2.

The *water content* of the clay is an important quantity. The differences in the operational sense, between 'one, two- and three-layer clays' are schematized in figure 3. 'Layers', in this context refer to the interlamellar water, though the precise chemical nature of this entrained water is not easily established and in any case is a function of the parent silicate. In some sheet silicates, the water is believed to take up an ice-like mono-layer (Hendricks *et al* 1940). What is clear from TGA and IR, however, is that primary and secondary hydration of the interlamellar cation, itself a rather mobile entity, takes place. Such water is rather readily, but not completely, displaced by various organic species, especially amines and carboxylic acids. As a consequence,
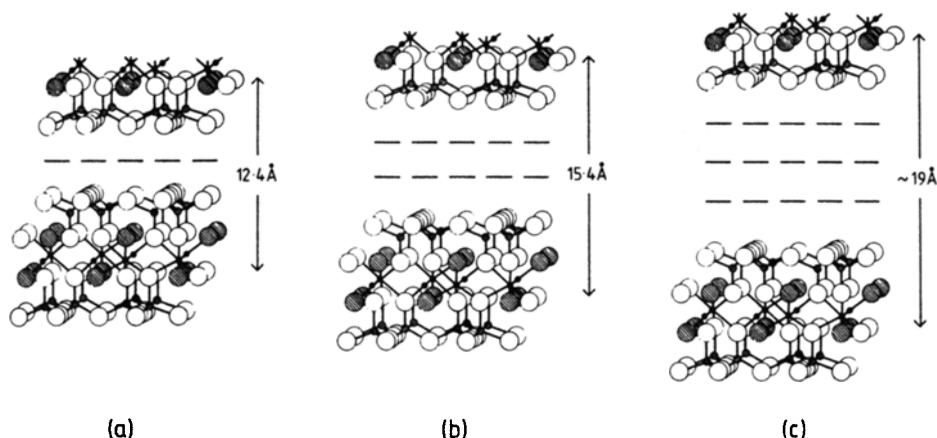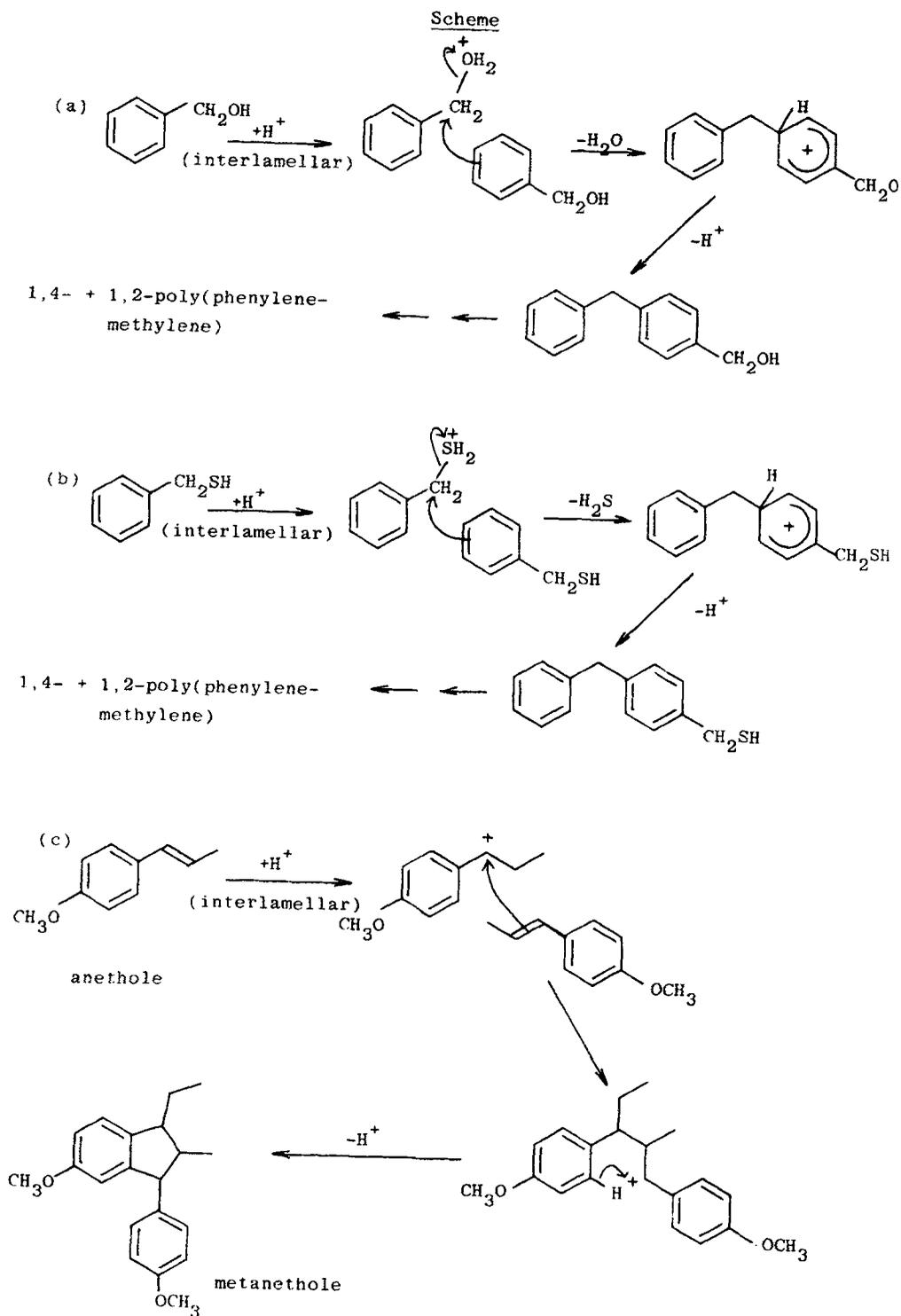

