strong doses of ionizing radiation. Furthermore, these inorganic ion exchangers possess a high ion exchange capacity and some peculiar selectivities. Layered phosphates are good intercalating agents of ionic or polar species. This allows the construction in the interlayer region of supramolecular assemblies with special functionalities in the fields of chromatographic supports, chemical and electrochemical sensors, ion exchange membranes, ionic and molecular recognition and catalysts. The delamination of layered phosphates has permitted the preparation of thin films and coatings and pillared layered structures with accessible microporosity. There are many more possibilities in layered phosphonate chemistry because functional groups may be inserted on alkyl chains or on aryl rings. The field of layered phosphates and phosphonates is in continuous expansion and these materials will find many applications as soon as their potential is realized.

See also: **II/Ion Exchange:** Catalysis: Organic Ion Exchangers; Historical Development; Inorganic Ion Exchangers; Novel Layered Materials: Non-Phosphates; Organic Ion Exchangers; Theory of Ion Exchange.

Further Reading

Alberti G (1978) Syntheses, crystalline structure, and ion-exchange properties of insoluble acid salts of tetravalent metals and their salt forms. *Accounts in Chemical Research* 11: 163–170.

Alberti G and Costantino U (1982) Intercalation chemistry of acid salts of tetravalent metals with layered structure and related materials. In: Whittingham MS and Jacobson JA (eds) *Intercalation Chemistry*, Chapter 5, pp. 147–180. New York: Academic Press.

Alberti G and Costantino U (1984) Recent progress in the intercalation chemistry of layered *a*-zirconium phosphate and its derivatives, and future perspectives for their use in catalysis. *Journal of Molecular Catalysis* 27: 235–250.

Alberti G and Costantino U (1991) Intercalates of zirconium phosphates and phosphonates. In: Atwood JL, Davies JED and MacNicol DD (eds) *Inclusion Compounds*, Vol. 5, *Inorganic and Physical Aspects of Inclusion*, Chapter 5, pp. 136–176. Oxford: Oxford University Press.

Alberti G and Bein T (eds) (1996) *Solid State Supramolecular Chemistry: Two and Three Dimensional Networks*, Vol. 7, *Comprehensive Supramolecular Chemistry*, Chapters 4 and 5, pp. 107–187. Oxford: Pergamon.

Alberti G, Casciola M, Costantino U and Vivani R (1996) Layered and pillared metal(IV) phosphates and phosphonates. *Advanced Materials* 8: 291–303.

Alberti G, Bartocci M, Santarelli M and Vivani R (1997) Zirconium phosphate chloride dimethyl sulfoxide, a reactive precursor of a large family of layered compounds. *Inorganic Chemistry* 36: 3574.

Amphlett CB (1964) *Inorganic Ion Exchangers*. Amsterdam: Elsevier.

Cheetham AK and Day P (eds) (1992) *Solid State Chemistry: Compounds*, Chapter 6, pp. 182–223. Oxford: Clarendon Press.

Clearfield A (ed.) (1982) *Inorganic Ion Exchange Materials*, Chapters 1–3, pp. 1–132. Boca Raton, FL: CRC Press.

Clearfield A (1990) Layered phosphates, phosphites and phosphonates of groups 4 and 14 metals. *Comments in Inorganic Chemistry* 10: 89–128.

Clearfield A (1998) Metal phosphonate chemistry. In: Karlin KD (ed.) *Progress in Inorganic Chemistry*, Vol. 47. New York: John Wiley.

Novel Layered Materials: Non-Phosphates

R. Mokaya, University of Cambridge, Cambridge, UK

Introduction

In this paper the structure and composition of layered materials (excluding those which contain phosphates) and their modified variants are described. Layered materials are made up of sheets or planes of atoms held together by interplanar forces which are weaker than intraplanar binding forces. This structural set-up allows the insertion of atomic or molecular guest species between the layers. Such insertion (or intercalation) provides a means for controlled variation of the physical and chemical properties of the host layered material over wide ranges to yield new variants of novel layered materials. The intercalated layered materials are also described.

