

Review Article

Spectroscopic Studies on Organic Molecules Intercalated into Clays^{*}

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Abstract. An overview of clay structures and characterization methods is followed by a discussion of some adsorption reactions of organic molecules which have been studied spectroscopically. These can be divided into two main classes: adsorption with and without reaction.

Key words: Clays, intercalation, montmorillonite, kaolinite, illite, vermiculite, intercalation, organic guests, XRD, TGA, FT-IR, FT-Raman.

1. Introduction

Two classes of naturally occurring aluminosilicates are of interest in host–guest chemistry: zeolites and clays. Although both can be based on aluminosilicate building blocks they have very different structures. Zeolites are crystalline microporous compounds with molecular-sized intersecting channels and cages. In addition to naturally occurring materials a wide range of synthetic materials are available, many of which have found widespread applications as ion-exchangers, molecular sieves and catalysts [1]. Although many clays are aluminosilicates they need not contain aluminium. The main interest in clays are with those having a layered structure i.e. the sheet silicates or *phyllosilicates*, although clays without a layered structure are also known [2].

The structural features of a typical clay, montmorillonite, are illustrated in Figure 1. The noteworthy features are:

- (i) The TOT (or 2 : 1) arrangement of atoms i.e. the silicon atoms in one layer are tetrahedrally (T) coordinated, the Al or Mg atoms in the next layer are octahedrally (O) coordinated followed by tetrahedrally (T) coordinated silicon atoms. An alternative arrangement is the TO or 1 : 1 arrangement (Figure 2).
- (ii) Each layer is negatively charged.

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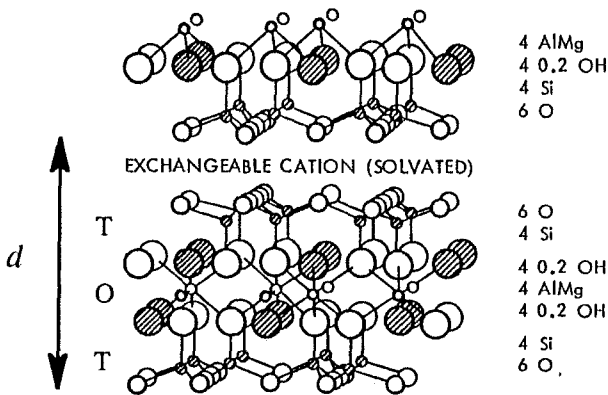


Figure 1. The structure of montmorillonite.

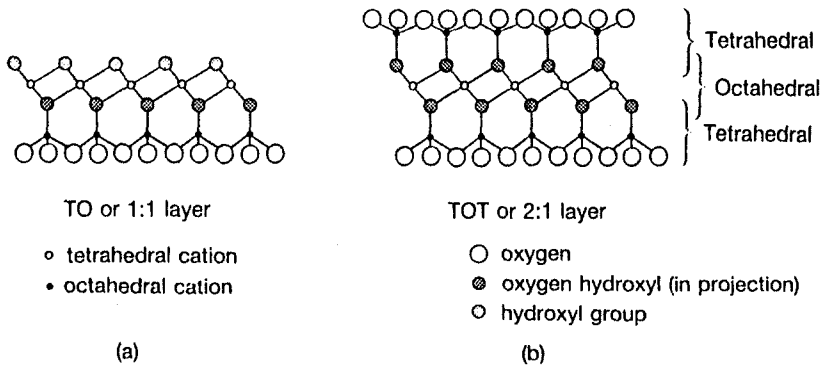


Figure 2. Illustration of the TO-type (a) and the TOT-type (b) layer structures.

- (iii) This charge is balanced by having counter cations in the interlayer space. These are usually exchangeable and clays can thus be used as ion-exchangers.
- (iv) The counter cations are hydrated. Additional water, termed *zeolitic water*, can also be present in the interlayer space. These water molecules play a prominent part in the reactivity of clays (Section 6.2).
- (v) The interlayer spacing, the d value, is a characteristic property of the clay.

A very large number of different natural clays exist depending on whether the Si atoms in the tetrahedral layer or the Al atoms in the octahedral layer have been replaced by other atoms. The oxidation number of the substituting atom will affect the net charge of the layer and thus determine how many exchangeable cations, characterized by the cation exchange capacity (cec), are present in the interlayer space.

Figure 3 illustrates the structures of a few of the numerous naturally occurring clays. Kaolinite has a 1:1 or TO structure, the layers are uncharged and the cec value is very low. Montmorillonite has a large cec value. Illite also has a TOT







MINERAL	STRUCTURE	COMPOSITION (idealized)	CATION EXCHANGE CAP. meq/100g
Kaolinite		$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	1 - 10
Montmorillonite		$\text{Ex}_x[\text{Al}_2 - x\text{Mg}_x] \langle \text{Si}_4 \rangle \text{O}_{10}(\text{OH})_2$	80 - 140
Illite		$\text{K}_{1-x}[\text{Al}_2] \langle \text{Al}_1 - x\text{Si}_3 + x \rangle \text{O}_{10}(\text{OH})_2$	10 - 40
Chlorite		$[\text{Mg}, \text{Al}]_3(\text{OH})_6[\text{Mg}, \text{Al}]_3 \cdot \langle \text{Si}, \text{Al} \rangle_4 \text{O}_{10}(\text{OH})_2$	5 - 30
Vermiculite		$\text{Ex}_x[\text{Mg}_3] \langle \text{Al}_x\text{Si}_{4-x} \rangle \text{O}_{10}(\text{OH})_2$	100 - 180
		Tetrahedral layer $\langle \rangle$ Octahedral layer $ $	

Figure 3. Schematic view of the structural units of the principal clay mineral groups, together with typical (idealized) chemical compositions and cation exchange capacities.

structure but with some of the Si atoms in the tetrahedral layer being replaced by Al, and a low cec value. Chlorite has a complicated layer structure, the so called 2 : 1 : 1 structure and a small cec value. Vermiculite also has a TOT structure where the octahedral layer is based solely on Mg and some of the Si in the tetrahedral layer has been replaced by Al. Another high cec value comparable to that of montmorillonite.