(a)   (b)   (c)

Figure 3. Diagram showing the arrangement of layers of water molecules (dashed lines) in hydrated montmorillonites, and the corresponding interlayer spacings of: (a) a one-layer clay, (b) a two-layer clay, (c) a three-layer clay.
The spacing adopted by a clay depends upon the nature of the silicate layer and the exchangeable cations, as well as the humidity and temperature.

Scheme

(a) ![chemical scheme showing benzyl alcohol CH₂OH +H⁺ (interlamellar) reaction] $-H_2O$ ... $-H^+$

1,4- + 1,2-poly(phenylene-
methylene)

(b) CH₂SH +H⁺ (interlamellar) $-H_2S$ ... $-H^+$

1,4- + 1,2-poly(phenylene-
methylene)

(c) CH₃O— anethole +H⁺ (interlamellar) ... $-H^+$

metanethole

Scheme (cont.)

(d)

$$C_3H_7-CH_2-CH=CH_2 \xrightarrow[\text{(interlamellar)}]{+H^+} C_3H_7-CH_2-\overset{+}{C}H-CH_3 \;\rightleftharpoons\; C_3H_7-\overset{+}{C}H-CH_2-CH_3$$

$$C_3H_7-CH_2-\overset{+}{C}H-CH_3 \xrightarrow{ROH} C_3H_7-CH_2-\underset{\overset{\mid}{\overset{+}{H-OR}}}{CH}-CH_3 \xrightarrow{-H^+} C_3H_7-CH_2-\underset{\overset{\mid}{OR}}{CH}-CH_3$$

$$C_3H_7-\overset{+}{C}H-CH_2-CH_3 \xrightarrow{ROH} C_3H_7-\underset{\overset{\mid}{\overset{+}{H-OR}}}{CH}-C_2H_5 \xrightarrow{-H^+} C_3H_7-\underset{\overset{\mid}{OR}}{CH}-C_2H_5$$

the interlamellar microenvironment is converted from a predominantly hydrophilic to an oleophilic state, making it more conducive to the further insertion of organic species which may otherwise be difficult to intercalate into the original, water-rich montmorillonite.

