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Layered Silicates as Catalysts

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The structure of layered silicates, mainly smectites, and the synthesis of similar minerals, including fixed clays with pores exceeding in size the inlet apertures in zeolites are examined. Such clays are capable of catalysing the reactions of even large molecules, having a kinetic diameter in excess of 1.0 nm, which cannot penetrate into zeolite cavities for steric reasons. Certain reactions occuring in the presence of layered and fixed clay minerals are considered.
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I. INTRODUCTION

Clays, which form part of the group of natural layered aluminosilicates, have long been used for the purification and clarification of petroleum fractions by virtue of their adsorption properties. Much later clays came to be used as catalysts of organic reactions.

The advances in catalysis in the presence of amorphous aluminosilicates[1] and then synthetic crystalline aluminosilicates (zeolites)[2-6] diverted attention from the application of clays as catalysts and greatly weakened the interest in research on these lines. However, during the last decade, numerous studies have again been published on the application of layered silicates as catalysts of organic reactions.[7-11] This was promoted by the brilliant successes in the synthesis of minerals, including clay minerals, and the appearance of new refined methods for the determination of their structure and properties. A new class of catalysts, which are called "pillared sheet silicates" and also cross-linked or fixed layered silicates, were created in the 1970s. There is virtually no information about them in the Soviet literature. The appearance of fixed layered silicates, including clays, coincided with the time when interest was aroused in compounds resulting from intercalation in layered substances such as graphite,[8-12] clays,[7-11] phosphates, and certain other compounds of quadrivalent metals.[8]

Layered silicates, including clays, constitute three-quarters of the sedimentary rocks in the Earth's crust.[1c] Their deposits have been created as a result of the weathering of hyperbarites, basalts, granites, and especially volcanic ash, glasses, tuffs, and different types of pumice. The principal chemical components of layered silicates are SiO_2 (30–70%), Al_2O_3 (10–40%), and H_2O (5–10%). Among the clay minerals constituting the basis of clays, which have found applications as adsorbents and catalysts, mention should be made of the kaolinite $[Al_4](Si_4O_{10})(OH)_8$.[9,10] Various smectites, capable of swelling, including the dioctahedral smectites[9,10] (see Fig. 2 below), montmorillonite $M^{n+}_{x/n}[Al_{4-x}Mg_x](Si_8)O_{20}(OH)_4$ and beidellite $M^{n+}_{x/n}[Al_4](Si_{8-x}Al_x)O_{20}(OH)_4$, and the trioctahedral smectites hectorite $M^{n+}_{x/n}[Mg_{6-x}Li_x](Si_8)O_{20}(OH, F)_4$ and saponite $M^{n+}_{x/n}[Mg_6](Si_{8-x}Al_x)O_{20}(OH)_4$ are of greatest interest. Vermiculites, which swell with much more difficulty, as well as the micas muscovite $K_2[Al_4](Si_6Al_2)O_{20}(OH)_4$ and phlogopite $K_2[Mg_6](Si_6Al_2)O_{20}(OH)_4$, where M are exchangeable cations are also layered silicates; the cations forming part of the composition of the octahedral layer are enclosed in square brackets (see Section II) and the cations forming part of the composition of the tetrahedral layer are indicated in round brackets (again see Section II). In reality, the composition of real clay minerals may differ from the idealised formulae quoted above. Furthermore, clays usually contain different admixtures: carbonate, gypsum, iron oxides, etc. as well as plant or animal residues. All the most important properties of clays and clay minerals depend mainly on the chemical and mineral composition and the proportions of different grain sizes.

Pure montmorillonite clays (bentonites), industrial deposits of which exist in various regions of the USSR, have acquired the greatest practical importance as sorbents and catalysts. Mainly montmorillonites and hectorites, both natural and synthetic, constitute the basis of a new type of fixed layered aluminosilicate catalysts.

II. THE STRUCTURE OF LAYERED SILICATES

The majority of layered silicates are made up mainly of two structural fragments:[16-19] a network of silicon–oxygen tetrahedra SiO_4 (the *T*-network) and the network of aluminium-oxygen octahedra $Al(O, OH)_6$ (the *O*-network). In the ideal model, it is assumed that the sizes of the tetrahedra and octahedra are comparable, the Si^{4+} ions being located in the centres of the tetrahedra whose vertices are occupied by oxygen ions. Each O^{2-} ion, lying in the basal plane (the plane comprising oxygen triads lying at the bases of the tetrahedra) of the *T*-network, made up in accordance with the hexagonal motif, joins together two tetrahedra (Figs. 1*a*, 1*b*, and 1*c*). The octahedra, in the centres of which aluminium or magnesium ions are located, sometimes substituted by the ions of other elements, have edges in common, on which there are two common oxygen ions, and form the *O*-network, also in accordance with a hexagonal motif (Fig. 1*d*). Depending on the valence of the cations and on the degree of occupation of the *O*-positions by them, dioctahedral networks arise (Fig. 2). The octahedra in the dioctahedral networks are populated mainly by tervalent cations (Al^{3+}, Fe^{3+}), pairs of such octahedra meeting at a common lateral edge; trioctahedral networks include predominantly bivalent cations and three octahedra meet at a common lateral edge in each case.

The Si^{4+} cations in the *T*-network can be isomorphously substituted by Al^{3+}, Fe^{3+}, etc. ions, while the Al^{3+} ions in the *O*-network can be similarly substituted by Mg^{2+}, Fe^{2+}, Li^{+}, etc. ions. The substitution of a cation by an ion with a lower valence leads to the appearance of one negative charge in the layer, which creates conditions for the manifestation of acid properties by the clays. In those cases where charge-compensated substitution takes place, for example, the substitution of $2Al^{3+}$ by $3Mg^{2+}$, the charge of the layer does not change [see Barrer[7] (p.538) and also Osipov[18]].

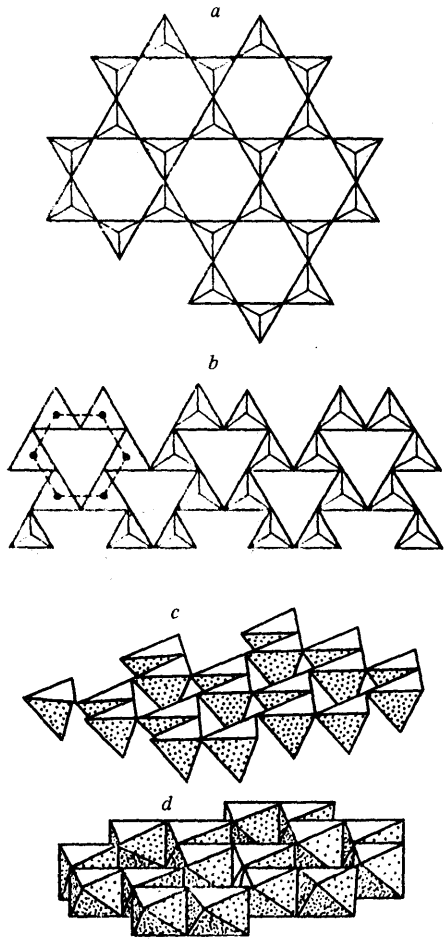


Figure 1. Models of the principal structural fragments of layered silicates:[7,8,17] *a*) and *b*) tetrahedral silicon–oxygen networks (*T*-network) (in the hexagonal motif in Fig.1*b*, the dots indicate the apical oxygen atoms of the tetrahedra and the dashed lines designate their hexagonal disposition); *c*) *T*-network in the axonometric representation; *d*) octahedral network (*O*-network) in the axonometric representation.

The *T*- and *O*-networks are joined together via the O^{2-} ions, forming layers made up of two, three, and more networks (Figs.3 and 4) constituting the basis of various clay minerals. All the vertices of the tetrahedra in each *T*-network are rotated towards the *O*-network. Kaolinite, for example, belongs to structures made up of two-network layers (1:1) and containing one *T*-network and one *O*-network in each case. Smectites (montmorillonites, hectorites, and hydromicas), vermiculites, as well as micas have a structure in which two *T*-networks are joined to an *O*-network between them (2:1, *TOT*-minerals). The distance *d* from the *T*-network of one layer to the *T*-network of an adjoining layer arranged in the same way and the size Δd of the gap between the layers are characteristic parameters of layered silicates (Figs.3 and 4).