2. Host Properties

A very diverse range of organic molecules can intercalate into these layered structures by a variety of mechanisms [3]:

- ion exchange: in the case of organic cations
- cation solvation by replacing the water of hydration
- dipole-dipole interactions with the layer atoms
- hydrogen bonding with the water molecules, with the Si—OH and Al—OH groups and with any organic cations exchanged into the clay.

Some guests can be accommodated by more than one of these mechanisms, an example being the adsorption of benzidine on ion-exchanged montmorillonites as reported by Lahav *et al.* [4]. Each of the illustrated modes of association (Figure 4), which is dependent on the degree of hydration and the cation present, has been detected spectroscopically.

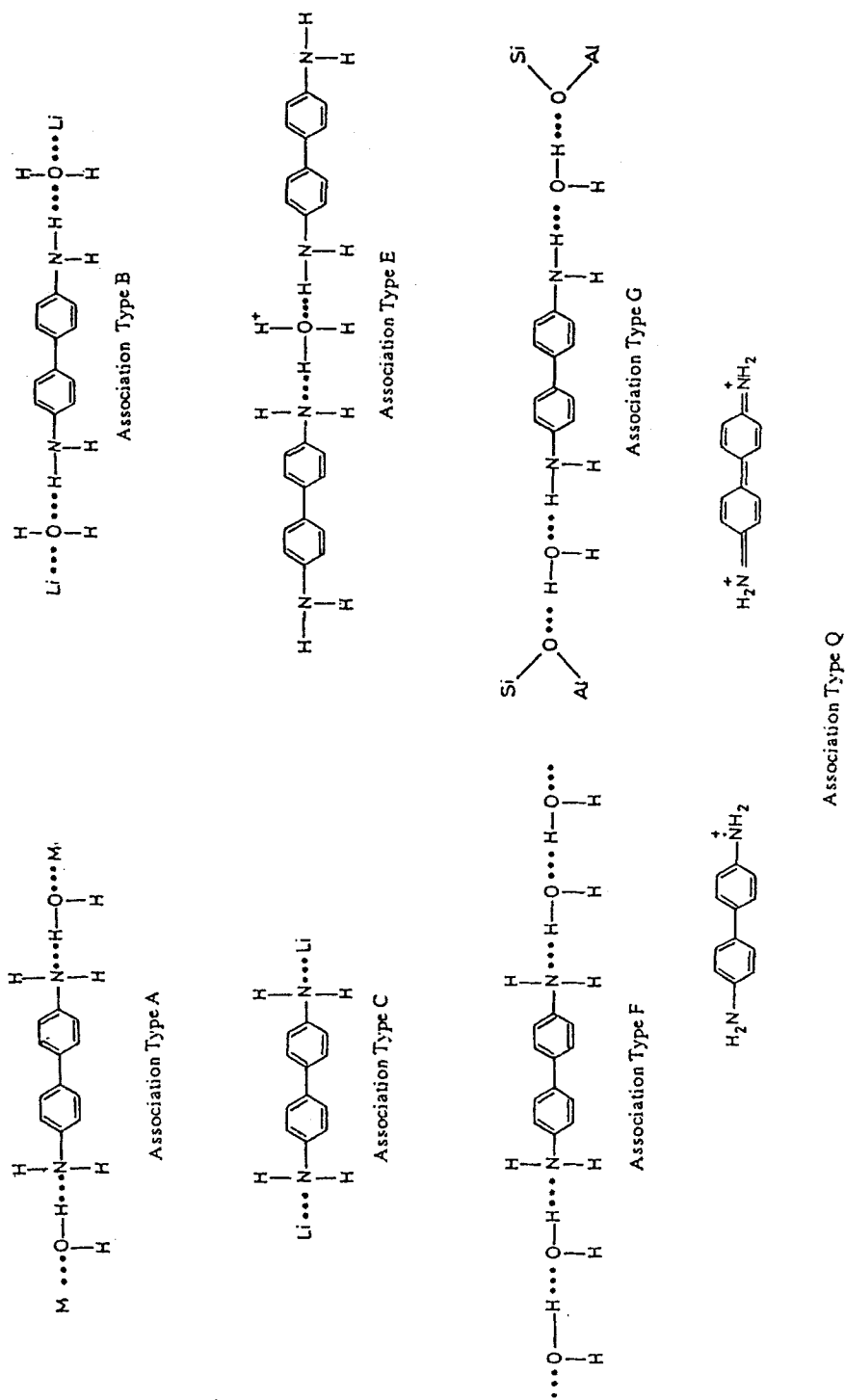


Figure 4. Modes of association of benzidine on clays. Reproduced with permission from *J. Therm. Anal.* **40**, 41 (1993).

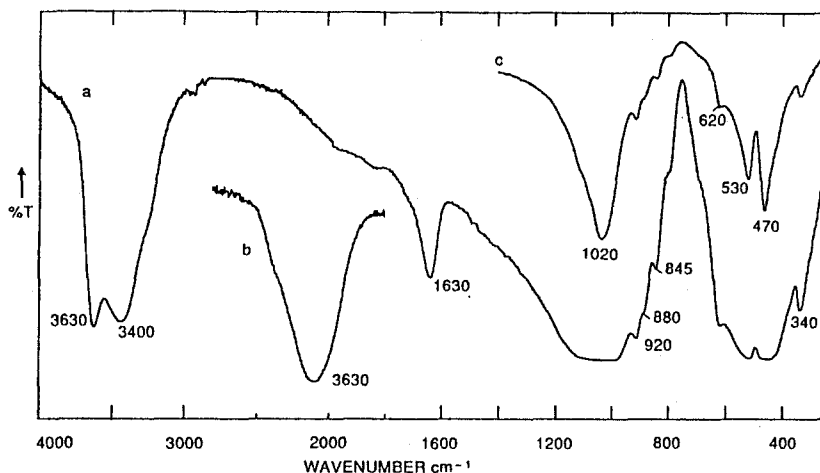


Figure 5. IR spectra of untreated montmorillonite in KBr discs: (a) unheated (b) heated for 16 hr at 150 °C (c) less concentrated disc than in (a).