Layered materials may be broadly classified into three groups according to the composition of their layers and the forces that hold the layers together. The interlayer forces determine the inherent ability of he layers to resist distortions involving displacements transverse to the layer planes.

1. Type I layered materials are made up of layers of atomically thin sheets. The neutral layers are held together by van der Waals forces. Examples are graphite and boron nitride. In graphite the layers tend to be 'floppy' and are easily separated with respect to distortions transverse to the layer
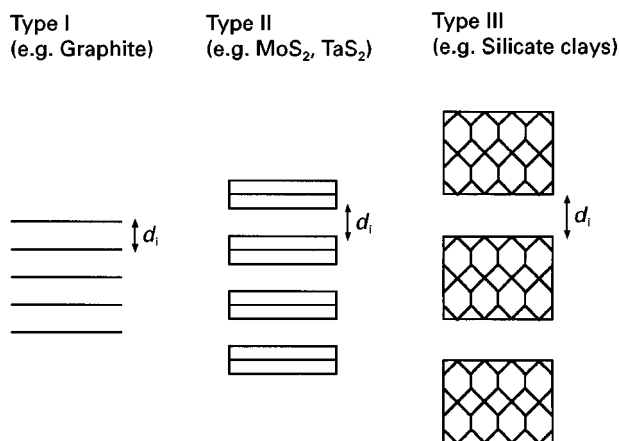
Type I
(e.g. Graphite)

Type II
(e.g. MoS$_2$, TaS$_2$)

Type III
(e.g. Silicate clays)

Figure 1 Schematic classification of layered solids (d_i = interlayer distance).

planes. Graphite is however rigid against longitudinal in-plane distortions.

2. Type II layered materials, such as dichalcogenides and lamellar oxyhalides, have layers composed of a few (usually three) distinct planes of strongly bonded atoms held together by van der Waals forces.

3. Type III layered materials have layers made up of dense (up to seven) assemblies of strongly bonded atoms. The layers may be charged in which case the interlayer forces are ionic resulting in layered structures, such as silicate clays and layer double hydroxides, which are quite rigid to interlayer distortion or expansion.

Figure 1 gives a schematic illustration of the three classes of layered materials.

In all cases the intralayer forces are much stronger than the interlayer forces and therefore guest species can be inserted into the interlayer region between the host layers without any change to the layers themselves. This attractive feature of layered materials has been extensively exploited. Indeed, the bidimensional character of many layered materials can be gradually modified by intercalation, grafting, or pillaring with a variety of guest species to yield new classes of novel layered materials. Type I intercalation materials, such as those of graphite, form stages in which n-multilayers of the host are separated by monolayers of guest intercalant to form expanded n-stage materials. Type II materials are able to accept guest species into random interlayer sites and may ultimately form a saturated stage-1 expanded material at sufficient guest species concentrations. In contrast type III materials always form intercalation compounds with a stage 1 stacking sequence in which the host layers are separated by one or more layers of the guest

species. Novel layered materials that have found use in separation processes are mainly (intercalated or otherwise modified) type III materials and this paper is therefore devoted to such materials with only a brief mention of type I and type II intercalated materials (using graphite and dichalcogenides as examples) given below.

Type I: Graphite

Graphite is known to be intercalated by both electron donors and acceptors and to a large extent the driving force for intercalation is electronic in nature. Thus depending on the guest species, positively charged carbon layers or negatively charged carbon layers may be obtained. Graphite intercalation compounds usually exhibit a high degree of ordering and are unique among layered host materials in that the intercalation occurs such that, depending on the extent of guest species incorporation, it is possible to observe the staging phenomenon (**Figure 2**). The staging phenomenon is defined by a periodic arrangement of n graphite layers (where n is the stage index) between sequential intercalant layers. Well staged graphite intercalated materials can be prepared up to $n \sim 10$. Strong interatomic intercalant–intercalant binding relative to the intercalant–graphite binding favours a close-packed in-plane intercalant arrangement and is the driving force for the staging phenomenon. Graphite intercalation compounds (GICs) have found use as catalysts, electric conductors, recording materials (in inks and coloured leads) and as lubricants and low friction coatings.

