

Expanded Clay Minerals: a Major Class of Molecular Sieves

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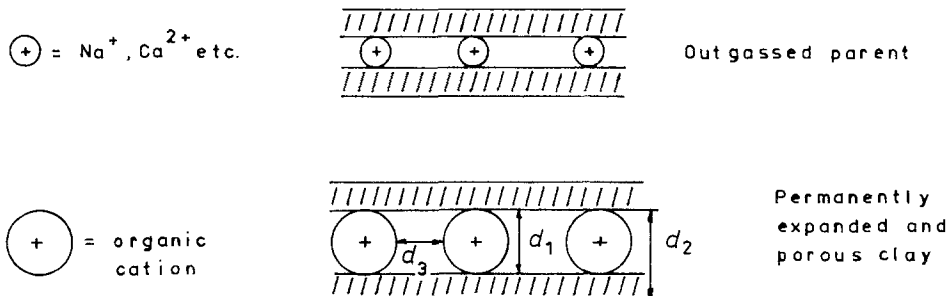
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Abstract. Clay minerals, such as smectites and vermiculites, can be permanently opened and made porous by exchanging interlayer cations with suitably large globular ions, as first reported in 1955. An account is given of some developments in this area. Initially a range of alkylammonium ions was used as props, and then large inorganic cations such as Co(en)_3^{3+} and polyoxo-cations of aluminium, zirconium and titanium. Very recently substituted silsesquioxanes have been intercalated for the same purpose. By varying the size, charge and shape of the entering ion, as well as the cation exchange capacity of the clay mineral, the molecular sieve character of the expanded clay mineral sorbents can be altered as required. The diversity of sieves thus produced can have free distances between siliceous sheets from ~ 2.6 to $\sim 10 \text{ \AA}$ and a comparable range of lateral free distances between adjacent pairs of interlayer cations.

Key words: clay minerals, molecular sieves, fluorhectorites, oxy-aluminium cations, silsesquioxanes.

1. Introduction

It was first reported in 1955 [1] that smectites can be expanded and made permanently porous on the scale of molecules. The resultant molecular sieve sorbents were then examined and characterised over a number of years [2–8]. Latterly, as will be described, interest in this class of sorbent has grown and research is in progress in a number of laboratories. Figure 1 gives the structure typical of a smectite, where parallel siliceous sheets are separated by charge balancing cations. In our work, referred to above, somewhat globular organic cations were used to replace the Na^+ , Ca^{2+} , etc. from the inter-layer regions. These because of their size, held the sheets apart by acting as props or supports, and there was sufficient distance between adjacent pairs of cations to allow penetration into the permanent interlayer pore space thus created. Schematically the situation is represented below:



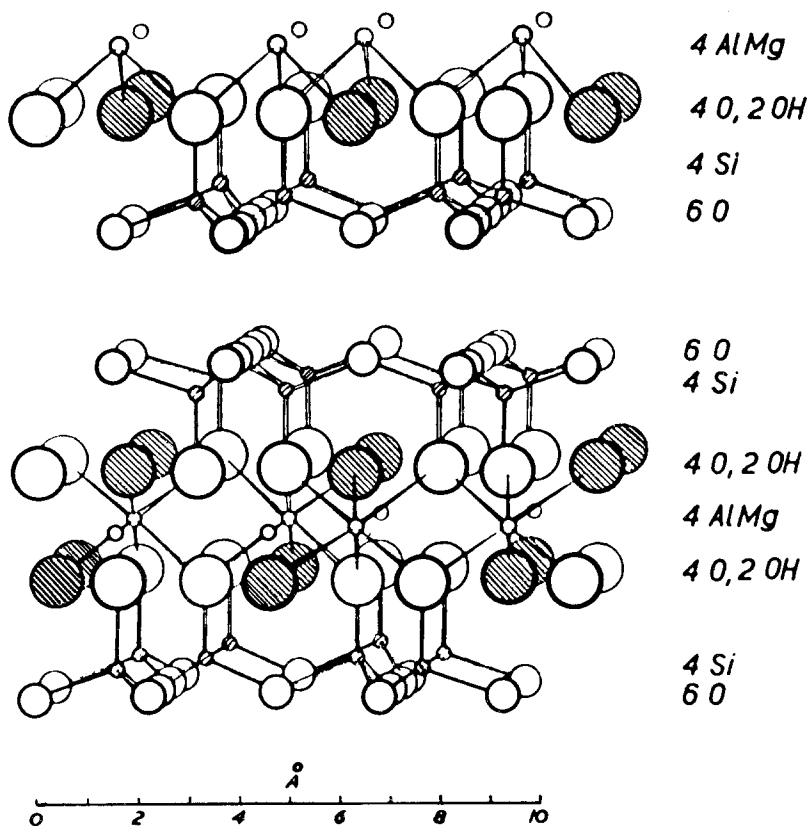
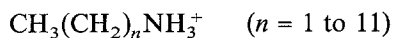
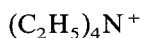
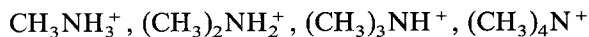
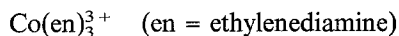