Type A: H bonding with the water of solvation, N---H type (benzidine acting as the proton acceptor).

Type B: H bonding with the water of solvation, H---O type (benzidine acting as the proton donor).

Type C: Interaction with the cation which acts as a Lewis acid site.

Type E: Benzidine/benzidinium cation/water interaction.

Type F: Extended H bonding with the zeolitic water.

Type G: Interaction with the framework atoms via water molecules.

Type Q: Formation of cationic guest species.

3. Characterization

Due to the wide range of possible host-guest interactions it is essential to use a combination of characterization techniques [5].

IR spectroscopy can easily identify water in materials. Figure 5 illustrates the IR spectrum of montmorillonite, where the presence of two bands at 3630 and 3400 cm^{-1} indicates two types of OH groups, with the latter band disappearing on heating the sample to 150 °C (Figure 5b). This points to the loss of water, both solvation and zeolitic, on heating leaving just the band from the clay OH groups. IR spectra give only qualitative information about the water content. Quantitative information is obtained using thermogravimetric analysis (TGA) where the weight loss of the sample on heating is followed (Figure 6). By 200 °C about 10% of the sample weight has been lost and heating to 700 °C leads to a further loss of 4%. This illustrates the advantage of using a combination of techniques.

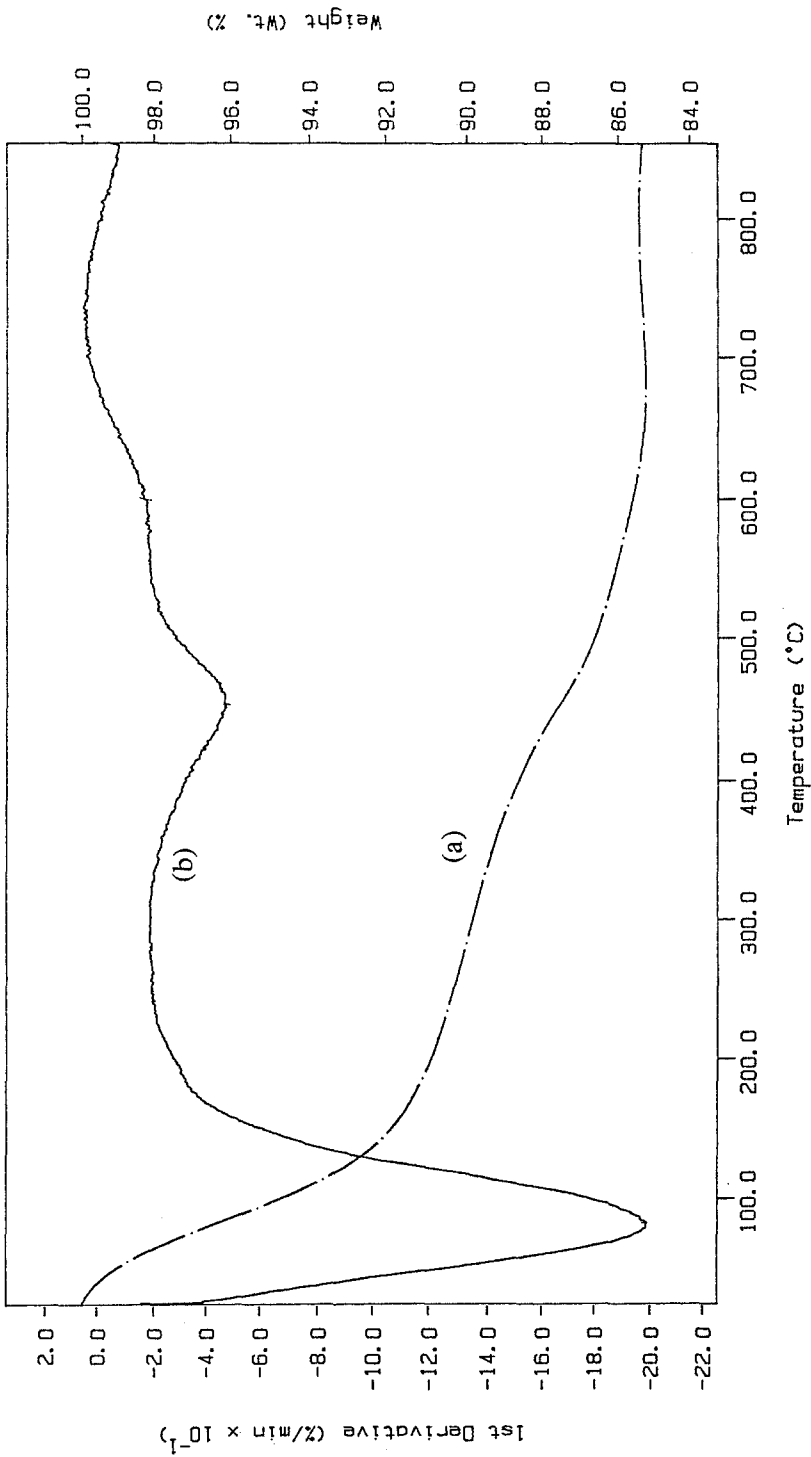


Figure 6. TGA (a) and DTG (b) traces of montmorillonite.