Type II: Dichalcogenides

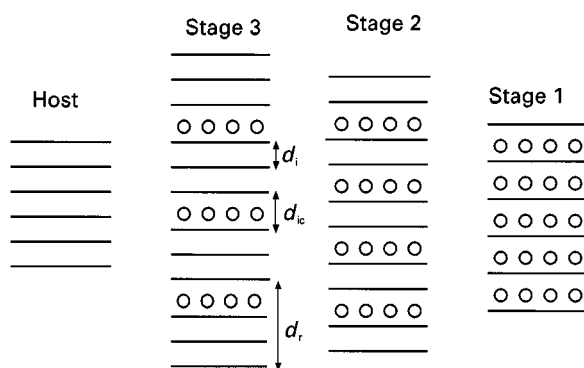Dichalcogenides, sometimes denoted TX$_2$, have layers made up of a sheet of metal atoms (T)

Figure 2 The staging phenomenon as exhibited by graphite (for stage 3, d_i = carbon interlayer distance, d_{ic} = intercalate distance and d_r = repeat basal distance).
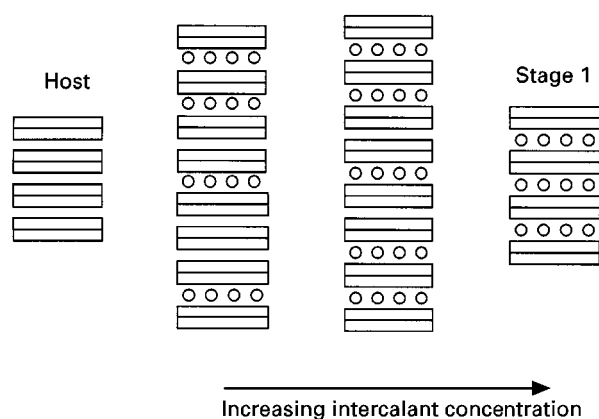
Figure 3 Schematic illustration of intercalant concentration dependent intercalation of type II layered materials.

sandwiched between two sheets of chalcogen (X) atoms. T is usually a transition metal and X may be S, Se or Te. The layers are largely neutral and separated by a van der Waals gap. As mentioned above, dichalcogenides are able to accept guest species into random interlayer sites and may ultimately form a saturated stage 1 expanded material at sufficient guest species concentrations (**Figure 3**). During intercalation, the guest species are inserted in the van der Waals gap and in most cases occupy interstitial sites. The intercalation is generally accompanied by charge transfer between the intercalant species and the host layers and therefore intercalation complexes are formed with electron donor species only. Such species include alkali metal atoms, transition metal atoms and organic molecules. The intercalation of metal atoms (especially alkali metal atoms) results in efficient transfer of electrons to the host compound resulting in unique electronic properties. For metal atom intercalation the increase in layer separation is not large but the weak host layer interactions are replaced by strong Coulomb (alkali metal) and covalent (transition metal) interactions yielding a quasi three-dimensional solid. The intercalation of organic molecules results in much larger layer separations. An example is the intercalation of amines in which the orientation of the amines in the van der Waals gap depends on the number of carbon atoms. Short chain amines, such as methylamine, pack parallel to the layers whereas intermediate chain amines (e.g. C_4–C_9) orient at an angle to the layers with the nitrogen with its lone pair of electrons adjacent to the layer. The angle of inclination generally increases with chain length and for chain lengths $> C_{16}$, the amines are arranged perpendicular to the host layers and form bilayers resulting in layer separations as high as 57 Å for stage 1 intercalation.