Fig. 1. The structure of the smectite montmorillonite, viewed along the a axis. The stacking of the triple sheets is believed to be irregular. Hydroxyl is distinguished from oxygen by hatching. The interlayer region is occupied by exchangeable cations and water molecules. Triple sheets of varied compositions are also found in all smectites, vermiculites and micas.

A wide range of molecular sieve sorbents was made in this way in which we used the cations



and



Subsequently, Mortland and Berkheiser [9] and Shabtai *et al.* [10] studied clay mineral sieves with the interlayer cation $\text{HN}^+(\text{C}_6\text{H}_{10})\text{NH}_3^+$, and more recently still interest has developed in inorganic cation props or pillars, as described later.

2. Some Results with Alkylammonium Smectite Sieves

We have demonstrated that in outgassed parent smectite non-polar molecules do not intercalate, but that in the permanently expanded smectite non-polar molecules of the right shape and size intercalate freely, just as in the case of zeolites. In the schematic representation of the previous section three distances are indicated:

d_1 = the free distance between siliceous layers

d_2 = the repeat 001 distance of the crystal

d_3 = the lateral free distance between adjacent cation pairs.

Molecular sieving and intercalation depend upon d_1 and d_3 . For a regular or lattice-like distribution of interlayer cations d_3 is expected to be a constant for a given type of spheroidal cation, but its value will change for each cation species. In principle, and to some degree in practice, d_1 can increase as a result of intercalation, if spatial requirements of the guest need this. Also, where the cations are elongated or chain-like, electrostatic repulsions will tend to keep adjacent centres of charge approximately equal distances apart, but variable free distances can arise between the parts of the alkyl chains [6]. For the ions referred to in the previous section d_1 ranges from ~ 2.6 to ~ 5.4 Å.

Where only part of the inorganic cations of the parent clay mineral were exchanged by the organic props the intercalation capacity increased linearly with extent of exchange [5]. This occurs because only some of the interlayer regions in partial exchange have been penetrated by the entering cations, but for those that have been invaded virtually all of the original cations are displaced. Random interstratification of this type appears to be a general feature of partially exchanged smectites.

3. Sieving and Selectivity

It was soon demonstrated that the distances d_1 and d_3 could be fine-tuned or tailored according to the size, shape and charge of the cation props, and the charge density of the anionic sheets of the smectite or vermiculite (which in turn determines the cation exchange capacity and so the interlayer cation density). As an example of the degree of fine-tuning achieved Figure 2 shows differences in rates of uptake of H_2 , D_2 , O_2 and Ne (at 77.3 and 90.2 K) on the one hand; and of N_2 , Ar (at 77.3 and 90.2 K) and CH_4 (at 90.2 K) on the other [8,11]. The sorbent was $Co(en)_3$ -fluorhectorite having 150 meq/100 g exchange capacity, where 'en' denotes ethylenediamine. (At 194.7 K rates for Kr and CH_4 are intermediate). The dramatic rate differences can be compared with similar differences between O_2 , N_2 and Ar found in leynite at ~ 90 K and in narrow port Ca-mordenite at ~ 195 K [12] (Figure 3). The Pauling values of the dimensions of the sorbates are, in Å,