The ^{57} *Fe Mössbauer spectrum* (taken with a transmission geometry) readily detects structural changes which may result in iron-containing smectites as a result of purification or ion-exchanged as well as during or after catalysis (Rozenson and Heller-Kallai 1978). There is little doubt that the silicate layers are modified during ion-exchange. Figure 4 demonstrates the complete absence of the initial structural ferrous species (a) following cation exchange by chromium (b). Although rigorous quantitative assessment of of site population is, in general, extremely difficult, such major changes in oxidation state are readily studied using this technique. At one time it was suspected
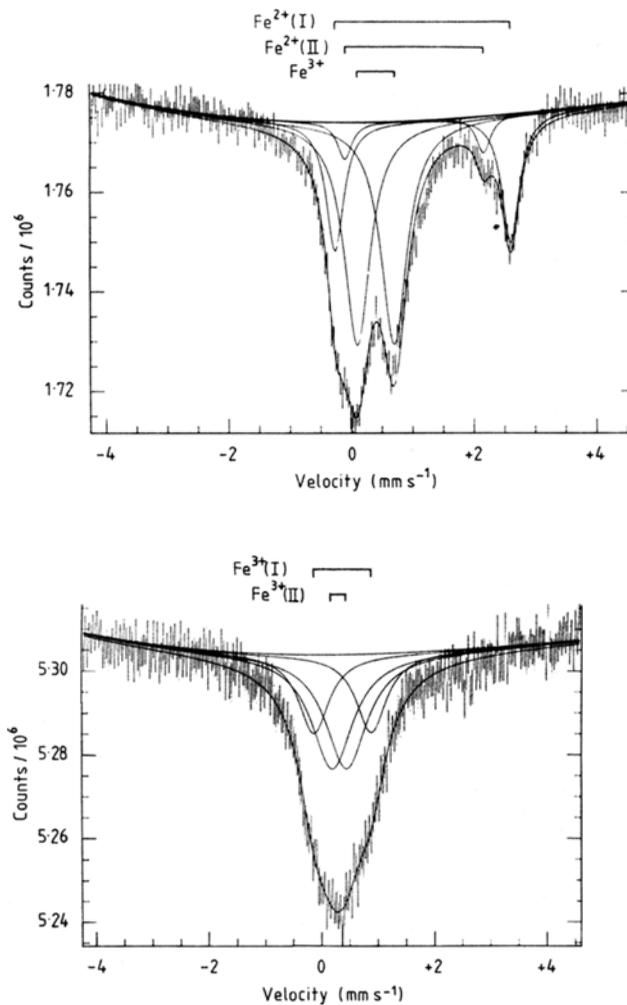

Figure 4. Mössbauer spectra of the naturally occurring montmorillonite before and after exchange by Cr^{3+}. The absence of a ferrous absorption after exchange is evident.
[Fe^{2+} (I) $\delta = 1.17$, $\Delta = 2.86$; Fe^{2+} (II) $\delta = 1.03$, $\Delta = 2.26$; Fe^{3+} (I) $\delta = 0.40$, $\Delta = 0.60$ mm sec^{-1} for natural montmorillonite].
[Fe^{3+} (I) $\delta = 0.34$, $\Delta = 1.08$; Fe^{3+} (II) $\delta = 0.31$, $\Delta = 0.33$ mm sec^{-1} for chromium exchanged montmorillonite].

(by us) that the constitutional iron was involved, either directly or indirectly, in certain of the reactions of the organic intercalates. This now seems unlikely, at least when Bronsted rather than Lewis acidity holds sway, as results we have obtained recently using a commercially available montmorillonite known as Gelwhite (which is essentially free from iron) are not significantly different from those obtained with iron-rich montmorillonites.