Type III: Layer Silicates (Clays) and Layer Double Hydroxides (LDHs)

Nature of Layer Silicates (Clay Minerals)

Clays are by definition fine grained solids with particle size generally $< 2\ \mu m$ and many of their properties result from their small particle size. The layers of clays are formed by condensation of sheets of linked $Si(O,OH)_4$ tetrahedra with those of linked $M_{2-3}(OH)_4$ octahedra, where M is a divalent or trivalent cation. A 1:1 condensation gives two sheet minerals such as kaolinite with a general layer formula of $M_{2-3}Si_2O_5(OH)_4$. A 2:1 condensation results in the octahedral sheet being sandwiched between two sheets of tetrahedra giving the mica type layer structure with a layer formula of $M_{2-3}Si_4O_{10}(OH)_2$. In both cases the tetrahedral sheets are linked in the unit structure to octahedral sheets and to groups of coordinated cations or individual cations. The apical oxygen at the fourth corner of the tetrahedron, which is directed normal or nearly normal to the sheet, forms part of an immediately adjacent octahedral sheet in which octahedra are linked by sharing edges. The junction plane between tetrahedral and octahedral sheets consists of the shared apical oxygens of the tetrahedra and unshared OH groups that lie in projection at the centre of each sixfold ring of tetrahedra. **Figure 4** shows a three-dimensional schematic illustration of layer silicates. Also possible, for example in chlorite, are four sheet clays in which the trimorphic units alternate with $M(OH)_{2-3}$ sheets of octahedrally coordinated M^{2+} or M^{3+} ions.

Smectite clays, which exhibit the property of intercalation, are made up of negatively charged layers and therefore possess an ion exchange capacity which distinguishes them from the mica and pyrophillite-talc groups of minerals (see below). The layer charge arises generally from isomorphous substitution of Si^{4+} by Al^{3+} in the tetrahedral sheet and/or Al^{3+} by Mg^{2+}, Fe^{2+} in the octahedral sheet. Some charge may also arise from broken bonds at edges of the clay crystal. Following below are ideal structural formulae of some clay silicates showing, where appropriate, isomorphous substitution:

1. Dioctahedral smectites (two-thirds of octahedral sites are occupied by trivalent cations)
   (a) Pyrophyllite
   $[(Si_8)(Al_4)O_{20}(OH)_4]$ No layer charge.
   (b) Montmorillonite
   $[M_x(Si_8)[Al_{4-x}Mg_x]O_{20}(OH)_4 \cdot nH_2O]$ Octahedral substitution.
   (c) Beidellite
   $[M_xSi_{8-x}Al_x(Al_4)O_{20}(OH)_4 \cdot nH_2O]$ Tetrahedral substitution.

Exchangeable cations

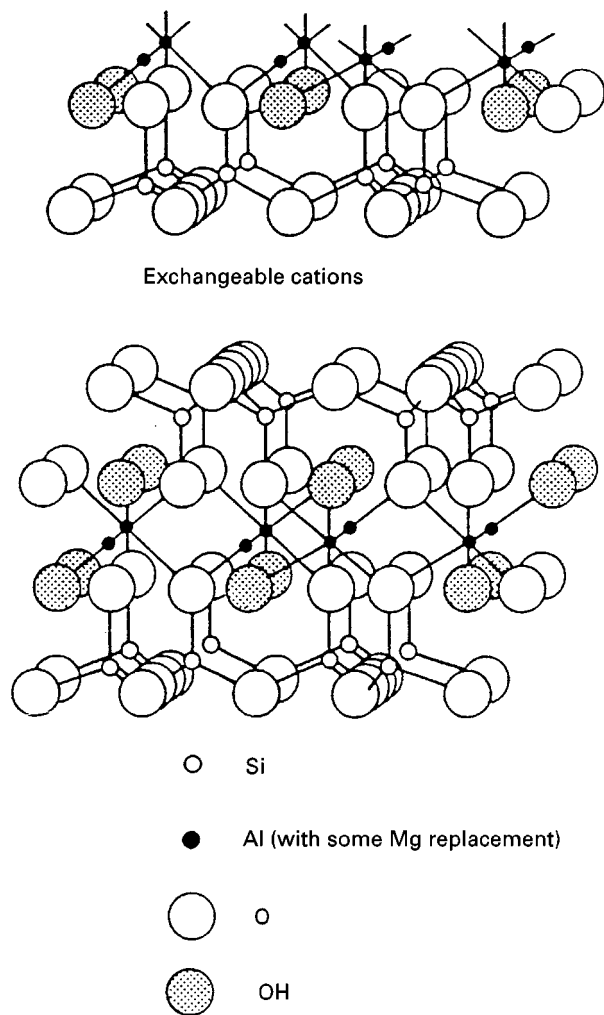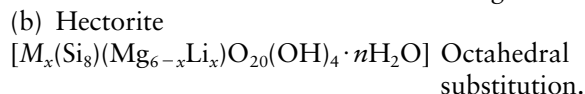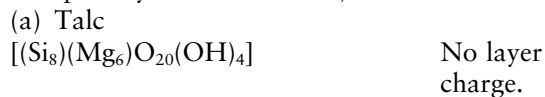○ Si