H_2, D_2	2.4×3.1	} very rapid uptake at 77.3 and 90.2 K
O_2	2.8×3.9	
Ne	3.2	
N_2	3.0×4.1	} very slow uptake at 77.3 and 90.2 K
Ar	3.8_3	
CH_4	4.0	

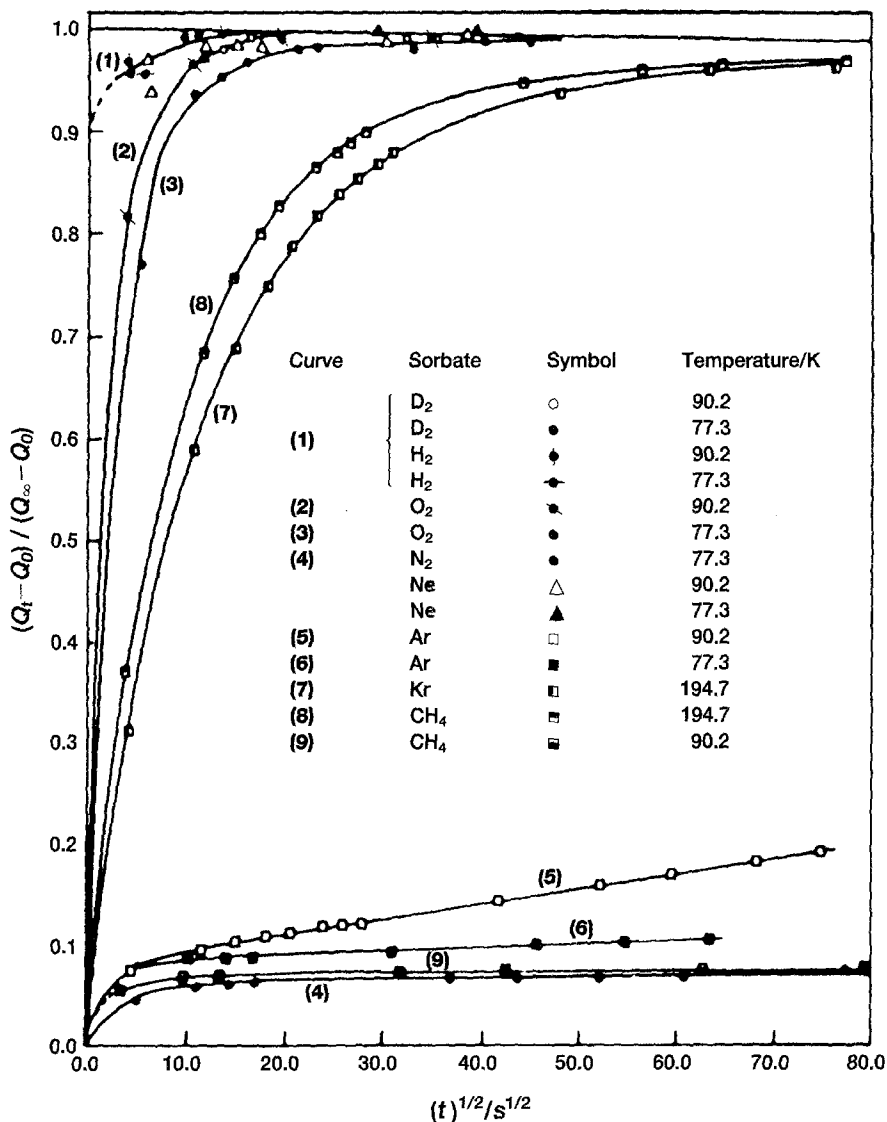


Fig. 2. Sorption kinetics for H₂, D₂, O₂, N₂, Ne, Ar, Kr and CH₄ in synthetic Co^{III}(en)₃-fluorhectorite of exchange capacity ~150 meq per 100 g [11]. At ~78 and ~90 K the group N₂, Ar, Kr and CH₄ is strongly differentiated from the group H₂, D₂, O₂, and Ne which are very rapidly intercalated. Q₀, Q_t and Q_∞ are respectively the amounts sorbed at times zero, t and at equilibrium.