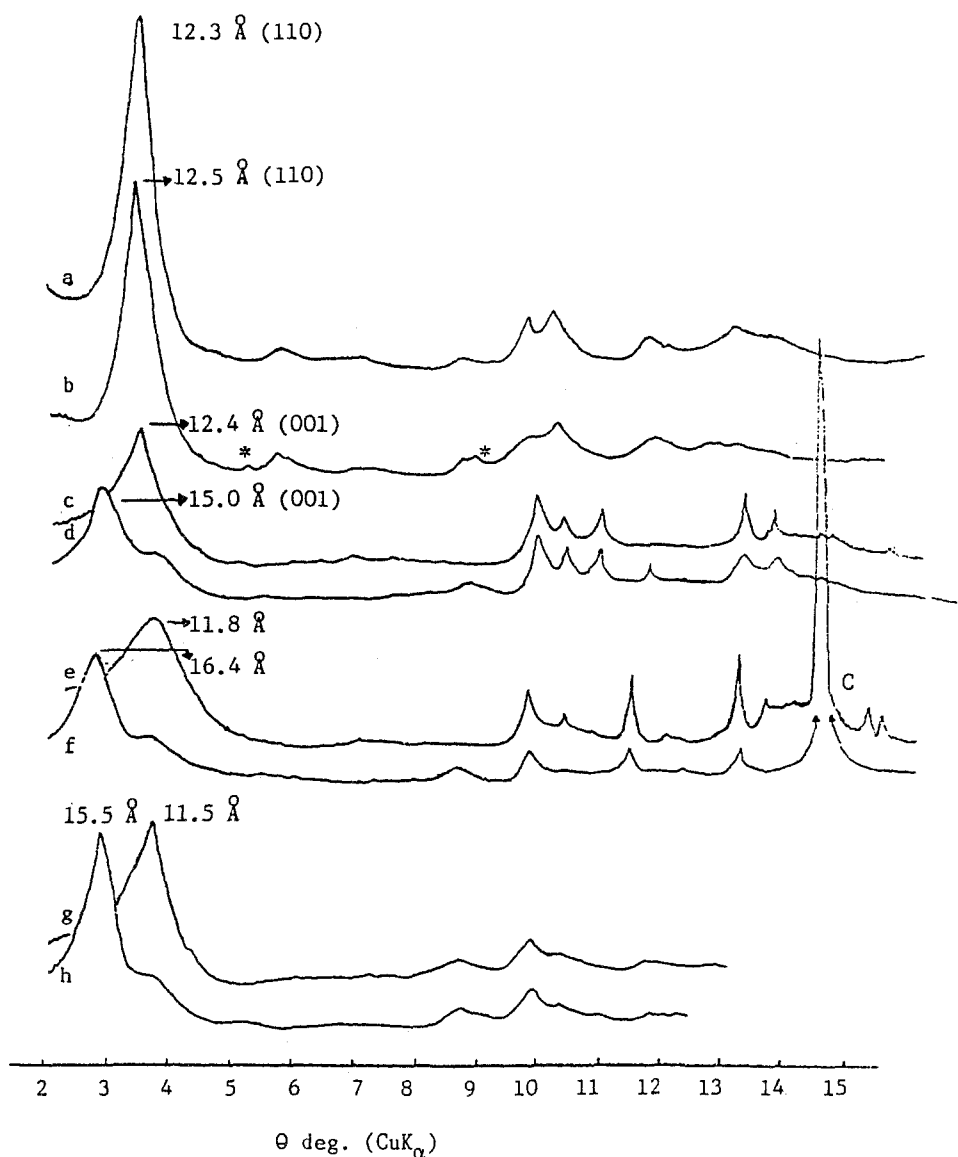


Figure 7. XRD patterns of (a) natural sepiolite (b) 4,4'-bipy treated sepiolite (c) natural bentonite (d) 4,4'-bipy treated bentonite (e) natural hectorite (f) 4,4'-bipy treated hectorite. C indicates a calcite reflection. (g) natural saponite (h) 4,4'-bipy treated saponite.

When a clay adsorbs a guest there will be an increase in the interlayer spacing which can be followed using X-ray diffraction (XRD). Figure 7 shows the XRD patterns for some clays before and after the adsorption of 4,4'-bipyridyl [6]. The most significant difference for bentonite (c,d), hectorite (e,f) and saponite (g,h) lies in the small angle region where the position of the band moves to lower θ value