● Al (with some Mg replacement)

○ O

⊙ OH

Figure 4 Three-dimensional illustration of the structure of silicate clays.

2. Trioctahedral smectites (all octahedral sites are occupied by divalent cations)
   (a) Talc
   $[(Si_8)(Mg_6)O_{20}(OH)_4]$ No layer charge.
   (b) Hectorite
 $[M_x(Si_8)(Mg_{6-x}Li_x)O_{20}(OH)_4 \cdot nH_2O]$ Octahedral substitution.

Smectite clays can intercalate other compounds in a three component system:

1. Host layer with an overall negative layer charge.
2. Exchangeable intercalates (ions) which compensate for the overall negative charge.
3. Neutral molecules (e.g. water) which occur between the layers and are associated with the interlayer cations and the layers.

Pillared Clays

Pillared clays are usually smectite clay minerals in which the interlayer cations are three-dimensional species which in some cases, after appropriate treatment, are fixed to the layers of the host clay. The shape and size of these cations allows them to function as molecular pillars which keep the layers apart at a fixed distance. The pillaring phenomenon therefore exposes much of the intercrystal basal surfaces for adsorption and molecular sieving purposes. Permanent porosity may be introduced in montmorillonite by replacing the interlayer alkali or alkaline earth cation with a variety of species such as tetraalkylammonium ions, tris-metal chelates, bicyclic amine cations and polymeric oxymetal cations. Clays pillared by oxycations or metal oxides are of greatest interest because they exhibit thermal stability in excess of 500°C and, depending on preparation methods, materials with large pore diameters and surface area (**Table 1**).

The most extensively studied pillared clays are those containing polymeric hydroxy-aluminium species as the pillaring cation. In this paper such Al pillared clays are used to illustrate the nature and properties generally possessed by metal oxide pillared clays. In the non-calcined so-called precursor pillared clay, layer charge is balanced by the pillaring polycations which in the case of Al pillared clays is the Keggin-like $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ion. On calcination this ion is converted into an oxide with the layer charge balanced by the release of an equivalent number of protons, i.e.

$$2[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+} \rightarrow 13Al_2O_3 + 14H^+$$
$$\text{pillar}$$
$$+ 41H_2O$$
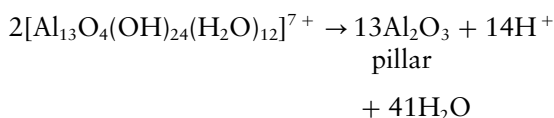
The formation of pillars fixed to the layers of the host clay is dependent on the calcination temperature. In general the basal (0 0 1) spacing of the precursor-Al pillared clay decreases to a fixed value upon

Table 1 Pillar type and corresponding basal spacing and surface area for montmorillonite pillared clays

Pillar type	Basal spacing (Å)	Surface area (m² g⁻¹)
Alumina	18–19	250–400
Iron oxide	17–18	~ 280
Chromia	19–21	350–400
Zirconia	18–22	250–300
Titania	18–20; 25–29	300–350
Silica	12–13; 16–20	40–200; 150–400
Silica/alumina	16–19	350–500
Titania/silica	38–40	250–400

heating at 500°C. Heating to temperatures up to 400°C causes some contraction but does not prevent re-expansion of the clay upon exposure to moisture. However, the pillared clay obtained by calcination at 500°C usually shows no tendency to expand. This is because in the temperature range 400–500°C an irreversible contraction in the layer spacing occurs, during which the pillars are held within the host aluminosilicate sheets resulting in cross-linked materials. Therefore the precursor pillaring species dehydroxylates progressively on heating to 400°C, releasing protons which migrate into the clay structure and at 500°C condensation takes place of terminal hydroxy groups present on the polymeric ions with the lattice hydroxy groups on the clay. The oxide pillars formed become linked directly via oxygen to the aluminium and magnesium atoms in the octahedral layer resulting in a rigid cross-linked structure resistant to expansion. These changes are illustrated in **Figure 5**.