At low temperatures, therefore, very small differences in molecular dimensions can make major differences in rates of intercalation.

Figure 4 [7] shows reversible isotherms and rapid uptakes of *n*-octane at 50°C in N⁺H₃CH₂CH₂N⁺H₃-exchanged fluorhectorites having exchange capacities of 90 and 150 meq/100 g (termed en-FH90 and en-FH150, respectively). Uptakes are substantial and rapid and desorption is readily achieved. As in zeolites the intercalation parts of the isotherms are of Type I in Brunauer's classification.

For larger molecules as for smaller ones molecule sieving behaviour is observed, according

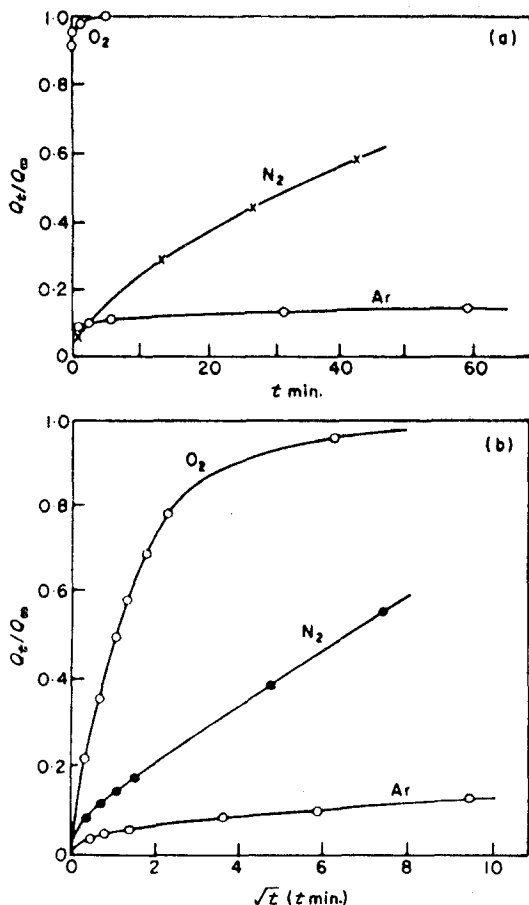


Fig. 3. (a) Sorption rates of O₂, N₂, and Ar in a natural levynite at 90 K [12]. For O₂, $Q_\infty = 10.02$; for N₂, $Q_\infty = 9.77$ and for Ar $Q_\infty = 10.01$, all in cm³ at stp g⁻¹. (b) Sorption rates of O₂, N₂, and Ar in a narrow port Ca-mordenite at 195 K [12].

to the dimension d_3 and d_1 characteristic of the expanded clay mineral, and the shape and dimensions of the intercalated species. This is illustrated in Table I.

The vertical free distance, d_1 , in the en-fluorhectorites was ~ 2.8 Å and the lateral free-distances, d_3 , were estimated as ~ 4.9 to ~ 7.5 Å for en-FH90 and ~ 3.8 to ~ 5.3 Å for en-FH150 (the cation $en^{2+} = H_3N^+C_2H_4N^+H_3$ is not spherical and, therefore maximum and minimum values of d_3 arise). The vertical free distances expand somewhat since the crystals are penetrated by molecules up to 4.6_5 Å in height, but not by those of height 5.9 Å. The lengths of molecules, especially of flexible n -paraffins which can thread their way among cations, appear less important than breadth in the intercalation process.