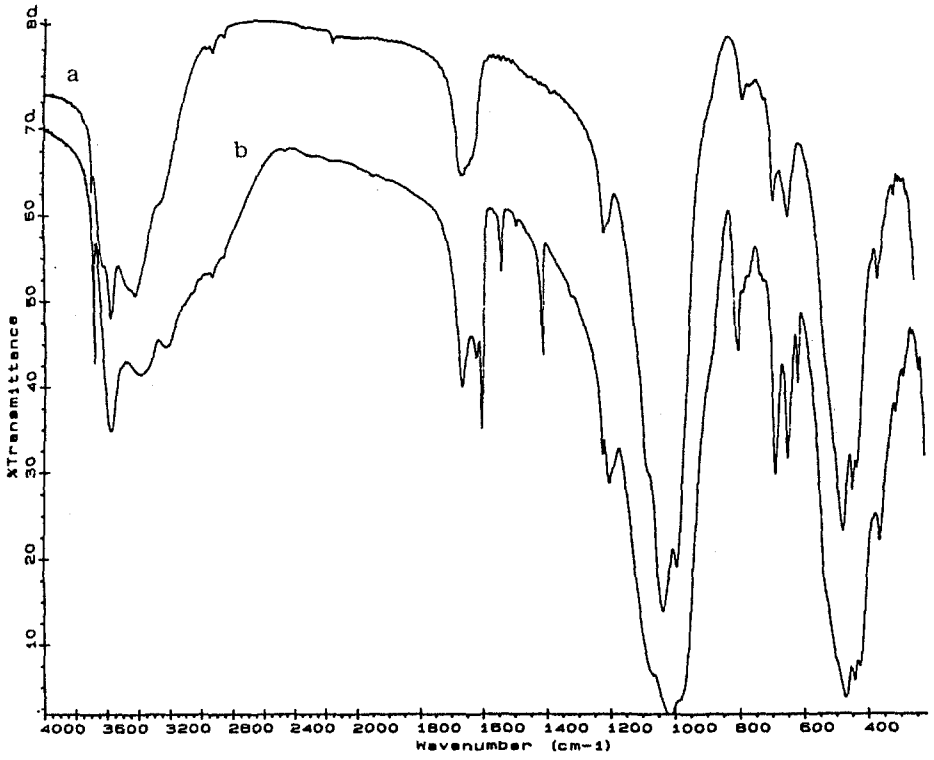


Figure 8. FT-IR spectra of (a) natural (b) 4,4'-bipyridyl treated sepiolite.

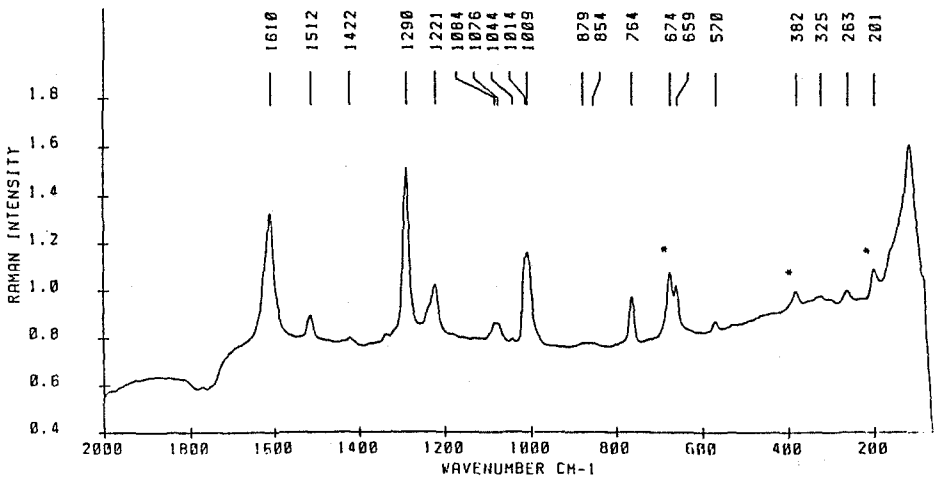


Figure 9. FT-Raman spectrum of 4,4'-bipyridyl treated sepiolite. * Indicates bands arising from the sepiolite structure.

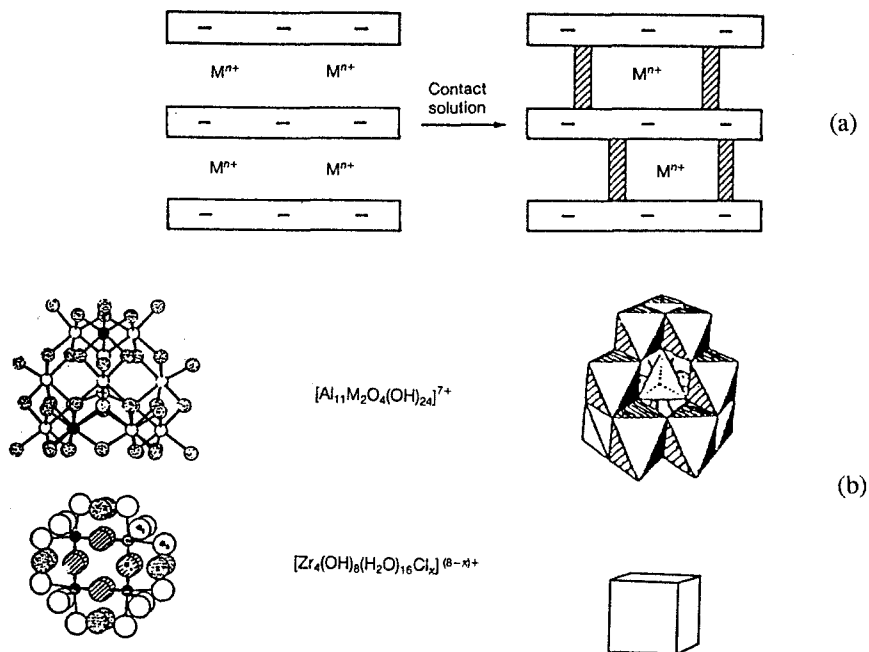


Figure 10. (a) Schematic representation of the pillaring process (b) typical inorganic pillars.

Table I. Reaction types that occur in sheet silicate interlayers

Reaction type	Example
Thermal decomposition	Breakdown of esters to acid and hydrocarbon
Dimerization	Formation of indane and anthracene derivatives from diphenylethylene
Reduction-oxidation	Conversion of diphenylethylene to diphenylethane and benzophenone
Hydrogen transfer	Between dihydroanthracene and diphenylethylene
Lactonization	Cyclo-octene carboxylic acid to 1,4- and 1,3-lactones
Ether formation	Formation of dialkylethers from alkenes (Figure 14) or alcohols
Ester formation	Ethyl acetate from ethylene and acetic acid
Amine transformations	Elimination of NH_3 from two amine molecules

after adsorption. As the θ value can be related to the interlayer spacing via Bragg's law, XRD detects the expansion of the spacing on adsorption. The XRD trace of sepiolite (a) does not change after exposure to 4,4'-bipyridyl (b). Sepiolite is an example of a clay which does not have a layered structure but rather a channel structure and adsorption does not lead to an appreciable change in dimension.