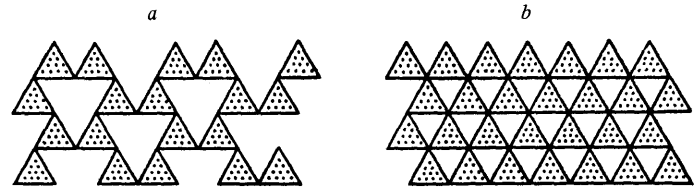


Figure 2. Types of octahedral networks:[16,17] *a*) dioctahedral; *b*) trioctahedral (only the upper faces of the octahedra are represented).

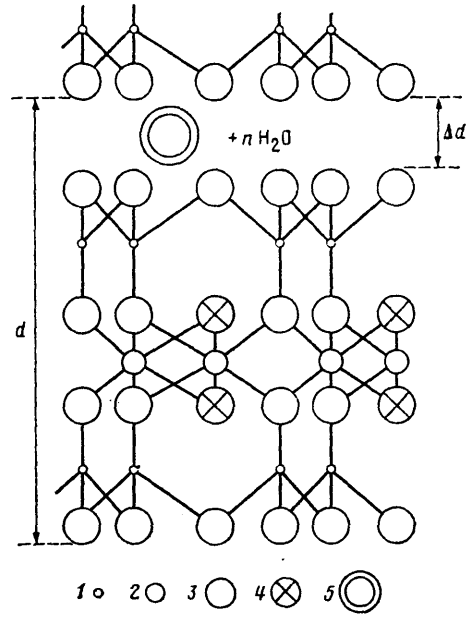


Figure 3. Schematic representation of the structure of montmorillonite:[7,8] 1) Si; 2) Al; 3) O; 4) OH; 5) intercalated cations.

In real clay minerals, the bases of the tetrahedra are not located in one plane, the cations being displaced relative to the tetrahedra and the pattern of the *T*-network differing from the ideal hexagonal motif. The octahedra are frequently flattened in the direction at right angles to the

planes of the networks. A twist in the arrangement of the octahedra in the dioctahedral network in the plane coplanar with the basal plane has been noted, which also distorts the planar surface and its hexagonal motif.[16] This influences strongly the structure of layered silicates: the dimensions of the tetrahedra and octahedra cease to be comparable, the surfaces of the octahedra become non-coplanar, and the basal surfaces of the layers acquire an irregular wavy structure.

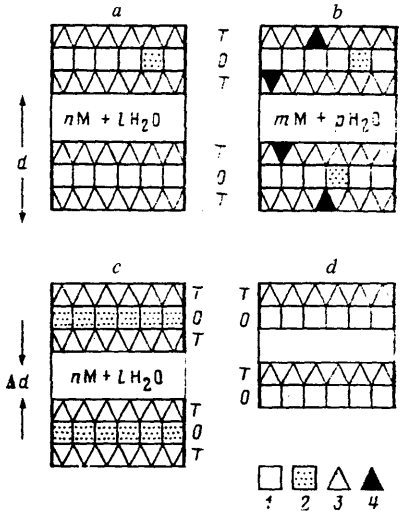


Figure 4. Schematic representation of the structures of certain layered silicates according to Frank-Kamenetskii et al:[16] *a*) montmorillonite; *b*) hectorite; *c*) vermiculite; *d*) kaolinite; 1) aluminium–oxygen octahedron; 2) magnesium–oxygen octahedron; 3) silicon–oxygen tetrahedron; 4) aluminium–oxygen tetrahedron; M = intercalated cations.

In the layered silicates having the *TOT*-structure, the gap between the layers is made up of the isotypical surfaces of the *T*-networks, which are held by the dispersion forces of the silicon–oxygen tetrahedra and by the electrostatic forces arising between the negative charges of the opposite layers and the cations (mostly Na^+ and Ca^{2+}) located between them. Depending on their size, the cations are fully or partly "pressed" into the free space between the tetrahedra, generating an additional force drawing the layers together. In terms of this capacity, the ions can be arranged in the series Li < Na < K < Mg < Pb < NH_4 < Co < Al [19] (p.179). However, this sequence frequently breaks down. Thus if the sizes of the cation and of the apertures of the *T*-network are similar, then such a cation is held more strongly.

The space between the layers in many layered minerals having the *TOT*-structure, such as smectites, vermiculites, etc. contains a certain number of water molecules involved in the formation of the mineral. These molecules prevent the collapse (complete adhesion) of the layers. The layered and two-dimensional primary porous structure arises in this way (it is denoted in the literature by 2*D* or 2*d* in contrast to the three-dimensional 3*D* or 3*d* porous structure of zeolites).

Cations are also located on the lateral surfaces of the crystals. Like the interlayer cations, these can be readily exchanged for a wide variety of inorganic and organic cations. Furthermore, as a result of the abrupt termination of the *T*- and *O*-networks, valence-unsaturated atoms capable of adsorbing ions and molecules are formed on the lateral surface. It has been suggested that up to 80% of the exchangeable cations are present in the interlayer space and up to 20% on the lateral surface [7] (p.537).

The crystals of clay minerals are joined together into small scale-like, ribbon-like, or tubular particles sometimes of colloidal size, which tend to aggregate and generate a secondary porous structure between the particles.[8,20,21] Table 1 presents data on the shapes and dimensions of the particles of certain clay minerals.

Table 1. The shapes and dimensions of the particles of certain layered silicates.[7,9]

Mineral	Shape of particles	Particle size, μm
Kaolinite	Hexagonal plates, frequently well formed, sometimes elongated	Width 100–4000; thickness 50–2000
Montmorillonite	Poorly differentiated shapes, rarely hexagonal, characteristic tendency towards formation of aggregates of particles	Diameter up to 1000 and above; thickness 1–20
Hectorite	Thin elongated plates	Length up to 3000; width ~100; thickness 1–2 and above

The occurrence of reactions between organic substances in the interlayer space in smectites at high temperatures (in excess of 200 °C) is prevented by the dehydration of the clays and the collapse of the layers induced by this. The temperature-dependent limitations imposed by the collapse can be overcome by introducing into the interlayer space thermally stable bulky cations which act as a kind of pillar and fix the layers at a specific distance preventing them from adhering closely after the removal of water or a solvent. This way of fixing the layers made it possible to create a new class of aluminosilicate catalyst—pillared sheet silicates.

III. THE SYNTHESIS OF LAYERED SILICATES

Clay minerals of constant composition, contaminated to a minimal extent by extraneous impurities (which is especially important for the development of catalytic systems), can be obtained synthetically. Layered silicates are synthesised under hydrothermal conditions (100–400 °C) or by fusing together mixtures of the initial oxides at 800–1500 °C.

The results of studies on the hydrothermal preparation of kaolin, montmorillonite, pyrophyllite, and other clay minerals at an increased pressure have been summarised in a review.[22] The conditions in the formation of montmorillonite have been examined and its properties described.[23] Montmorillonite is formed in alkaline media and the results of the synthesis are appreciably influenced by magnesium (in contrast to other cations).

It has been established that the dioctahedral montmorillonite is formed with a relatively small MgO content in the mixture of the initial oxides. With increase in the MgO content

in the mixture, a small admixture of a trioctahedral smectite is formed initially and this is followed by the appearance of large amounts of the latter. In order to obtain a well crystallised product, the hydrothermal treatment is carried out for several (6–7) days.[31] A decrease in the duration of the hydrothermal treatment entails a proportionate decrease in the exchange capacity of the mineral.[31] The influence of temperature and pressure on the formation of montmorillonite in the SiO_2–Al_2O_3–H_2O[29] and SiO_2–Al_2O_3–MgO–H_2O [30] systems has been studied in detail and the regions corresponding to the formation of montmorillonite and other minerals have been described with the aid of phase diagrams.[30] Depending on the pH of the mixture, it is possible to obtain a clay mineral with the *TO*- or *TOT*-structure. Thus the addition of HCl to the initial mixture leads to the formation of kaolinite, while the addition of NaOH induces the formation of montmorillonite.[32]

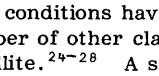
Hydrothermal conditions have also been used in the synthesis of a number of other clay minerals, for example, kaolinite and beidellite.[24–28] A simple method of synthesis of various clay minerals from a mixture of natural sand (or artificially precipitated SiO_2) and aluminium hydroxide (or $AlCl_2$) has been described.[32] The methods of synthesis of the so called "fluorotetrasilicate micas", in which some or all the hydroxy-groups have been replaced by fluorine atoms, have been developed vigorously in recent years,[33–36] especially by Japanese investigators. The fluorotetrasilicate micas constitute the basis of catalysts of a new type with a high thermal stability. The fluorohectorites obtained after the replacement of OH groups by fluorine are stable up to 800 °C [7] (p. 469). The OH groups can be replaced by fluorine atoms also in the hydrothermal treatment of a freshly prepared smectite with a solution of NH_4F or other water-soluble fluorine compounds.