4. Thermal and Hydrothermal Stability

For exploitation as sorbents and catalysts there must be adequate stability. We examined this aspect for some alkylammonium smectites by determining the BET areas for N₂ relative to that of the given smectite outgassed at 50°C [2]. The results are shown in Figure 5, for

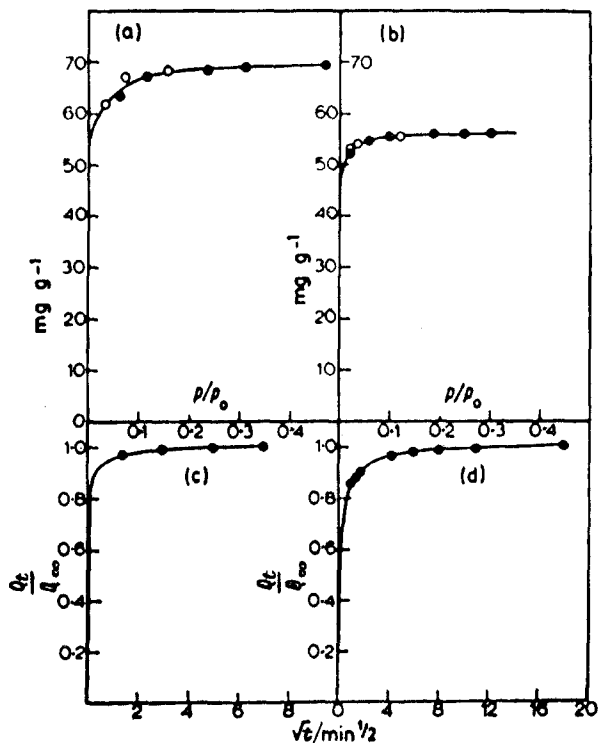


Fig. 4. Sorption of *n*-octane at 50°C [7]. (a) Isotherm in en-fluorhctorite of 90 meq exchange capacity per 100 g ($\text{en} = \text{H}_3\text{N}^+ + \text{CH}_2\text{CH}_2\text{N}^+ + \text{H}_3$). (b) Isotherm in en-fluorhctorite of 150 meq exchange capacity per 100 g. (c) Rate of uptake in en-fluorhctorite 90. (d) Rate of uptake in en-fluorhctorite 150. \circ = sorption; \bullet = desorption. Q_t , Q_∞ are, respectively, uptakes at time t and at equilibrium.

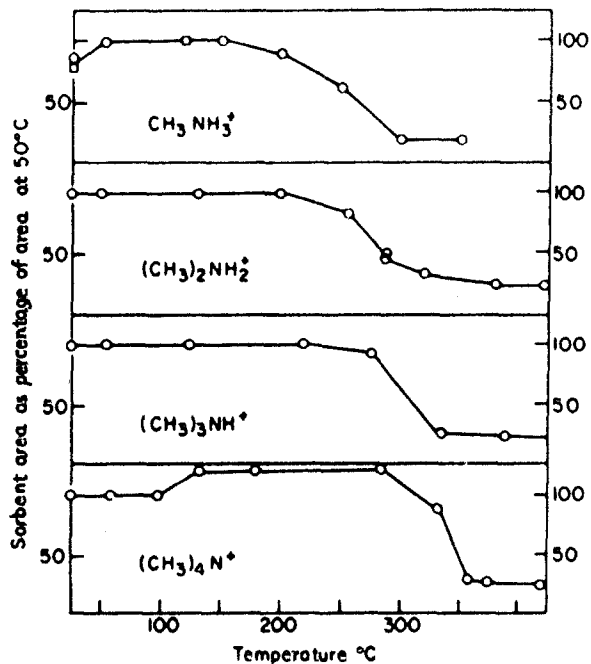
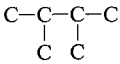
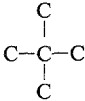
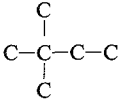
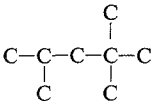


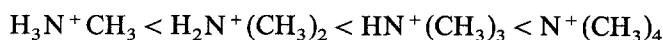
Fig. 5. The variation with outgassing temperature of the relative BET area measured with N_2 . This area after outgassing at 50°C is taken as 100 [2].