Confirmation that sepiolite has nevertheless adsorbed bipyridyl can be obtained using IR spectroscopy [6]. Figure 8 shows the IR spectra of sepiolite before and after treatment with 4,4'-bipy; the additional bands in the bottom spectrum confirm

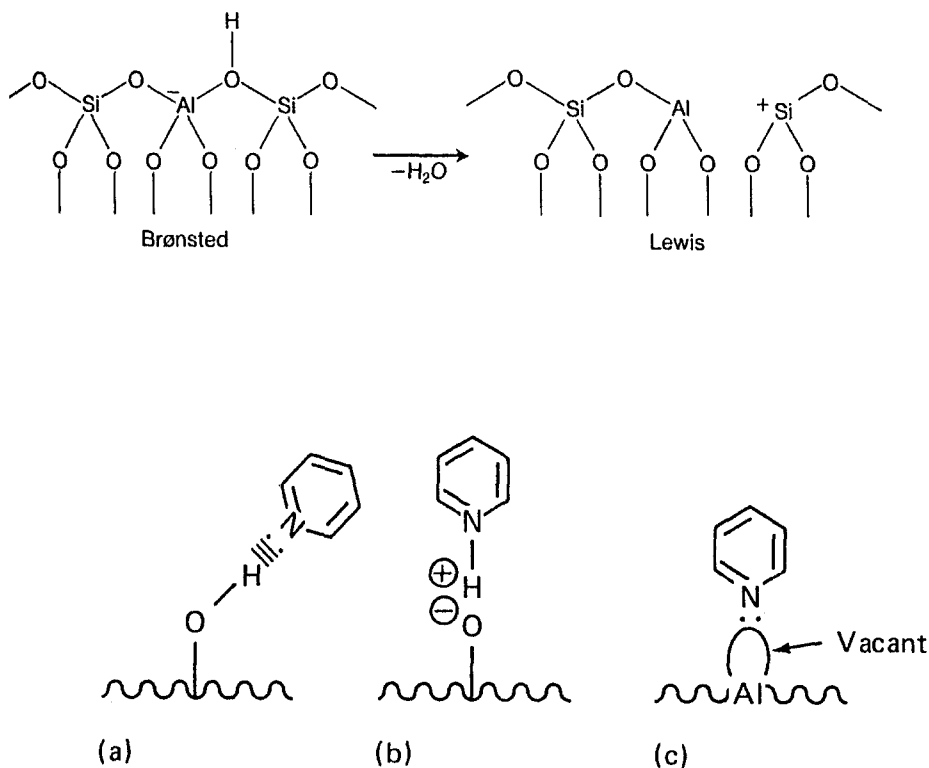


Figure 11. Top: illustration of the Brønsted and Lewis sites. Bottom: different modes of adsorption of pyridine to (a) hydrogen bonding (b) Brønsted acid and (c) Lewis acid sites.

that 4,4'-bipy has been adsorbed. Notice however the changes in the spectrum of sepiolite itself in the 3600 cm^{-1} region, which is characteristic of the OH groups. The band at 3688 cm^{-1} , for instance, has increased significantly in intensity. The changes in this region indicate that 4,4'-bipy is interacting with the OH groups of sepiolite. Thus the IR spectrum not only confirms the adsorption of the guest but also indicates the adsorption site on the clay.

Figure 9 shows the FT-Raman spectrum of 4,4'-bipy treated sepiolite [6]. Although the IR and Raman spectra give similar information in that both techniques analyse the vibrations of the molecules, there are marked differences. In the IR spectrum the strongest bands arise from the clay whereas in the Raman spectrum the strongest bands arise from the vibrations of the guest. Thus complementary information is obtained from these two techniques, again illustrating the advantage of using a combination of techniques.

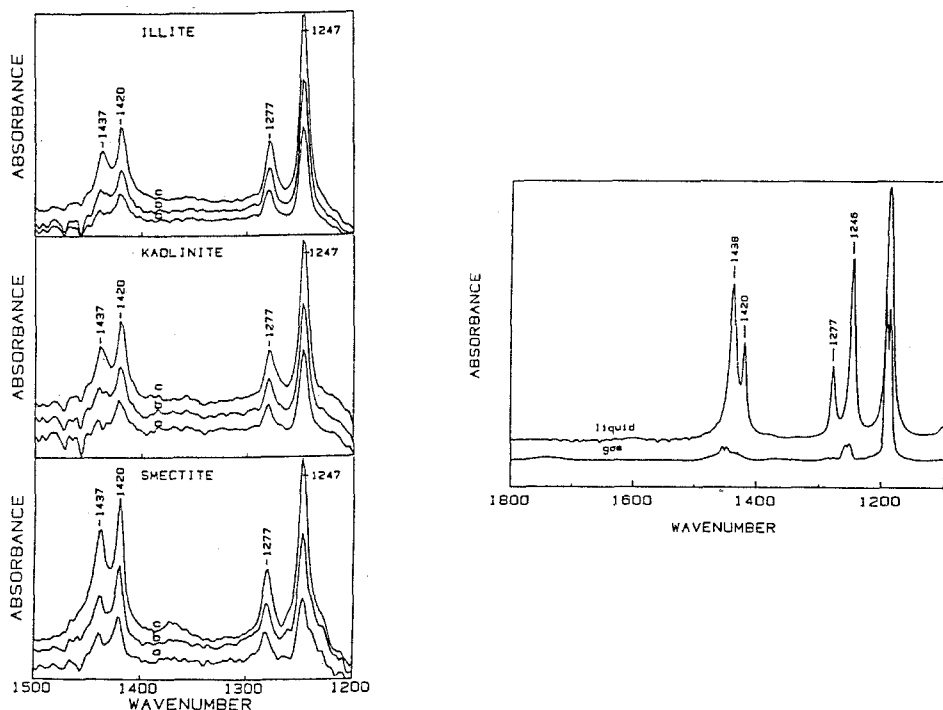


Figure 12. IR spectra of 1,2-dibromoethane on illite, kaolinite and smectite (left) and in the liquid and gaseous phases (right). Reproduced with permission from *Envir. Sci. Technol.* **26**, 329 (1992).