Much attention has been devoted to the synthesis and study of the catalytic properties of the so called mica-montmorillonite,[37–40] which consists of a multilayered mineral with a random packing of mica and montmorillonite layers and an overall mica content ranging from 1/6 to 5/6. This mineral is frequently synthesised in such a way that it contains transition metal ions,[41–43] mainly nickel ions,[41,42] in the octahedral network. The composition of the product obtained by Heinerman's method[41] corresponds to the chemical formula $(Al_{1.08}Ni_{4.38})(Si_{6.62}Al_{1.38})O_{20}(OH)_{3.24}F_{0.76}(NH_4)_{1.38}$. As mentioned above, to prevent the layers from sticking together on raising the temperature, they are fixed at an appropriate distance.

The fixation of clays was first proposed more than 30 years ago.[44] In order to attain a constant porosity in clays, tetraalkylammonium ions have been used. However, the prospects for the employment of clay minerals in order to develop catalysts of a new type arose only when the fixation was achieved with the aid of inorganic compounds, namely the oligomeric aluminium and zirconium and then bismuth, chromium, etc. hydroxo-cations (Table 2). The insertion of an oligocation in clay minerals takes place fairly readily as a result of exchange with the interlayer cations. At the same time, in the presence of an excess of Al_{13} oligocations, the amount of bound aluminium calculated per unit cell varies within narrow limits (2.78–3.07), is not correlated with the charge determining the exchange capacity of the clay, and is independent of the charge distribution among the layers, which is extremely non-uniform in smectites and can vary from layer to layer by a factor of two.[60,61] This led to the hypothesis[62] that the adsorption of the oligocation entails the formation of a more or less uniform monolayer of polyoxo-cations on the surface of the clay. In this case the distance between the pillars is determined by the radius of the hydrated cations, which can in fact account for the uniform distribution of the pillars in the interlayer space after the dehydration of the fixed smectite.

The introduction of aluminium and zirconium oligocations leads to the formation of thermally stable clays exhibiting molecular-sieve and catalytic properties and having a specific surface of 200–500 $m^2\ g^{-1}$ and an interlayer gap Δd in excess of 0.9 nm.[49,50,63–68]

Table 2. Compounds used for the fixation of clays.

Name	Formula	θ, °C *	Refs.
Tetraalkylammonium	Alk_4NH	<250	[7, 44]
Bicyclic amines		<250	[45, 46]
Fe(II) and Cu(II) metal chelate complexes	$[Fe(2,2'\text{-bipyridyl})_3]^{2+}$; $[Cu(1,1'\text{-phenanthroline})_3]^{2+}$	<450	[47, 48]
Al oligocations	$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$; $[Al_{26}O_8(OH)_{52}(H_2O)_{20}]^{10+}$	>500	[49]
Zr oligocation	$[Zr_4(ON)_{12}(H_2O)_{12}]^{4+}$	~800	[50–52]
Bi oligocation	$[Bi_6(OH)_{12}$	>500	[13]
Cr oligocation	—	>500	[53, 54]
SiO_2 polymers	—	>600	[55–58]
Nb and Ta complexes	$[M_6Cl_{12}]^{2-}$	>600	[59]

* Thermal stability of fixed clays (natural clay is stable up to ~200 °C[7]).

As can be seen from Table 2, fixation increases the upper limit to the thermal stability from 200° to 550–800 °C. The fixation of clay minerals by oligomeric hydroxo-cations makes it possible to obtain aluminosilicates with a regular structure, the size of the cavities in which is significantly greater than in coarsely porous zeolites, including faujasites. This led to the possibility of using fixed clays for the catalytic reactions of large molecules, to which the internal surface of zeolites is inaccessible.

The aluminium oligocation (known in the U.S. industry as "chlorohydrol") is used most widely as a fixing agent and has been more thoroughly investigated than other such agents. It can be obtained by various methods: by dissolving metallic aluminium in a boiling solution of $AlCl_3$ [69] or in an NH_4Cl solution[70] and by hydrolysing $AlCl_3$ dissolved in water with sodium carbonate (either solid or in solution) at 90–100 °C.[71] The use of different aluminium salts yields similar results.[62] It has been suggested that the principal species in the aluminium oligocation is the so-called Keggin cation $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$,[69,72] consisting of a central tetracoordinate Al^{3+} ion surrounded by twelve AlO_4 octahedra joined via the common edges.

In order to increase the molecular weight of the oligocation, chlorohydrol is subjected to ageing by boiling the solution for 1–48 h or by treating it with ammonia, alkali, and metallic magnesium.[66] The Al_{13} oligocation then dimerises with formation of the cation $[Al_{26}O_8(OH)_{52}(H_2O)_{20}]^{10+}$.[66]

The zirconium oligocation is obtained by hydrolysing zirconyl chloride $ZrOCl_2 \cdot 8H_2O$ in sodium carbonate solution. After the solution has been aged for 24 h, an oligomer having a molecular weight of ~1000 is obtained.[66] The method of fixation of clays described by Vaughan et al.[66] has been used virtually without change in many investigations.

The high thermal stability of the smectites fixed by the Al_{13} and especially Zr_4 oligocations is attributed to the formation of metal oxide clusters as a result of the dehydroxylation of the hydroxo-cations at an elevated temperature. In the case of the Al_{13}-montmorillonite, this reaction proceeds in accordance with the mechanism[73]

$$[Al_{13}O_4(OH)_m \cdot p\,H_2O]^{n+} \rightarrow 6.5\,Al_2O_3 \cdot q\,H_2O + n\,H^+$$

However, there is no information about the structure of the cluster (the so called pillar) or about the disposition of the protons in the oxide compound.

Chromium is also included among the metals capable of forming oligocations.[53,54] The transparent solution of the chromium oligocations obtained from chromium nitrate and ammonium hydroxide is violet in colour. The bentonite fixed by such cations has a specific surface of 165 $m^2\ g^{-1}$ and a micropore volume of 0.03 $cm^3\ g^{-1}$ and d amounts to 1.2–1.4 nm (0.96 nm in the initial clay).

There have been reports[74–76] of the synthesis of Fe-fixed smectites prepared using the trinuclear hydroxoacetato-iron(III) nitrate complex $[Fe_3(OAc)_7(OH)_2(H_2O)].NO_3$. After the clay has been heated, the complex cations, introduced by ion exchange, are converted into oxides, which serve as the pillars; the value of d established is 1.66 nm.

Although fixation with the aid of polynuclear hydroxo-cations makes it possible to obtain stable clays with a large free space between the layers, the number of elements capable of forming the oligomers is limited. Ways of extending the number of fixing agents are therefore being sought. For example, the silicic acid obtained by the hydrolysis of silicon acetylacetonate cations in the interlayer gap[56,57] or of polychlorosilanes[58] can be introduced into montmorillonite. In such cases the clay is usually allowed to swell beforehand in an organic solvent (amine or alcohol). After heat treatment, the inserted SiO_2 is capable of maintaining the layers at a distance of 1.26 nm from one another; the specific surface of the clay fixed by silica and measured with respect to nitrogen is 240 $m^2\ g^{-1}$.

It has been suggested that aluminium and zirconium as well as aluminium and silicon copolymers be used for fixation.[66] The properties of catalysts prepared on the basis of clay minerals cannot be improved by the fixation of the latter. Thus a decrease in the activity of the catalyst was noted[77] when a copolymer of aluminium and silicon was used as the fixing agent. The hydrolysis and oxidation of the cations $Nb_6Cl_{12}^{2+}$ and $Ta_6Cl_{12}^{2+}$ make it possible to obtain fixed clays with an interlayer gap $\Delta d > 1.0$ nm. These clays are stable up to 400 °C.[59]

Whereas the fixation of clay minerals determines their primary interlayer porosity, the secondary porosity between the clay particles depends greatly on the conditions in the drying of the fixed mineral.[62] Thus drying in air gives rise to a product in which the size of the external secondary pores is 0.6–0.9 nm, while the mineral dried by subliming water from the specimen frozen beforehand is capable of adsorbing molecules with a kinetic diameter† greater than 1.0 nm. It has been suggested that drying in air entails close layer-by-layer adhesion of the mineral particles and the volume of secondary pores becomes small. Drying by sublimation promotes a disordered agglomeration of the particles, which gives rise to a larger free pore volume between them.