Table I. Sorption at 50°C in en-FH90 and en-FH150 [7]

Guest	Critical Dimensions ^a (Å)			en-FH90 Intercalation and wt%	en-FH150
<i>n</i> -C ₄	4.9(<i>b</i>)	4.0(<i>t</i>)	7.7 ₇ (<i>l</i>)	yes	yes
<i>n</i> -C ₆	4.9(<i>b</i>)	4.0(<i>t</i>)	10.3(<i>l</i>)	yes	yes 6.7
<i>n</i> -C ₈	4.9(<i>b</i>)	4.0(<i>t</i>)	12.3(<i>l</i>)	yes 6.9	yes 6.4
<i>iso</i> -C ₄	4.6 ₅ (<i>h</i>)	6.1 ₈ (<i>b</i>)	6.1 ₈ (<i>l</i>)	yes	yes
	4.6 ₅ (<i>h</i>)	6.1 ₈ (<i>b</i>)	7.7 ₇ (<i>l</i>)	yes 5.1	yes 4.5
	5.9(<i>h</i>)	6.1 ₈ (<i>b</i>)	6.1 ₈ (<i>l</i>)	no	no
	5.9(<i>h</i>)	6.1 ₈ (<i>b</i>)	7.7 ₇ (<i>l</i>)	no	no
	5.9(<i>h</i>)	6.1 ₈ (<i>b</i>)	9.0 ₃ (<i>l</i>)	no	no
cyclo-C ₅	6.4(<i>b</i>)	4.0(<i>t</i>)	6.5(<i>l</i>)	yes 7.2	yes 7.6
cyclo-C ₆	6.4(<i>b</i>)	4.9(<i>t</i>)	7.2(<i>l</i>)	yes 5.9	no
Benzene	6.7(<i>b</i>)	3.7(<i>t</i>)	7.4(<i>l</i>)	yes 12.9	yes 7.6
Toluene	6.7(<i>b</i>)	4.0(<i>t</i>)	8.6(<i>l</i>)	yes 9.6	no
<i>m</i> -xylene	7.9(<i>b</i>)	4.0(<i>t</i>)	8.6(<i>l</i>)	yes 5.6	no
Mesitylene	9.0(<i>b</i>)	4.0(<i>t</i>)	8.6(<i>l</i>)	yes 5.4	no

^a The dimensions of the guest are in three directions at right angles. *h* = height; *t* = thickness; *b* = breadth; *l* = length.

increasing outgassing temperatures. The temperatures at which loss of N₂ begins are in the sequence



It is from these results expected:

- that alkylammonium smectites have adequate thermal stability for applications involving selective sorption; and
- that they have sufficient stability for low temperature catalyses only, and not for more rugged needs of the petrochemical industry.

An example of a low temperature catalysis taken from the work of Weiss [13] is shown in Figure 6, for the oligomerisation of oleic acid, using N(CH₃)₄⁺-montmorillonite, plotted against charge density expressed as charge *e* per (Si, Al)₄O₁₀ unit. One could expect catalytic activity at first to increase with layer charge; the decline after maximum activity at *e* ~ 0.3 per (Al, Si)₄O₁₀ unit could be due to increasing difficulties in intercalating the parent oleic acid and of desorbing the products as *e* and so the number of interlayer N⁺Me₄ cations increases and, hence, *d*₃ decreases.