The microstructure of pillared clays is controlled by the wet chemistry of synthesis and, to a large
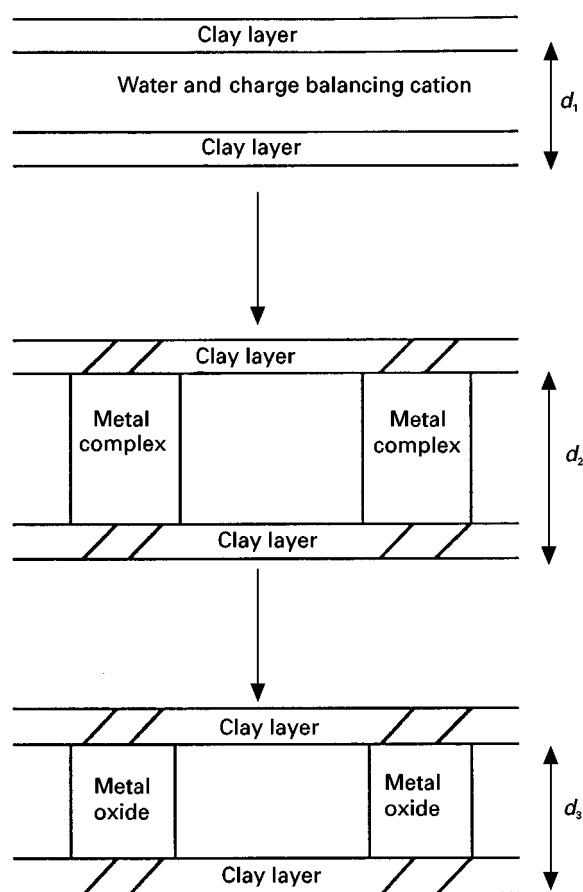

Figure 5 Schematic description of pillaring. In the case of an alumina pillared clay prepared from Ca-montmorillonite, $d_1 = 14.4$ Å, $d_2 = 20.5$ Å, $d_3 = 19.0$ Å.

extent, the method used to dry the precursor pillared clay. The basal spacing of the pillared clays depends on the age of the pillaring reagent, the degree of hydrolysis (polymerization) of the pillaring reagent, the amount of reactants (i.e. Al/clay ratio) and the temperature of pillaring. Pillaring of clays increases their surface area from as low as $30 \text{ m}^2 \text{ g}^{-1}$ to $500 \text{ m}^2 \text{ g}^{-1}$ (Table 1) and generates a microporous structure similar but less constrained than that of zeolites. The volume created can be used for adsorption purposes; the adsorption characteristics are known to vary with the method employed in drying the pillared clay. Air-dried pillared clays are zeolite-like products which cannot adsorb molecules of kinetic diameter 9.2 Å (e.g. 1,2,5-triethylbenzene) but can adsorb molecules of kinetic diameter 6.0 Å. Freeze-dried pillared clays can, however, adsorb appreciable amounts of molecules with kinetic diameter of 10.0 Å. Freeze-dried pillared clays therefore contain a significant fraction of pore openings > 10.0 Å whereas all the pore openings of air-dried pillared clays are < 9.0 Å. This is related to the mechanism of layer aggregation during drying. The aggregation may be face to face (for air-dried materials) or edge to face and edge to edge layer contact for freeze-dried materials. Air-dried pillared clays therefore exhibit long range lamellar order with a regular and relatively narrow pore size distribution while freeze-dried pillared clays, on the other hand, exhibit less lamellar order and a broad pore size range.