†The kinetic diameter[62] or the critical diameter[7] (p. 293) is the diameter of the van der Waals section through the molecule.

IV. CERTAIN PHYSICOCHEMICAL PROPERTIES

The most characteristic and important property of clay minerals, especially montmorillonites and to a lesser extent hectorites and vermiculites, is their ability to swell both in water and water vapour as well as in certain polar organic liquids. The molecules of the substances inducing the swelling are inserted into the interlayer space and move the layers apart. For example, when one, two, or three layers of water molecules are inserted in montmorillonite, d increases from 0.95 to 1.24, 1.54, and 1.9 nm respectively. The montmorillonite in which the intercalated cations have been exchanged for Sr^{2+} can give rise to several intercalation compounds with butyrolactone (single-layer, two-layer, and three-layer), for which d is 1.3, 1.8, and 2.3 nm respectively.[19]

Some workers believe that paraffinic hydrocarbons are not sorbed by smectites containing small intercalated cations[7] (p. 434). According to other data,[15] intercalation does occur, but extremely slowly, and traces of moisture are essential for this purpose. Apparently, the presence of intercalated water leads to the delocalisation of alkali metal cations and intensifies their polar effect on hydrocarbons. The nature of the intercalated cation, which is important for the adsorption of polar compounds, does not influence appreciably the intercalation of n-alkanes.[78] Evidently the adsorption of saturated hydrocarbons is not due to ion exchange; their insertion in the space between the layers in smectites can be accounted for from the standpoint of the interactions of the molecular dipoles, induced by the mineral ions, with the surfaces of the clays.[15,78,79] There are data showing that the Ca- and NH_4-montmorillonites do not sorb n-hexane.[79] However, montmorillonite with intercalated $CH_3NH_3^+$, $(CH_3)_4N^+$, and $(C_2H_5)_4N^+$ ions sorbs saturated hydrocarbons, while montmorillonite containing a quaternary ammonium base with a long chain, for example, the didodecyldimethylammonium ion, adsorbs selectively paraffinic and aromatic hydrocarbons, and is used in gas–liquid chromatography.[7]

The intercalation of C_6–C_{10} paraffins in fixed clays takes place fairly readily,[81] is independent of temperature and the number of carbon atoms in the molecule, and leads to the filling of 50–60% of the pore volume. The heats of sorption in such clays are much lower than in zeolites and the rate of diffusion of the sorbates is several times higher.

The study of the adsorption of hex-1-ene on the Cr^{3+}-exchange montmorillonite by IR spectroscopy[82] shows that the alkene is protonated in this instance and that the 2-carbonium ion formed is linked to the primary coordination sphere of the intercalated cation. One of the hydrogen atoms in the water molecules in this primary sphere is involved in the formation of strong hydrogen bonds with the silicate layers, while others do not form such bonds and are directed into the interlayer space. These hydrogen atoms are in fact labile and protonate the alkene molecule.

Benzene and its substituted derivatives as well as tetralin and naphthalene are fairly readily intercalated in certain smectites, forming even a double layer.[78,83] The interaction of benzene with Cu^{2+}-montmorillonite results in the formation of coloured complexes:[84,85] in the green complex, benzene retains its aromatic character, while in the red complex its aromaticity is infringed, since the π-electrons become localised.[84,85]

Non-aromatic non-polar molecules are intercalated very slightly or not at all in layered silicates containing intercalated cations of small diameter, for example, Na^+ and Ca^{2+}. On the other hand, in the presence of large cations, for

example, the Cs^+ ion, intercalation takes place to an appreciable extent[7] (p.436). Another smectite, Ca-montmorillonite, swells effectively in saturated alcohols and glycols, which are capable of displacing water from the interlayer space, including water hydrating the cations. When a single layer of C_4–C_{18} alcohol molecules is intercalated in the smectite, the hydrocarbon group is arranged parallel to the basal plane (Fig. 5a). The hydrogen of the hydroxy-group is linked to the oxygen of the *T*-network via a hydrogen bond. On the other hand, if many molecules are intercalated, they are arranged almost at right angles to the basal plane (Fig. 5b) and the hydrogen atoms of not only the hydroxy-group but also of the methyl group at the opposite end of the chain form a hydrogen bond with the oxygen of the second *T*-network. With increase in the length of the hydrocarbon chain of the alcohol, the distance between the layers therefore increases. The layers move apart to an even greater extent after the intercalation of aliphatic acids.

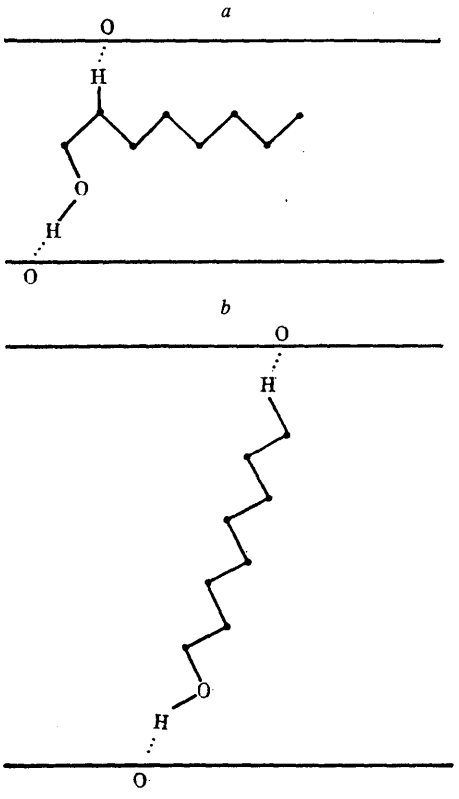


Figure 5. Models of the arrangement of n-alcohols in the interlayer space:[86] *a*) for the single-layer intercalation of the alcohol; *b*) for the maximum intercalation.

The removal of water and of intercalated organic substances, for example, on heating unfixed layered silicates, leads to a marked decrease in the interlayer space (the layers adjoin one another closely), which hinders the subsequent intercalation of substances and sometimes completely rules it out. On the other hand, if the inorganic intercalated cations have been exchanged for the ions of quaternary ammonium bases, then, after the removal of the intercalated substances, for example, water or alcohols, the distance *d* remains the same as before swelling[7] (p.461): the bulky ions prevent the layers from sticking together.

The ability of the intercalated cations to exchange, which was already mentioned in Section III, is important for the chemistry of layered silicates. The cation exchange takes place mostly in aqueous salt solutions, which can be achieved also in non-aqueous solutions, for example, alcoholic solutions. With increase in temperature, the rate of exchange also rises, but the exchange capacity diminishes, since some of the compensating cations move deeper into the network.[21] The exchange capacity diminishes particularly markedly when the specimen is heated above 300–400 °C; after such heating, the exchange capacity of clays is not as a rule restored, since the mineral is partly decomposed.

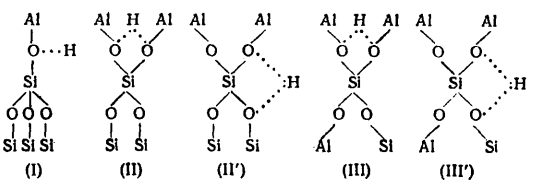
V. THE NATURE OF THE ACTIVE SURFACE

It follows from the data described in Section II that the active surface of layered silicates is extremely inhomogeneous. It is based on the basal surface of the *T*-networks with the lower valence cations built into these and the *O*-networks, which generates negative charges in the layer, the latter being neutralised by the intercalated cations. These *T*-networks bound both the crystal as a whole (part of the external surface) and the individual layers of the *TOT*-structure (internal surface). Another part of the external surface is made up of the lateral surface of the layers made up of the valence-unsaturated atoms of the *T*- and *O*-networks. Although the lateral surface of the cleaved layers does not exceed 20% of the total specific surface of the layered silicate (see Section II), nevertheless it has an appreciable influence on the character of the adsorption and of the catalytic action of the layered silicates.

It is known that the surface of a pure silicon–oxygen compound, for example quartz or ignited silica gel, is neutral. (Freshly prepared silica gel, heat-treated at a temperature not exceeding 500 °C, exhibits a weak acidity and catalyses the reactions of hexatrienes via an acid mechanism[87,88]). On isomorphous substitution of an Si^{4+} ion by Al^{3+}, the resulting aluminosilicate acquires acid properties, the nature of which is the same for all aluminosilicates, including zeolites; it has been most thoroughly investigated for the latter.

The aluminium atom inserted into a hydroxylated silicon–oxygen surface draws the electrons in the Al–O–Si–O–H group towards itself in an effort to fill its unoccupied *p* orbital, which polarises the –O–H bond[4] and, in the interaction with a water molecule, leads to the formation of an additional proton centre.