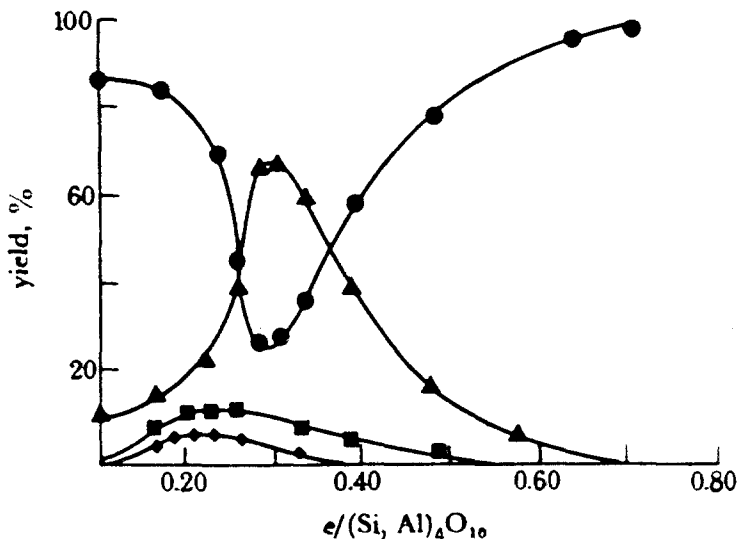


Fig. 6. Yields in the oligomerisation of oleic acid with $\text{N}(\text{CH}_3)_4^+$ -montmorillonite as catalyst [13]. The yield of each product is plotted against the charge, e , per $(\text{Si, Al})_4\text{O}_{10}$ unit. ● = oleic + stearic (C_{18}), ▲ = dicarboxylic acids (C_{36}), ■ = tricarboxylic acids (C_{54}) ◆ = oligocarboxylic acids ($\geq \text{C}_{72}$). The oleic acid reactant was 98% pure. 0.5 g of catalyst was used with 100 ml oleic acid.

5. Thermally Stable Synthetic Fluorhectorites

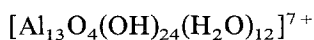
Clay minerals containing (OH) groups are not very stable thermally. Greatly increased thermal stability was achieved by Barrer and Jones [14] in synthesising two series of heat-stable fluorhectorites with c.e.c.'s of ~ 90 and ~ 150 meq/100 g (the FH-90 and FH-150 already referred to). These materials do not contain the intra-sheet OH groups of other smectites. The OH is replaced by F. The synthesis temperatures were in the range $800\text{--}850^\circ\text{C}$, so that thermal stability seems assured at least to this temperature. The materials were water-swelling, excellent cation exchangers, and yielded molecular sieve sorbents as already referred to.

However, in the alkylammonium forms the thermal decomposition of the exchange ions still limits the upper temperature of their use as catalysts. Also thermal stability and stability in superheated steam are different. Clay minerals of the smectite type are not in general stable in steam.

6. Pillared Clays

In part due to the thermal instability of organic cations, and in part to vary further the distances d_3 and d_1 , there has been growing interest in inorganic props or pillars in production of expanded clays, associated with the names of Brindley and Sempels [15], Vaughan and Lussier [16], Pinnavaia *et al.* [17], Ocelli *et al.* [18] and others [19,20].

The inorganic props which have been introduced have been oxocations of Zr, Ti and Al; and very recently silsesquioxanes. The oxo-cation of Al thought to be present in chlorhydrol, which was used in a number of preparations of pillared clays, is the Keggin cation



Twelve Al octahedrally co-ordinated to oxygens surround one Al tetrahedrally co-ordinated to oxygens.

Some properties of clay minerals initially exchanged with oxo-Al cations are as follows:

- (1) The free distance between clay layers, d_1 , after exchange varied between about 8 and 10.2 Å (Vaughan and Lussier). The variability suggests more than one oxy-cation could be involved, according to acidity and conditions of treatment. The Keggin cation has a van der Waals diameter of ~ 9 Å.
- (2) The products made from chlorhydrol showed only ~ 0.2 Å shrinkage on heating, even to 650°C (Vaughan and Lussier).