IR *spectroscopy* carried out using thin self-supporting films (Farmer 1974) ($\leq 50 \mu$ m thickness) of the appropriate purified montmorillonite, has proved most illuminating, as may be seen from figures 5 and 6. Figure 5 shows the spectrum of a purified sample of Wyoming montmorillonite and figure 6 shows the effect on the spectrum as the
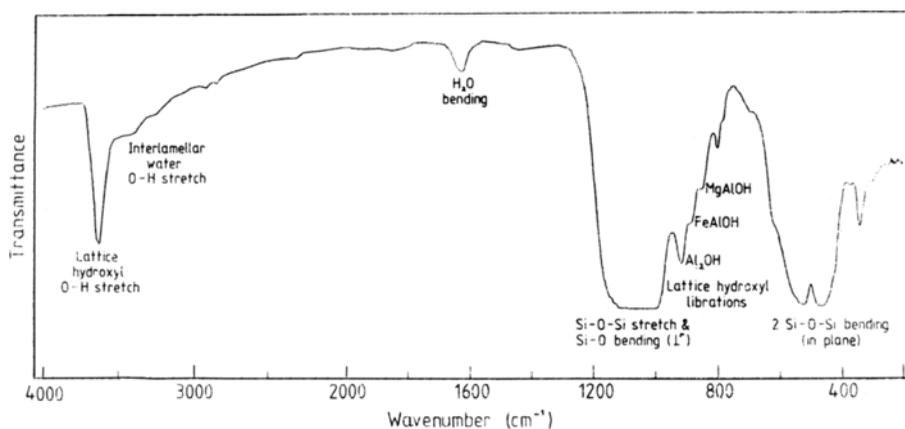

Figure 5. Infrared spectrum of a typical natural bentonite. Small amounts of residual silica (absorbing at $\sim$ 797, 760 and 695 cm^{-1}) are present.
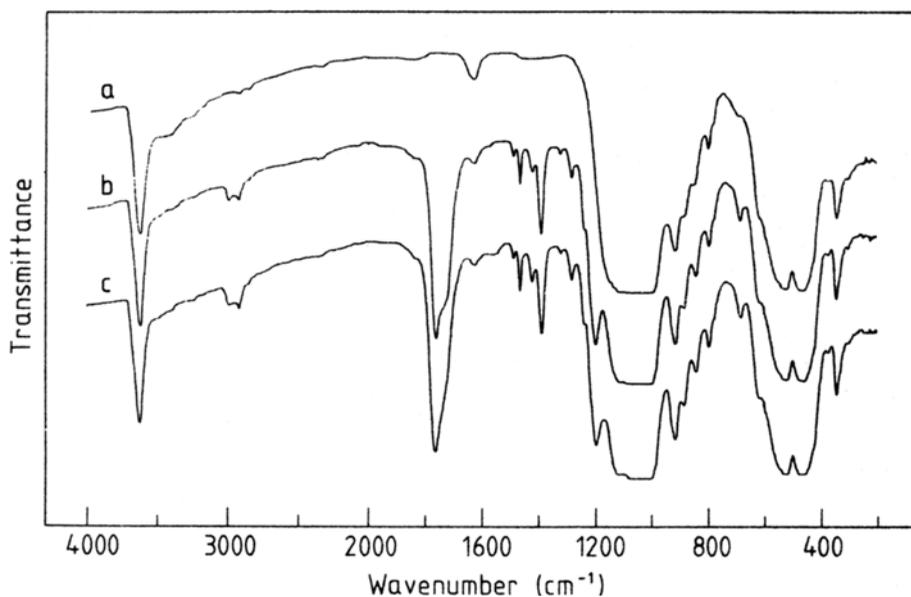

Figure 6. Intercalation of sedimented bentonite by γ-butyrolactone: (a) before exposure, (b) after 90 min exposure to vapour at 25° C, (c) after 14 days exposure to vapour.

sample is exposed to γ-butyrolactone (γ-BUL) vapour. It can be seen that the intensities of the interlamellar water vibrations are decreased, and that new absorptions, due to the organic molecule, have arisen. X-ray diffraction indicates that intercalation has indeed occurred: the interlamellar spacing changes from 12.4 Å for the hydrated material to 18.22 Å after 10 days in the vapour of γ-BUL. This spacing corresponds to a double layer of γ-BUL molecules between the sheets. After 1½ hr in the vapour, the x-ray diffraction pattern has an irrational series of peaks, indicating that a mixture of at least two different spacings is present. The shoulder on the low wave number side of the carbonyl absorption at *ca* 1760 cm^{-1} in the IR spectrum indicates that γ-BUL molecules exist in two types of environment in this sample, and is consistent with the existence of a proportion of one-layer intercalated material.