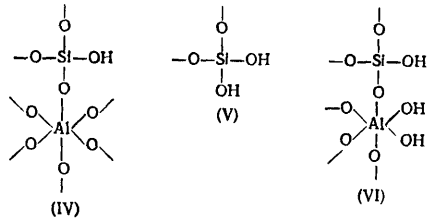
On the basis of quantum-chemical calculations for cluster models and the study of the IR spectra of aluminosilicates, it has been suggested[89,90] that there are several types of acid centres in both amorphous and crystalline aluminosilicates:



The highly acid centres are linked to the terminal siloxane OH group. The acidity of the bridging OH groups in centres of type (I) and especially (II) and (III) is somewhat reduced. The acid centres of types (II) and (III) can exist in the isomeric forms (II) and (II') and (III) and (III').

It is to be expected that acid centres are also present in layered silicates. The distance between them in such silicates usually exceeds the size of the aluminium ion and even the radius of action of the valence bonds.

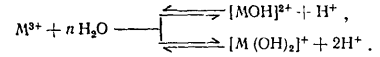
Valence-unsaturated atoms, giving rise to single (IV) and paired (V) and (VI) Brønsted acid centres differing in strength, appear on the lateral surface of the layers, especially when the crystal is cleaved:



(IV) (V) (VI)

The hydroxy-groups in (VI) can become capable of either cation exchange or anion exchange depending on the pH of the medium[9] (p.25). Furthermore, there are Lewis acid centres in montmorillonite both on the lateral surface of the crystal and on the basal surfaces.

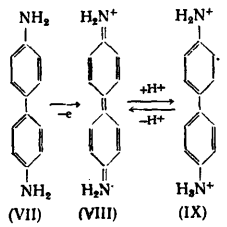
Acid centres arise in layered silicates also as a result of the interaction of water with intercalated cations, especially tervalent cations:



The degree of dissociation increases with increase in the polarising power of the cation in the sequence K < Na < Mg < Al.[93,94] In the presence of a large amount of water, the polarisation effect, arising when water is acted upon by the cation, weakens, since the influence of the cation is dissipated among a larger number of molecules and the pH of the medium approaches the values characteristic of the ion in solution. However, the concept of such a major role of exchange cations in generating the acidity of layered silicates has been questioned[18] (p.33). The hydroxy-groups of minerals can also serve as centres for the adsorption of polar organic compounds. Brønsted acidity predominates on clays containing 0.5–1.0% of water. For a lower level of hydration, the strength of the acid centres increases and the clay behaves more like a Lewis acid.[95,96]

The study of the interaction of clays with various amines led to the elucidation of the nature of the catalytic activity of layered silicates. Acid–base and oxidation-reduction reactions, leading to the formation of coloured radical-cations, take place when certain amines are adsorbed on clays.[97] The acid–base mechanism is especially characteristic of acid-washed clays. These clays act as proton donors, because their activity is greatly suppressed by treatment with bases, for example, ammonia. Oxidation-reduction reactions are relatively insensitive to treatment with acids and bases, but they are appreciably influenced by the presence of reducing agents such as $SnCl_2$.

The study of different types of treatment showed that colour reactions of clays with aromatic amines proceed with participation of Lewis and Brønsted acid centres. The reaction of benzidine with layered silicates has been most thoroughly investigated:[86,92]

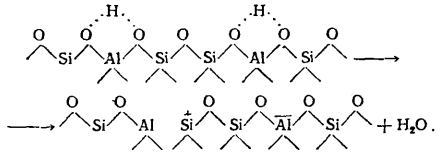


(VII) (VIII) (IX)

The proposed reaction mechanism involves electron transfer from the initial diamine (VII) (i.e. its oxidation) to the mineral with formation of the blue radical-cation (VIII) (a semiquinone). The stability of the colour can be explained by the conjugation of the unpaired $2p_z$ electron of the nitrogen atom with the π-electron system of the aromatic ring enhanced by the resonance of both rings. The blue colour is observed only at pH 2.5–6. At pH < 2, the proton adds to the unshared electron pair of the nitrogen atom in the radical-cation, giving rise to the yellow radical-dication (IX).

The adsorption of sodium polyphosphate or reductive treatment of the clay inhibits the colour reaction only partially. Its complete inhibition occurs only when both these factors act simultaneously. The hypothesis was put forward on this basis[86,92] that the diamine is oxidised on the valence-unsaturated aluminium atoms on the lateral surface, the process being inhibited specifically by polyphosphates, and on Fe^{3+} ions located in the octahedral network which react with the diamine in the interlayer gap via the *T*-network.

The similarity of the chemical nature of layered silicates and other aluminosilicates suggests that they all contain isotypical active centres and not only acid active centres. Thus strong electron-accepting centres, formed by the triply charged Si^{3+} and Al^{3+} ions of the defect structures, as shown below in the two-dimensional scheme for zeolites and aluminosilicates,[98,99] should arise on the lateral surfaces of layered silicates, particularly in the case of mechanical cleavage of the layers or in topochemical reactions occurring when smectites are heated and in the presence of the strain in the Si–O–Si and Si–O–Al linkages induced by this:



Indeed the presence of oxidation-reduction centres, whose number increases with increasing heat treatment temperature of the mineral, has been established by EPR using diphenylamine, anthracene, and chloranil probes[90] (p.55). Their presence in layered silicates has been suggested, as mentioned above, on the basis of the study of the colour reactions.

VI. CATALYSIS IN THE PRESENCE OF LAYERED SILICATES

In recent years there has been a growth of interest in clays as catalysts of various processes and at the present time numerous catalytic reactions involving their participation are known. Certain examples of catalytic reactions carried out in the presence of layered silicates as well as specific reactions with participation of large molecules on fixed clay minerals are presented in Table 3. The majority of these reactions have not been investigated in the presence of other aluminosilicates, including zeolites.

Clays, acting mainly as acid catalysts, initiate a wide variety of reactions of hydrocarbons, such as cracking, β-elimination, the shifts of the methyl group, and others. The catalytic properties of clays have also been investigated in connection with the elucidation of the genesis of petroleum. For example, the conversion of n-octacosane $C_{28}H_{58}$ in the presence of montmorillonite has been investigated.[102] Heating at 375 °C led to the formation of alkanes and olefins of smaller size, the yield of n-alkanes increasing and that of

branched and cyclic alkanes and aromatic hydrocarbons falling with increase in the duration of heat treatment. The olefins formed in the cracking process underwent isomerisation, rearrangement, and cyclisation.

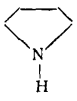
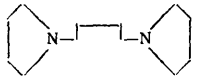
Table 3. Catalytic reactions in the presence of clays.