In preparations by other authors (Pinnavaia *et al.*) partially base-hydrolysed AlCl_3 and Al chlorhydrate with OH/Al ratios 2.42 and 2.50 respectively were sources of oxo-Al cations. Notable observations on the products were:

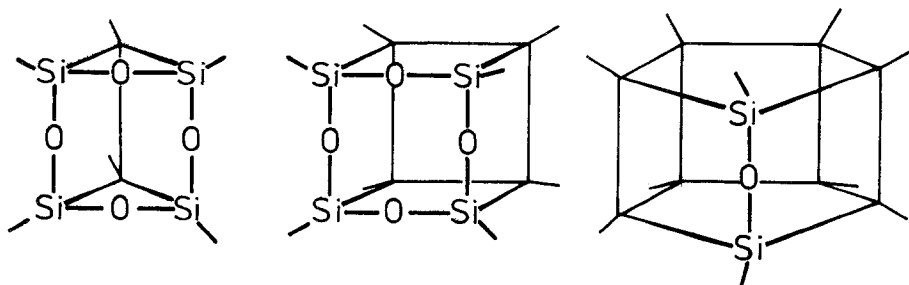
- (4) *Air drying* yielded zeolite-like sorbents with pore openings > 6.2 Å and < 9.2 Å (Pinnavaia *et al.*).
- (5) *Freeze-drying* yielded delaminated products (likened to a house of cards). *Laponite* (i.e., synthetic hectorite) was particularly prone to de-lamination (Pinnavaia *et al.*).
- (6) The pattern of cracking selectivity of a *delaminated* product suggested that, despite absence of 001 X-ray reflections and the presence of appreciable macro-porosity, similarity was to zeolite more than to amorphous alumina-silica catalyst [18]. Thermal stability of the catalysts after 10 h heating in air was limited to 550°C [19].
- (7) Plee *et al.* [20] differentiated between pillared clays in which the parent clay mineral had Al replacing some Si in the tetrahedral layer of the silicate sheet (montmorillonite, beidellite) and those which did not (hectorite, laponite).

In the former, calcination caused the oxo-Al cation to graft on to the tetrahedral layer, giving a firm three-dimensional net; in the latter there was little interaction between pillar and clay mineral sheets.

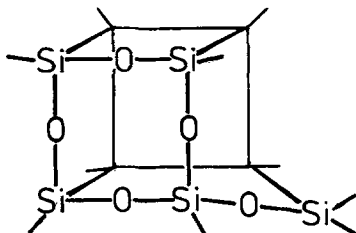
The acid properties of the grafted three-dimensional net were much stronger than those of the clays where there was little interaction between pillar and clay mineral.

7. Silsesquioxane-Clay Mineral Intercalates

The silsesquioxanes are among the products of controlled hydrolysis of substituted silico-chloroforms RSiCl_3 , where R = H or an organic moiety. They are exemplified by



where the dangling bonds are engaged by the R-groups. There are also related products, termed homosilsesquioxanes such as



In a recent patent [21] 'pillaring agents' were made by controlled hydrolysis of the substituted silico-chloroforms, 4-(2-trichlorosilylethyl)pyridine and 2-(2-trichlorosilylethyl)pyridine. Montmorillonites were then impregnated by the 'pillaring agent' solutions, calcined, and examined in various ways. The observations include the following:

- (1) Before calcination in air the surface areas were limited, but, as the organic moiety was burnt out the areas increased to values in the range $200\text{--}400\text{ m}^2\text{ g}^{-1}$, with limited change in the free distances, d_1 , between layers. These distances were between ~ 7 and $\sim 10\text{ \AA}$, according to the preparation. Pore volumes up to $\sim 0.3\text{ cm}^3\text{ g}^{-1}$ were observed.
- (2) Thermal stability and hydrothermal stability were improved over other pillared clays. Thus, after 1 h of steam treatment the results reported were:

$T^\circ\text{C}$	Steam stability (as % of 001 reflection retained)
700	95.7
750	84.6
800	40.4
850	0

Up to $\sim 700^\circ\text{C}$ steam-stability appears good.

- (3) Catalytic studies of hydroisomerisation of hexane, and of cracking, were made, using a bentonite exchanged with cerium prior to pillaring.

8. Conclusion

From layer silicates sorbents can be prepared with molecular sieving properties which cover the whole range found in zeolites, from those with narrow ports or windows up to and probably beyond the most open zeolites so far known. Sieves and sorbents based on such materials should find a place in separation technology and as catalyst carriers or catalysts.

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