IR is particularly useful in determining (a) the relative amounts of protonated and unprotonated organic species (see figure 7) or of dissociated and undissociated or dimerized acids, and (b) the rate of uptake of organic species (in a given molecular form) as a function of the interlamellar cation. Figure 8 reveals the important role played by the interlamellar ion in governing uptake kinetics.

Another essential characterizing tool is *x-ray diffractometry* since it provides generally reliable clues as to the occurrence of intercalation by the change in *d*-spacing*. Also one-dimensional Fourier projection maps, which may be extracted from the intensity of (00l) reflexions when highly oriented films (and hence large values of l) of the intercalate are formed yield instructive information pertaining to the 'time-averaged' orientation of the relatively rigidly held guest species in the interlamellar space (see figure 9). Thus, figure 9 (a) shows the electron density projection along the z-direction of a sample of vermiculite, obtained by Fourier synthesis using the observed intensities of the 00l reflections (up to $l = 17$) and calculated phases based upon the accepted framework structure. Figure 9 (b) is an electron density projection obtained by Fourier synthesis of calculated structure factors (to 00, 17) for a model structure of the vermiculite (see also legend to figure).

X-ray diffractometry is of additional value, however, since it may be utilized to characterize the clay catalysts under conditions close to, or the same as, those that prevail under actual reaction conditions. Thus figure 10 shows the variable temperature X-ray diffractometric traces, in the region of 2θ corresponding to reflections from the basal (00 l) planes of an Al^{3+}-exchanged montmorillonite intercalate containing (a) water and (b) 1-pentanol. Clearly this tool gives some insight as to whether a three-layer, two-layer or single-layer or a collapsed (9.5 Å repeat distance) clay exists under certain circumstances. 1-Pentanol which yields principally either 1,1 dialkyl ether or 1-pentene, depending upon the precise reaction conditions, is still retained as a 'one-layer' intercalate, with a d-spacing of 12.6 Å giving a van der Waals gap (or interlamellar space) of about 3.1 Å, at 175° C, at which temperature the heterogeneous reaction (pentanol vapour/solid Al^{3+}-exchanged montmorillonite) proceeds briskly to yield considerably more 1-alkene than when the reaction is carried out in presence of surplus liquid pentanol, in a bomb at 180°.

NMR, using conventional spectrometers (*i.e.* without 'magic-angle spinning'and/or cross-polarization techniques (Fyfe *et al* 1981; Andrew 1981) which are, in general, the preferred aids for extracting chemical shift data from solids), may be profitably used to reveal instructive information about guest entities in sheet silicates. For relatively mobile organic molecules within the interlayer region dipolar broadening is

*This is not an infallible guide: sometimes, when intercalation is known to have occurred, there is essentially no change in d–spacing (Adams 1974).
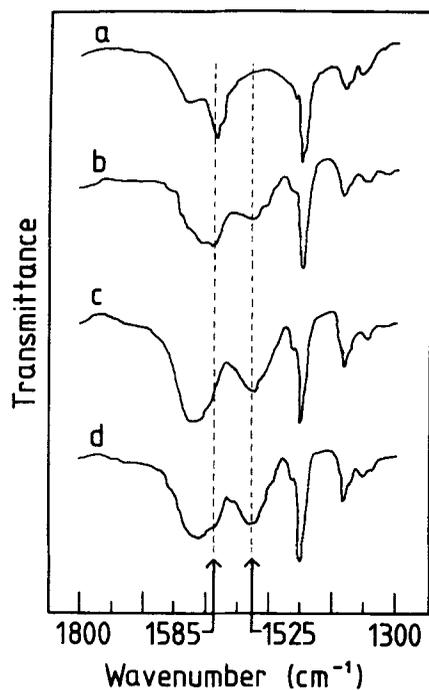
Figure 7. NH and CH bending absorptions in the infrared spectra of cyclohexylamine intercalated into bentonite: (a) naturally occurring clay (exchangeable cation principally Na^+) (b) after Cu^{2+} exchange, (c) Ni^{2+} exchange, (d) after Al^{3+} exchange.