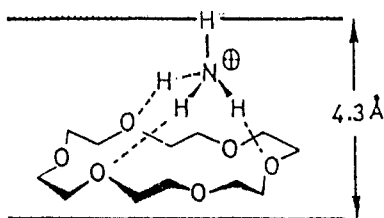


Figure 13. Schematic representation of the NH_4^+ -18-crown-6 complex in the interlayer space of montmorillonite. Reproduced with permission from *J. Chem. Soc., Faraday Trans. 1* **80**, 2225 (1984).

4. Pillared Clays

XRD studies show that the interlayer separation in clays varies with the adsorption/desorption cycle, while thermal analysis studies show that heating leads to expulsion of the guest and ultimately to the collapse of the interlayer space. If clays are to be used at high temperatures then some way of maintaining the interlayer

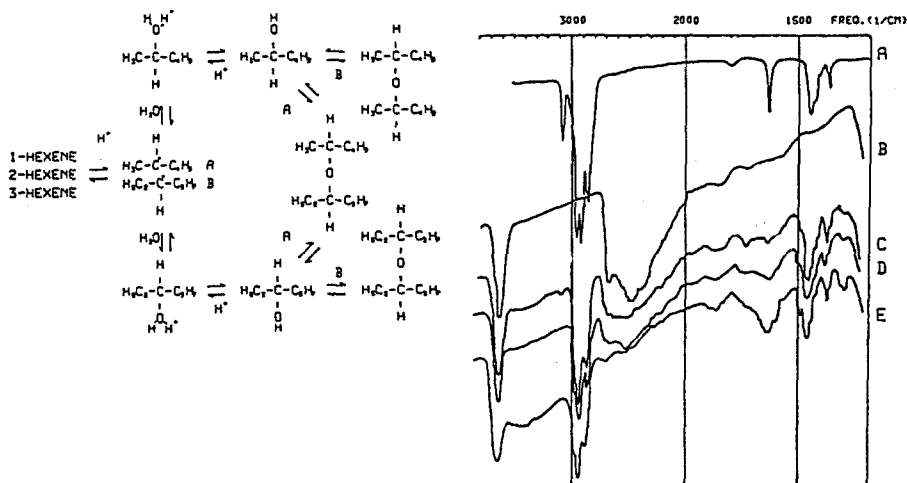


Figure 14. Right: IR spectra of (A) liquid 1-hexene (B) D_2O exchanged montmorillonite; 1-hexene on the clay (C) 15 minutes (D) 24 hours (E) 96 hours after exposure to 1-hexene. Left: proposed mechanism for the production of di-2,2'-hexyl ether from 1-hexene. Reproduced with permission from *Clays Clay Miner.* 33, 15 (1985).

space is needed. One way of achieving this is to exchange the interlayer cation with a very bulky organic or inorganic cation giving the so-called pillared clays (Figure 10a). The use of inorganic pillars such as Al or Zr complexes (Figure 10b) results in clays having higher thermal stability than those with organic pillars. These pillared clays thus have a more rigid structure than the parent clay and contain permanent pores which can lead to shape selective catalysis, as in the case of zeolites [7].

5. Catalytic Activity

Clays can catalyse a wide variety of organic reactions as illustrated in Table I [8]. The guest-host interactions usually involve the surface acid sites of the clay which are classified as Brønsted or Lewis sites which are interchangeable by dehydroxylation (Figure 11). The distribution of the different types of sites can be determined by reacting the clay with a simple base such as pyridine. Pyridine can be adsorbed by hydrogen bonding to a surface OH group, or by interacting with a Brønsted or Lewis site (Figure 11). The usefulness of pyridine is that each of these interactions affects the vibrations of the adsorbed pyridine in different ways. Thus recording the IR or Raman spectrum of pyridine treated clay gives the distribution of the different sites which can be related to the reactivity of the clay.

6. Adsorption Studies

This section deals with a few examples of spectroscopic studies of molecules adsorbed onto clays. These can be divided into two main classes: adsorption with and without reaction of the guest.

6.1. ADSORPTION WITHOUT REACTION

The IR and Raman studies on the adsorption of 4,4'-bipyridyl indicated that with sepiolite (a channel structure clay) the interaction is with the surface OH groups (Figures 8, 9). With the layered clays the bipyridyl is however coordinated to the exchangeable cations, both directly and via the water of solvation [6].

There are a few interesting examples of clays showing some selectivity. Figure 12 shows the IR spectra of 1,2-dibromoethane on three different clays, illite and smectite (2:1 TOT structures) and kaolinite (1:1 TO structure). Of particular interest are the two bands at 1420 and 1437 cm^{-1} . Comparison of these spectra with that of dibromoethane in the liquid phase (Figure 12) shows that the relative intensities of these bands have been reversed. In the liquid phase the 1437 cm^{-1} band is the stronger; for the adsorbed species the stronger band is the 1420 cm^{-1} band. These two bands arise from different rotational isomers of dibromoethane: the 1420 cm^{-1} band from the *gauche* isomer and the 1437 cm^{-1} band from the *anti* isomer. Thus in the liquid phase the *anti* rotamer is the more abundant while for the adsorbed species the more abundant rotamer is the *gauche* rotamer [9]. The main controlling influence here is the effective dielectric constant of the clay rather than a steric effect.