Field of application	Examples		Catalyst	Refs.
	starting materials	products		
Study of the genesis of petroleum. pyrolysis	Kerogen	–	Montmorillonite	[100, 101]
Ditto	Higher paraffins	–	Argillaceous rocks	[102]
"	Higher aliphatic acids	Hydrocarbons	Bentonite	[103]
Cracking of petroleum fractions	Distillates, gas oils	–	Bentonite clays	[104, 105]
Ditto	Various petroleum fractions	–	(0.5–4%) Al_2O_3/bentonite, with HNO_3	[106]
"	Higher paraffins	–	Ni-mica-montmorillinite	[107–109]
"	Gasoils, high-molecular-weight compounds in petroleum residues	–	Al-, Al-Zr-, Zr-, Al-Si-, and Si-fixed *montmorillonite*	[53, 55–57, 63–68, 110–115]
Hydroisomerisation of hydrocarbons	n-Pentane	Isopentane	0.2% Pd/mica-montmorillonite	[70, 116–118]
Ditto	*n*-Pentane	"	Beidellite	[28]
"	But-1-ene	Isobutenes	Al(Ti, Zr, Ho)-fixed montmorillonite	[119]
Hydrocracking	Higher paraffins	–	Ni-mica-montmorillonite	[67]
Ditto	n-Decane	–	Al(Ti, Zr, Ho)-fixed montmorillonite	[119]
"	Gasoil	–	Al(Zr, Si)-fixed montmorillonite	[115]
Hydropurification	Petroleum raw material	–	Ni-mica-montmorillonite	[120, 121]
Ditto	Petrol (gasoline)-ligroin fraction	–	Ni–Mo/bentonite	[122]
"	Aromatic raw material	–	1% Al_2O_3/montmorillonite	[123]
"	Mazut	–	Bentonite activated with HNO_3	[124]
"	Dibenzothiophen	Biphenyl	Mo-montmorillonite	[125]
Alkylation of aromatic compounds	Liquid benzene and toluene	Alkylbenzenes	Bentonite	[126]
Ditto	Benzene (with alcohols and olefins)	Ditto	Modified gumbrin	[127]
"	Benzene (with ethylene)	Ethylene	Silanised Al-fixed montmorillonite	[128]
"	Benzene (with propene)	Cumene	Al-fixed mica-montmorillonite	[129]
"	Benzene (with C_8–C_{18} olefins)	C_{14}–C_{24} alkylbenzenes	$Al^{3+}(In^{3+}$–$Cr^{3+})$-exchange montmorillonite	[130]
"	Benzene (with benzyl chloride)	Diphenylmethane	Vermiculite	[131]
"	Phenol (with 2-chloro-octane)	Octylphenol	Bentonite	[132]
Dealkylation	Isopropylnaphthalene	Naphthalene	Al-fixed montmorillonite	[62]
Transalkylation	Benzene + diisopropylbenzene	Cumene	Bentonite activated with H_2SO_4; fixed smectites	[133]
Disproportionation	1,2,4-Trimethylbenzene	Durene + *o*-xylene	Al-fixed montmorillonite	[134]
"	Oleic acid	Dieonic + steric acids	Ni-exchange montmorillonite	[135]
Reduction	Hex-1-ene	Hexane	Rh-phosphine/Na-hectorite	[136]
"	SO_2 (reaction with natural gas)	Elemental sulphur	Bauxite/bentonite	[137, 138]
"	CO	CO_2 + CH_4	$Ru(NH_3)_6^{3+}$/Al-fixed smectite	[139]
"	CO	Lower hydrocarbons, predominantly methane	$Ru(CO)_{12}$/montmorillonite	[140]
"	Biphenyl oxide	Benzene	Clay	[141]
Dehydrogenation	Butene	Butadiene	$Fe^{3+}(Sn^{4+})$-fluorotetrasilicate mica	[142, 143]
Intermolecular hydrogen transport	9,10-Dihydroanthracene + 1,1-diphenylethylene	Anthracene + 1,1-diphenylethane	Synthetic fluorohectorite	[144]
Ditto	Dihydroanthracene + stilbene	Anthracene + 1,2-diphenylethane	Al^{3+}-exchange montmorillonite	[144]

Table 3. (cont'.)

Field of application	Examples		Catalyst	Refs.
	starting materials	products		
Oxidation	1,1-Diphenylethylene	1,1-Diphenylethane + benzophenone	Synthetic fluorohectorite	[8]
Ditto	Leuco-bases (*in* coloured copy paper)	Dyes	Clays	[145]
Hydration	Ethylene	Ethanol	$Al^{3+}(Fe^{3+}, Cr^{3+}, H^+)$-exchange montmorillonite	[146]
Dehydration	Ethanol	Ethylene	Natural montmorillonite	[147]
Di- and tri-merisation	Hexene	Methylundecenes	Cu^{2+}-exchange montmorillonite	[148]
Ditto	1,1-Diphenylethylene	1-Methyl-1,3,3-triphenylindan	Cu^{2+}-exchange montmorillonite	[149]
"	*trans*-stilbene	9,10-dibenzyl-9,10-dihydroanthracene	Cu^{2+}-exchange montmorillonite	[8]
"	Indene	Dimers and trimers	Cu^{2+}-exchange montmorillonite	[8]
"	Oleic acid	Di- and tricarboxylic acids	Montmorillonite	[135]
"	Aliphatic acids in tall oil	Dimers with M.W. ≈ 560–590	Bentonite activated with H_2SO_4	[150]
Cis-trans isomerisation	Oleic acid		Cr^{3+}-exchange montmorillonite	[135]
Oligomerisation	Cyclohexene	Liquid products	$CH_3NH_4^+$-exchange montmorillonite	[151]
"	Propene	Ditto	Al-fixed montmorillonite	[152]
"	"	"	H^+-exchange montmorillonite	[153]
"	Olefins	"	0.2% Pd/mica-montmorillonite	[154]
"	Butenes	Petrol (gasoline)	Montmorillonite/kaolin	[155]
"	Isobutene	Dimer (18%), trimer (56%), tetramer (17%)	Acid clay	[156]
Polymerisation	Propene	–	Bentonite	[157]
"	Styrene	–	Acid-washed montmorillonite	[158–160]
"	Methyl methacrylate	–	H-bentonite	[161]
"	Phenol	–	$Al^{3+}(Fe^{3+}, Cr^{3+})$-exchange montmorillonite	[162]
"	Benzyl alcohol	Polyphenylenemethylene	Cu^{2+}-exchange montmorillonite	[163]
Synthesis of ethers	Olefins (with participation of intercalated water in the mineral)	–	Cu^{2+}-exchange montmorillonite	[164, 165]
Ditto	Olefin + primary alcohol	–	Al^{3+}-exchange montmorillonite	[165]
"	Primary alcohols	–	Al^{3+}-exchange montmorillonite	[163, 165]
"	Primary diols	Dioxan + triethylene glycol	Al^{3+}-exchange montmorillonite	[165]
"	Epoxyethane	Dioxan	Al^{3+}-exchange montmorillonite	[165]
"	Phenol + isobutene	*p*-t-Butylphenol	Activated clay	[166]
"	Methanol + isobutene	t-Butyl methyl ether	$Al^{3+}(Fe^{3+}, Cr^{3+})$-exchange montmorillonite	[167]
Condensation	Phenol + benzyl alcohol	Benzylphenoxide	Fluorotetrasilicate mica	[168]
Synthesis of esters	Carboxylic acid + olefins	–	$Al^{3+}(H^+, Cr^{3+})$-exchange montmorillonite	[148, 169]
Conversion of mercaptans into thioethers	Alkanethiol	Dialkyl sulphide	Al^{3+}-exchange montmorillonite	[170]
Ditto	Benzenethiol	Diphenyl sulphide	Al^{3+}-exchange montmorillonite	[170]
"	Toluenethiol	Polyphenylenemethylene	Al^{3+}-exchange montmorillonite	[170]

Table 3. (cont'.)

Field of application	Examples		Catalyst	Refs.
	starting materials	products		
Lactonisation	Cyclo-octene-carboxylic acid	1,3 + 1,4-Cyclo-octane carbo-lactone	$Al^{3+}(Co^{2+})$-exchange montmorillonite	[171]
Conversion of amines	Alkylamines RCH_2NH_2	$RCH_2.NHCH_2R$	Al^{3+}-exchange montmorillonite	[172]
Ditto	Primary cyclo-alkylamines $C_6H_{11}NH_2$	$C_6H_{11}.NHC_6H_{11}$	Al^{3+}-exchange montmorillonite	[172]
"	Secondary cyclo-alkylamines 		Al^{3+}-exchange montmorillonite	[172]
Cycloaminolysis	Acetylene	Pyridine	Bentonite activated with H_2SO_4	[173]
Conversion of methanol	MeOH	C_1–C_6 olefins, predominantly C_2–C_4 olefins	Ti-exchange montmorillonite	[174, 175]
Ditto		Ditto	SiO_2-fixed montmorillonite	[58]
"		"	Zr-fixed montmorillonite	[176]
"		$CO + H_2$	Pd(Ru, Ni, Rh)/fluorotetrasilicate mica	[177]
Conversion of synthesis gas	$CO + H_2$	Lower olefins	Fe-fixed montmorillonite	[75]

The hypothesis that aliphatic acids are precursors of the petroleum n-paraffins stimulated research into the catalytic decomposition of aliphatic acids. Thus, the decomposition of behenic acid $C_{21}H_{43}COOH$[103] on bentonite in the presence and absence of water at 200 °C yielded C_3–C_5 hydrocarbons. The total amount of saturated hydrocarbons increased with increase in the duration of heat treatment (90–760 h), while the yield of olefins fell. According to the authors,[103] the decarboxylation reaction is catalysed by the Lewis centres located on the lateral surfaces of montmorillonite, while the cracking is associated with the Brønsted acidity.