The absorptions at 1585 and 1525 cm^{-1} are characteristic of the neutral and protonated cyclohexylamine molecules, respectively.
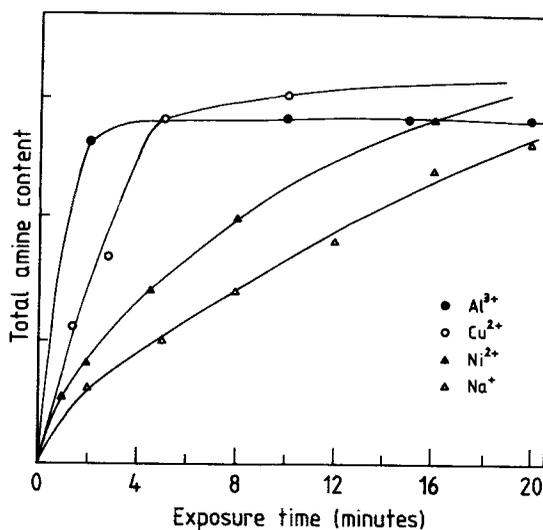

Figure 8. Comparison of rates of cyclohexylamine uptake by differently exchanged bentonite samples. Ordinate proportional to intensity of a CH breathing absorption and hence to the total amount of amine absorbed (protonated and non-protonated).
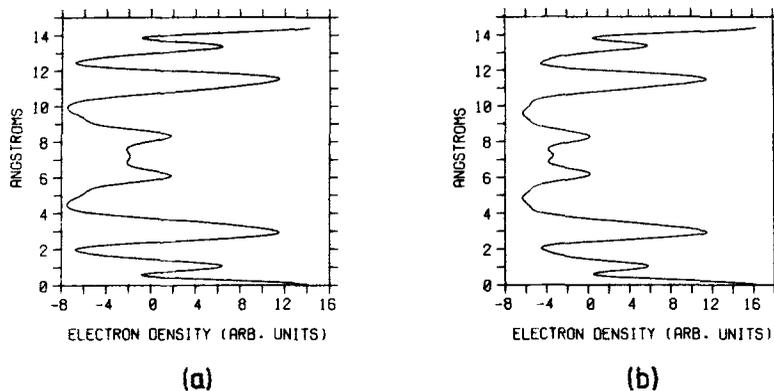
Figure 9. (a) Experimentally based and (b) theoretically deduced electron density projections for a vermiculite: water intercalate. The framework composition and structure follows closely that used by Mathieson and Walker (1954). The amount of water present in (b) was obtained by thermogravimetric analysis and the positions of the water molecules were obtained by refinement using our recorded intensity data.
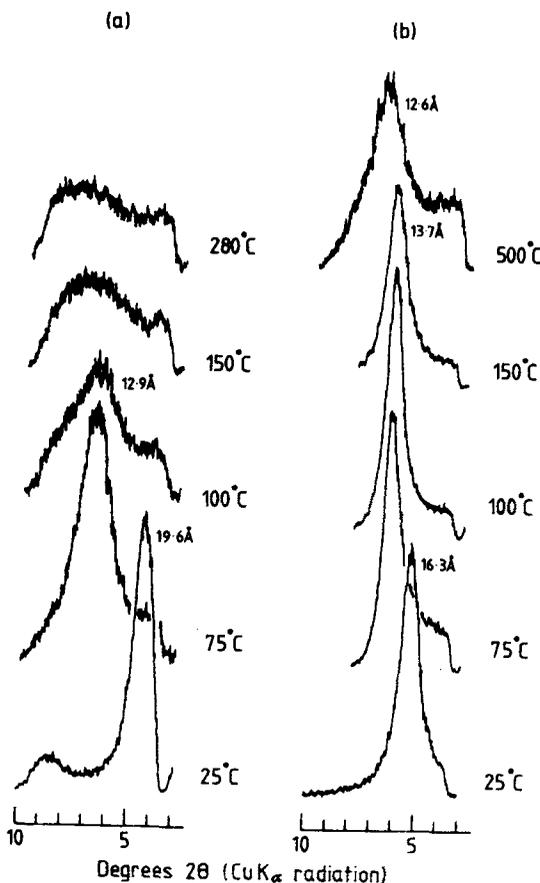