A final example of straightforward adsorption is shown in Figure 13 with a situation quite common in host-guest systems, *viz.* a case of a molecule within a molecule: the ammonium complex of 18-crown-6 within the montmorillonite structure [10].

6.2. ADSORPTION WITH REACTION

Clays can catalyse a wide range of reactions [8]. Below are given a few examples of such reactions which have been studied spectroscopically.

6.2.1. 1-Hexene on Montmorillonite

Figure 14 shows the IR spectra of 1-hexene itself (A), montmorillonite (B) and of hexene on montmorillonite after different time periods (C-E) [11]. The bands at about 3100 and 1650 cm^{-1} disappear after as short a time as 15 minutes after exposure. These bands are characteristic of the double bond in the molecule indicating that the molecule is losing its unsaturation, the final product being an ether: di-2,2'-hexyl ether. The mechanistic steps shown involve acidification and hydration. The source of the protons in clays is the water molecules solvating the cations.

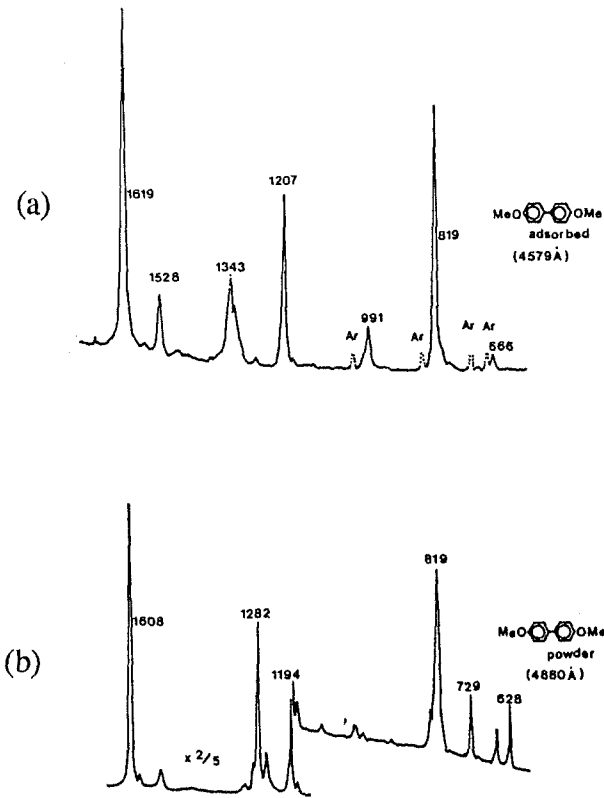


Figure 15. Raman spectra of (a) 4,4'-dimethoxybiphenyl adsorbed on Cu²⁺-montmorillonite (b) 4,4'-dimethoxybiphenyl powder. Reproduced with permission from *J. Phys. Chem.* **89**, 738 (1985).

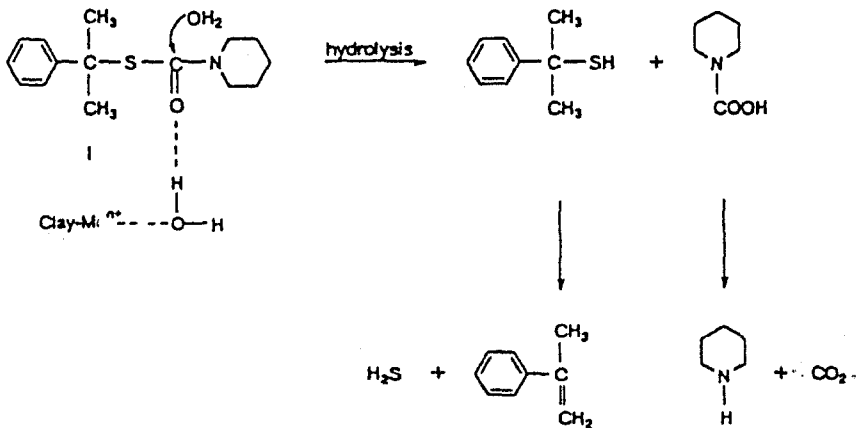


Figure 16. Proposed mechanism for the hydrolysis of dimepiperate on Fe³⁺ and Al³⁺ montmorillonites. Reproduced with permission from *Clays Clay Miner.* **41**, 335 (1993).

Depending on the cation these are polarized and can easily dissociate to yield protons.

6.2.2. Aromatics on Montmorillonite

Aromatics adsorbed onto transition metal ion-exchanged montmorillonites frequently give rise to coloured products. When 4,4'-dimethoxybiphenyl is adsorbed onto Cu^{2+} montmorillonite a dark green colouration is produced [12]. The Raman spectra of the neat powder (Figure 15b) and of the green product on montmorillonite (Figure 15a) are generally similar with a small difference in the 1200–1300 cm^{-1} region. These differences are consistent with the formation of the radical cation formed by oxidation by the transition metal ion.

Benzene itself on adsorption on Cu^{2+} montmorillonite also gives coloured products, but in this case the resulting spectrum is very different from that of benzene itself [13]. Here the initial step is the formation of the radical cation but this now undergoes a further polymerization reaction to give poly(paraphenylene) as the product. In the case of 4,4'-dimethoxybiphenyl no polymerization was possible because the para positions were blocked with methoxy groups.

6.2.3. Hydrolysis of Dimepiperate on Montmorillonite

A final example of a hydrolysis reaction is that of the herbicide dimepiperate on Fe^{3+} and Al^{3+} montmorillonites (Figure 16). This reaction is again initiated by the polarized water molecule solvating the cation so that the final products are H_2S , CO_2 , α -methylstyrene and piperidine [14].

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