The ability of clay minerals to effect the cracking of petroleum fractions is well known.[105] However, the development of methods whereby clays can be fixed has led to new possibilities for the creation of catalysts for the conversion of high-molecular-weight compounds with a kinetic diameter >0.9 nm,[110] which are present in heavy petroleum fractions. The active catalysts for the cracking of the heavy raw material (petroleum residues, coal liquefaction products, coal tar) should have pores larger than 0.8 nm and a large internal surface.[111] The advantages of the fixation of clay minerals are manifested precisely in the cracking of large molecules. Thus the zeolite Y in the Ce-form and the fixed Ce-montmorillonite both sorb alkylbenzenes with a kinetic diameter <0.9 nm [including cumene (0.68 nm), t-butylbenzene (0.68 nm), *m*-diisopropylbenzene (0.79 nm), and tricyclodecane (0.81 nm)] and large differences between the activities of the two catalysts are not observed.[110] On the other hand, the degree of cracking of dodecahydronaphthalene (with a kinetic diameter of 1.15 nm) on fixed Ce-montmorillonite (in which the size of the inlet apertures and pores is 1.6–1.9 nm) is higher by several orders of magnitude than on the zeolite Ce-Y (with a size of the inlet apertures of 0.9 nm), on which the sorption of this compound is sterically hindered.

With decrease in the degree of cross-linking from 2.0 to 1.6 mmol of Al per gram of the Ce-montmorillonite, the activity of the fixed clay increases still further.[112] The explanation is that, under the conditions of incomplete exchange, a large amount of free space remains between the layers and is sufficient for the penetration of the reactants into the interlayer space and at the same time a certain number of cations remain and polarise the molecules of the residual water with formation of protons. In such cross-linked montmorillonite, the distance between the pillars is 1.1 to 1.9 nm, depending on the degree of cross-linking (the distances were determined from the adsorption of planar condensed aromatic compounds), while the distance between the layers is 0.8–1.0 nm. Further decrease in the degree of cross-linking to 1.25 nm lowers the thermal stability of the catalyst and decreases the total pore volume and leads to the loss of catalytic activity.

Wide-scale studies have been carried out[113] on the application to petroleum processing of montmorillonites fixed by aluminium or zirconium oligocations. However, the montmorillonite fixed by the Al_{13} oligocation lost its activity rapidly in the cracking of gasoil as a consequence of not only coke formation but also of the breakdown of its structure. With increase in temperature from 560° to 760 °C, the specific surface of the clay fixed by the Al_{13} oligocation gradually fell from 200–300 to 55 $m^2\ g^{-1}$.[114] The deactivation caused by the formation of coke can be avoided by introducing into the catalyst small amounts (0.05%) of palladium and by carrying out the reaction in a stream of H_2.[134] Judging from the literature data,[134,178] by varying the conditions in the preparation of the specimens, especially from synthetic hectorite, it is possible to increase greatly the stability of the catalyst. Under optimum conditions, it is possible to obtain a catalyst whose specific surface remains fairly large (130 $m^2\ g^{-1}$) even at 800 °C.[178] However, one should note that there is little information about the thermal stability of the catalysts of the new type considered here—fixed clay minerals.

The stability of the montmorillonite cracking catalyst is also increased by adding to it 30% of the zeolite HY.[115] It has been suggested that the mica-montmorillonite mentioned above be used as a component of the cracking catalyst.[109,119] There are data concerning the application of clays, including fixed clays, to the hydrocracking of paraffinic hydrocarbons, from C_{10} upwards, and the hydroisomerisation of the C_4–C_5 hydrocarbons,[67,115,119,171,175] and also as carriers of catalysts for the hydropurification of heavy petroleum raw material.[125] Molybdenum catalysts deposited on bentonite showed a much greater activity in the hydrocracking of diphenylmethane and the hydrodesulphurisation of dibenzothiophen than those deposited on Al_2O_3. However, the activity of the Mo/Al_2O_3 catalyst was much greater in the hydrogenation of 1-methylnaphthalene.

Layered silicates have been used to alkylate aromatic compounds.[126–132] The overall characteristics of the alkylation process on clays and zeolites are the same. The reaction is usually carried out[159] at temperatures up to 400 °C and pressures ranging from 20 to 50 atm in order to maintain the reaction mixture in the liquid phase. The aromatic hydrocarbon:olefin molar ratio was varied from 2:1 to 15:1 in different investigations.[127,129] The alkylation of phenol requires a somewhat lower temperature—in the range 100–200 °C,[129,132] but in each specific case the reaction conditions depend on the catalyst used and on the type of alkylating agent. In the alkylation of benzene with ethylene under flow conditions on the Al_{13}-fixed montmorillonite (384 °C, contact time 10 s, benzene : ethylene molar ratio 7 : 4), the degree of conversion of ethylene into alkylbenzenes (diethylbenzene and ethylben-

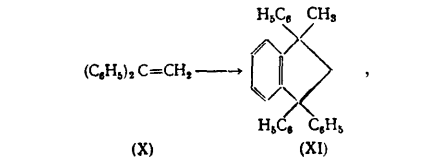
zene in proportions of 16:1) was 25.4%.[159] On montmorillonite in the H-form, treated with tetraethoxysilane, ethylbenzene was formed in 13% yield in a static system (40 atm. 200 °C, 2.5 h).[128]

Natural smectite clays (hectorite, saponite) in the cation-exchange form are used to alkylate benzene by higher olefins.[130] Under optimum conditions, the yield of the corresponding alkylbenzenes (with respect to the olefin) reaches 50%. Clays containing a cation with the highest Pauling electronegativity (Al^{3+}, In^{3+}, Cr^{3+}) are the most active. Minerals in which the cation has an electronegativity less than unity are inactive in the alkylation reaction. In the alkylation of phenol with chloro-octane (150–155 °C, 20 h) in the presence of natural bentonite, the yield of octylphenol (with respect to the alkane) reaches 92%.[132] Overall, comparative tests of the zeolitic catalysts H–ZSM and of fixed bentonite[179] showed that the latter is most suitable as the catalyst of the alkylation of benzene by olefins.

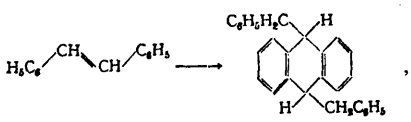
Dealkylation of isopropylnaphthalene[62] has been investigated in the presence of the Al-fixed montmorillonite dehydrated by the vacuum sublimation of a frozen specimen or by drying the specimen in air at room temperature. The reaction was carried out in a flow reactor at 300–400 °C and with a contact time of 0.6–3.6 s. The initial activities of the two specimens were similar (conversion 90–100%), but the catalyst dried by sublimation proved to be much more stable, The specimen dried in air rapidly lost its activity as a consequence of coke formation.

The transalkylation[124,163] and disproportionation[125,134] reactions of aromatic hydrocarbons have been carried out on bentonite activated by H_2SO_4 and on fixed smectites. A number of other catalytic reactions of hydrocarbons in the presence of clays are also known: hydrogenation,[136] dehydrogenation,[142,143] hydration of olefins,[146] oxidation,[8,45] etc.

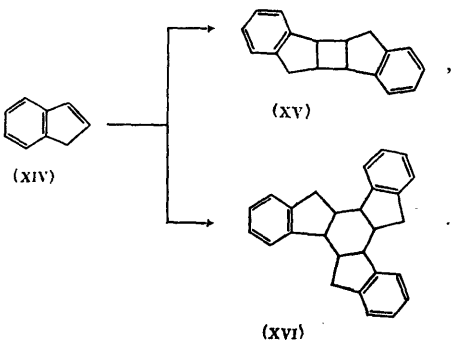
Studies of the dimerisation, oligomerisation, and polymerisation of olefins in the presence of layered silicates are of interest. As in the case of cracking, the use of layered and especially fixed silicates in these reactions makes it possible to introduce into the reaction or obtain large molecules:[8,149]



(X) (XI)



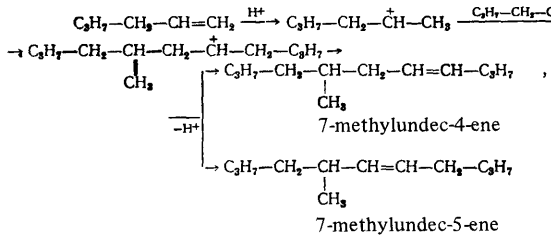
(XII) (XIII)



(XIV) (XV) (XVI)

For example, 1-methyl-1,3,3-triphenylindene (XI), whose molecule contains four aromatic rings, has been obtained[149] by dimerising 1,1-diphenylethylene (X) on Cu^{2+}-montmorillonite. The even larger 9,10-dibenzyl-9,10-dihydroanthracene (XIII) molecule is formed on the same catalyst from *trans*-stilbene (XII).[8] The dimerisation and especially the trimerisation of indene (XIV) leads to compounds (XV) and (XVI),[8] which cannot be obtained in comparatively narrow pores and cannot emerge from pores of moderate size and coke is gradually formed. Admittedly, one cannot rule out the possibility that such molecules can be assembled from the monomers on the lateral surface of the smectite crystal carrying acid centres of different strengths.