Figure 10. Positions and relative intensities of the (00*l*) reflections obtained with: (a) an Al-montmorillonite:water intercalate, and (b) an Al-montmorillonite:pentanol intercalate as a function of temperature. The presence of 1-pentanol clearly results in a more temperature-stable expanded structure. The shoulder present within these traces at *ca* 3.5° (2θ) is an instrumental artefact.

minimal so that quite good resolution may be achieved, adequately, in fact, to yield chemical shifts and relaxation times which, in turn, afford information pertaining to the precise degree of molecular freedom, keto-enol equilibria of certain organic species loosely constrained in the micro environment of the interlamellar space and the composition of the guest (especially if there are mixtures of organic species). ^{13}C-spectra recorded at 20 MHz, as well as straight forward ^{13}C spin-lattice relaxation time measurements of a *p*-xylene intercalate of a synthetic hectorite point (Fyfe *et al* 1981; Andrew 1981) to the integration of the xylene guest into the sheet-silicate host–all three structurally distinct carbon atoms have relaxation times (*ca* 450 msecs) that are essentially indistinguishable from one another. The ^{13}C NMR spectrum of cyclohexylamine intercalated within the sheets of a synthetic hectorite is shown in figure 11. Mass analysis and x-ray diffraction (the interlayer spacing increasing from *ca* 12 Å to *ca* 16Å) clearly support the view that the signal originates from intercalated material. Loss of motional freedom, compared with that of the liquid state, is suggested by the increased line widths.

Other techniques, such as acidity measurements using probe molecules (van Roos-malen 1980) are potentially of use in distinguishing one particular clay catalyst from another. As well as Hammett indicators and pyridine, which have been used to determine acidity, an IR absorption at *ca* 1290 cm^{-1} which appears when *t*-butylamine is introduced into a clay catalyst, could in principle also be used to compare the Brönsted acidity of related clays, since the intensity of this absorption increases with the polarising power of the exchangeable cations (*e.g.* $I_{Na^+} < I_{Ni^{2+}} < I_{Al^{3+}}$). This band may be attributable to the *t*-butyl carbenium ion: the fact that NMR measurements did not confirm its presence might be ascribed to either the low probability of such a cation having sufficient mobility in the interlamellar space to give an observable resonance or to a very short lifetime associated with the carbenium ion. Another method as yet inadequately exploited, is the protonic conductivity of the clay (Sheffield and Howe 1979): this too reflects directly the Brönsted acidity of the catalyst. Lastly high-resolution electron microscopy, as a post-mortem implement, reflects directly (Williamson 1980) the extent of intercalation and its uniformity, or otherwise, within individual crystallites.
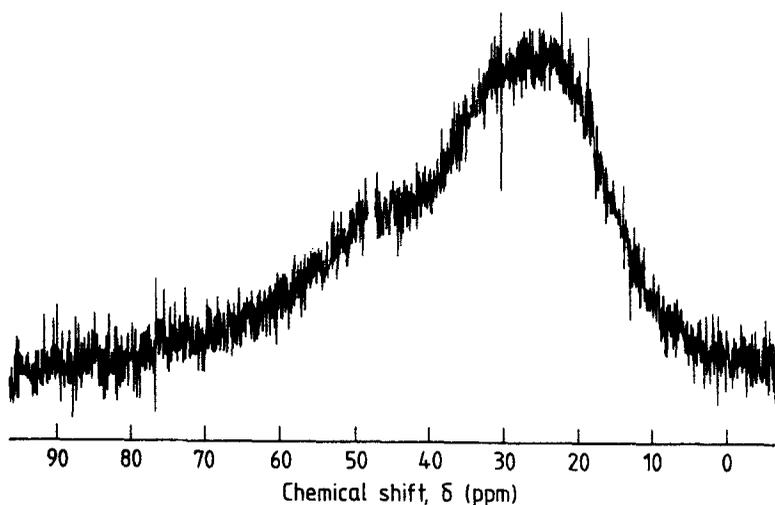

Figure 11. ^{13}C NMR spectrum of 0.16 g cyclohexylamine intercalated into 0.75 g of a synthetic hectorite. The ppm scale is relative to TMS.

5. Summary of catalytic features

We now proceed to enumerate the kinds of conclusion that may be drawn pertaining to reaction conditions and mechanisms from the application of one or more of the techniques discussed in the preceding section. Thus:

(a) *Proof* of the occurrence and nature *of intercalation* comes from x-ray diffractometry and infrared spectroscopy (both of which may be utilized under conditions that closely simulate those that prevail under actual reaction conditions) as well as from NMR studies. TGA provides further circumstantial evidence.

(b) *Proof* that protonation of at least one of the species is an essential requirement for certain reactions comes from infra-red measurements. Moreover, infrared has shown directly the coexistence of protonated and unprotonated amines, a feature which is responsible in part for the unique character of chemical conversions of organic molecules using sheet silicate intercalates.

(c) *Proof* of motional freedom of the intercalated entity comes partly from x-ray diffraction but more directly from NMR line shape and relaxation time data (^{13}C and ^{1}H, see Fyfe *et al* 1981 and Andrew 1981).

(d) *Proof* of the direct or indirect *participation* of certain framework ions (*e.g.* Fe^{2+} or Fe^{3+} in the octahedral or tetrahedral sub-lattices of the sheet silicate) is sometimes provided by spectroscopic measurements, especially Mössbauer absorption technique (Tennakoon *et al* 1974). (By taking two distinct kinds of montmorillonite, one rich in iron the other relatively free of it we have shown that the facile production of ethyl acetate from acetic acid and ethylene is not significantly influenced by so-called lattice iron).

6. Significance of results

The overwhelming majority of novel reactions that may be effected with the agency of sheet silicate intercalates are proton-catalyzed. Some typical examples are shown in the scheme. The production of 1,4- and 1,2-poly (phenylenemethylene) from benzyl alcohol and thio benzylalcohol (Ballantine *et al* 1981a) ((a)and (b)) as well as metanethole from anethole (Adams *et al* in preparation) (c) and sec-ethers from l-alkenes (Adams 1978, 1979) (d) are shown to have common mechanistic features. In this sense clay catalysts may be pictured in broadly the same mechanistic terms as zeolite catalysts. The solid silicate serves principally as a rich source of protons. But whereas a zeolite possesses a well-defined pore structure (and connectivity between the pores) with access only to relatively small organic molecules, the sheet silicate is in principle capable of 'opening' to accommodate reactant and product molecules of much greater dimensions. A delicate balance of opposing forces dictates whether or not intercalation of a guest by a layered host may take place: energy has to be expended whenever the distance between a central, interlamellar cation and the sheet-anion is increased, but energy is released if the guest is strongly bound to the cation or the interior surface of the silicate. Quantitative discussions of the various factors involved, including identification of separate energetic terms, have recently been given (Barrer 1978; Jenkins and Hartman in press). But it is not yet possible accurately to predict which reactant species will be preferentially intercalated for a given type of cation-exchanged sheet silicate. Greater understanding of the principles of clay catalysis are likely to emerge from the development of techniques for the *in situ* study of chemical reaction by XRD, IR and Mössbauer spectroscopy.

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