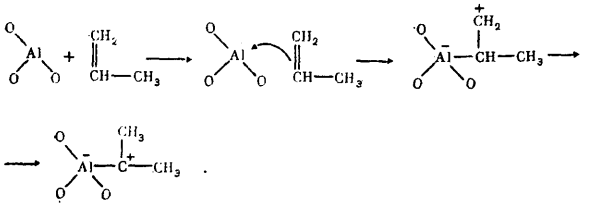
The mechanism of the dimerisation of olefins can be represented as follows in relation to hex-1-ene:[148]



7-methylundec-4-ene

7-methylundec-5-ene

Evidently, the oligomerisation of olefins under mild conditions can also be considered from the standpoint of the proton-donor mechanism. However, according to Occelli et al.,[152] the oligomerisation of propene on a fixed bentonite at temperatures up to 400 °C proceeds with participation of Lewis acid centres, which predominate on the surface even at temperatures above 300 °C. In this case, the reaction begins with the interaction of a highly active Lewis acid centre with a propene molecule and the formation of a stable π-complex. Electron transfer to an unoccupied orbital of the aluminium atom leads to the appearance of a σ-complex in which the propene fragment carries a positive charge:



After the addition of a propene molecule to this carbonium ion, chain propagation begins.

The elucidation of the cause of the activity of clays in polymerisation reactions[157–160] was assisted by a study of the interaction of leuco-bases with clay minerals.[92] This investigation resulted in the development of a donor–acceptor mechanism of the interaction of organic compounds with clays,[86,92,180] an example of which is presented in Section V.

The activity of montmorillonite in the styrene polymerisation reaction is appreciably suppressed after treatment with polyphosphates,[160] which is explained, as for the colour reactions (see Section V), by the presence on the lateral surface of electron-accepting (Lewis) centres consisting of aluminium atoms in an octahedral coordination. Since the polymerisation reaction has features characteristic simultaneously of free-radical and ionic mechanisms, it has been suggested[160] that electron transfer from the adsorbed styrene to aluminium results in the appearance of a radical-cation, which is rapidly converted into a dimer. Both the radical-cation and its dimer initiate the process, but the polymerisation itself proceeds via a cationic mechanism. Alcohols and amines inhibit

the polymerisation: being stronger Lewis bases, they are adsorbed preferentially.[158]

On the other hand, it has been suggested[181] that Brønsted and not Lewis acidity is responsible for the initiation of the polymerisation. However, whereas alkaline treatment suppresses the polymerisation completely, the adsorption of triphenylmethyl chloride on the Lewis centres on the lateral surfaces only reduces the yield of the polymer. It would therefore be an oversimplification to relate the activity of montmorillonite to its Lewis or Brønsted acidity only.

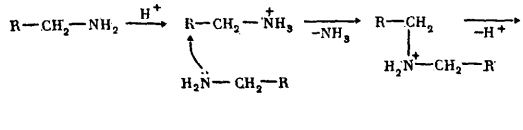
Various reactions of olefins, alcohols, thiols, and amines on layered silicates at low temperatures have been studied recently.[182] The reactions of olefins with water and alcohols afford ethers, those with carboxylic acids give rise to esters, and those with thiols produce thioethers (sulphides). Olefins do not react with amines on layered silicates.

It is noteworthy that the formation of an ether from an olefin and water requires an intermediate stage in which an alcohol is formed.[164] This reaction takes place with participation of the intercalated water after the exhaustion of which the reaction ceases; the catalyst cannot be regenerated. Smectites containing an exchange cation with the maximum polarising effect (Al^{3+}, Fe^{3+}, Cr^{3+}) exhibit the highest activity. However, the greatest selectivity in the formation of ethers has been attained on Cu^{2+}-exchange montmorillonite. For each cation, there is an optimum content of the intercalated water for which the yield of the ether is a maximum. The optimum $Cu:H_2O$ ratio for Cu^{2+}-montmorillonite is 1 : 12.[171]

The reactions of alcohols on layered silicates, which proceeds via an acidic mechanism, lead to the formation of ethers, alkenes, and alkene dimers.[163] Primary alcohols then give rise preferentially to ethers, secondary alcohols yield mainly alkenes, while tertiary alcohols give rise to alkenes and their oligomers exclusively. The fixation of montmorillonite and beidellite by the Al_{13} oligocation (d then increases to 1.8 nm) leads to a sharp fall in their catalytic activity in the reaction involving the formation of ethers from alcohols and of esters from an olefin and a carboxylic acid.[27]

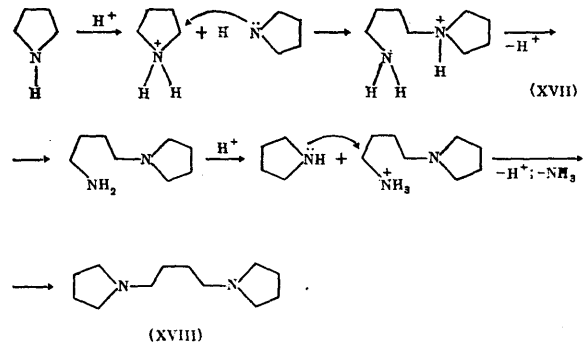
The reaction of benzyl alcohol on Cu^{2+}-montmorillonite takes place in an interesting manner:[62,163] polyphenylenemethylenes containing between 10 and 100 phenylenemethylene fragments are formed. The reaction of an aromatic thiol is of the same type.[170] The dimerisation of epoxyethane on Cu^{2+}-montmorillonite leads to the formation of a cyclic ether—dioxan.[109,182]

The reaction in which secondary amines are formed from primary anions on Cu^{2+}- or Al^{3+}-montmorillonite[172] has also been considered from the standpoint of a proton mechanism:



The formation of alkenes from amines was not then observed.

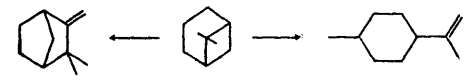
The rate of conversion of 2-alkylamines and cyclic amines is higher than that of 1-alkylamines (aniline is known to form complexes with clays,[172] but the nucleophilic substitution reaction does not occur). Cyclic secondary amines, for example, pyrrolidine, also split off ammonia in the presence of the Cr^{3+}-exchange montmorillonite, but in this case three amine molecules are involved in the reaction:[172]



(XVIII)

With increase in reaction time, the yield of compound (XVIII) increases and that of compound (XVII) falls, which indicates the intermediate character of the latter. The formation of piperidine and pyridine from acetylene and ammonia has been observed on bentonite activated with H_2SO_4.[173]

It is noteworthy that certain compounds react on layered silicates in a way which is different from that on zeolites. For example, α-pinene affords up to 20% of camphene and a large number of polymers on layered silicates, 50–62% of camphene has been obtained under industrial conditions on clays treated with acid, while on a synthetic zeolite the main product is dipentene:[183]



Camphene α-Pinene Dipentene

The "chemistry of C_1 compounds", which is based on the reactions of methanol and the synthesis gas, has acquired considerable importance in research and for practical purposes in all countries during the last decade. The possibility of using layered silicates as catalysts in this field has therefore been frequently investigated. For example, olefins, mainly having the C_2–C_4 composition, have been obtained from methanol in high yields on montmorillonites—both containing different exchange cations and fixed.[174–177] In this reaction too, the activity of the catalysts is related to their acidity. Preliminary treatment of the clay which enhances its acid properties, such as for example, the exchange of the Na^+ and Ca^{2+} cations for Ti^{4+} ions, greatly increases the degree of conversion of methanol.[174] Certain questions of the mechanism of the formation of higher olefins from methanol on zeolites have been examined in detail.[184] The similar nature of the active centres on zeolites and layered silicates (see Section V) suggests that the reactions on the latter proceed via the same mechanism.

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The data presented in this review show that the uses devised in recent years for layered silicates, in particular clays, in the preparation of catalysts have greatly expanded the scope of catalysis, mainly acid–base catalysis. This is due to the ready availability and low cost of the widely occurring natural raw material, the thermal stability of fixed clays, and the possibility of accelerating with their aid the reactions of large molecules. The latter is especially important at the present stage of development of the chemical, petrochemical and coal-chemical industry, which requires the creation of a

waste-free ecologically clean industry and hence the development of processes for the utilisation of the heavy residues remaining after the processing of different types of organic raw material containing large molecules.

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