Metal oxide pillared clays in general tend to possess pores in both the micropore and mesopore size range. The ratio of micropore to mesopore volume largely depends on the interlayer spacing (pillar height) and the interpillar distance. The interpillar distance may be controlled by varying the ion exchange capacity of the host clay; this in turn determines the number of pillaring polycations required to balance the host layer charge. A low exchange capacity favours a low pillar density and vice versa. The interlayer spacing, on the other hand, may be controlled by varying the pillar type. **Figure 6** gives a diagrammatic representation of two common pillar types and Table 1 gives some examples of pillar type and basal spacing for montmorillonite clay.

The porosity of pillared clays may also be varied by combining the pillaring process with other treatments such as competitive ion exchange with monocations or acid activation. Indeed acid activation of clays (see below) prior to pillaring yields a different class of materials, generally referred to as pillared acid-activated clays, with quite distinct properties.

An important characteristic of pillared clays (and clays in general) which is in some cases crucial to their
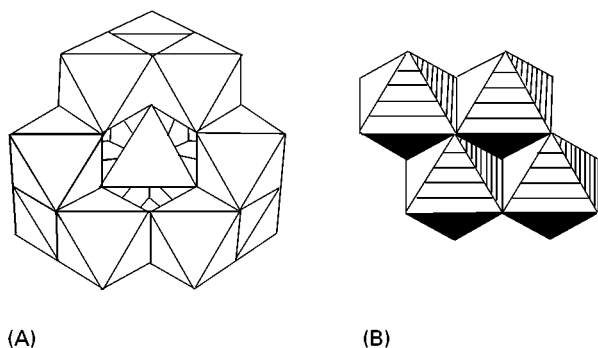
Figure 6 Diagrammatic illustration of polymeric hydroxy-Al (A) and -Ti (B) pillaring cations.

use in separation processes is that they possess considerable acidity and may be classified as solid acids. For example non-calcined precursor-alumina pillared clay possesses Brønsted acidity which arises through the following mechanisms:

1. Polarization of interlamellar water by initial exchangeable cations not replaced by the hydroxy-Al polycations. This is especially the case if the initial exchangeable cation is acidic.
2. The pillaring polymer may hydrolyse to release protons, i.e.

$$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$$
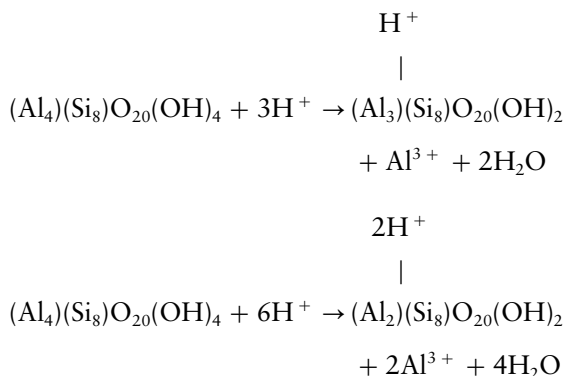$$\rightarrow [Al_{13}O_4(OH)_{24+x}(H_2O)_{12-x}]^{7+} + xH^+$$
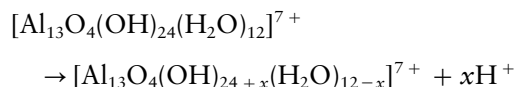
3. The OH groups of the clay lattice and the pillar may also act as Brønsted acid sites.

However, for a pillared clay calcined at temperatures above 400°C, Brønsted acidity is weaker than Lewis acidity. This is due to the migration of protons from the interlayer region into the layer structure where they neutralize the negative layer charge thus removing some Brønsted acid sites.

Acid activated clays When 'activatable' clay minerals are treated in acid, their chemical composition and physical properties are altered. The activation process enhances properties already present in the clay minerals and gives them certain desirable properties with respect to their applicability as adsorbents and catalysts. The clays of choice for acid activation are non-swelling bentonites containing montmorillonite as the major component. In general terms the acid activation of montmorillonites proceeds via the removal of octahedral ions and any isomorphously substituted tetrahedral ions. The changes that take place in an idealized montmorillonite with no isomorphous substitution may be

expressed as:

$$\overset{\displaystyle H^+}{\underset{|}{}}$$
$$(Al_4)(Si_8)O_{20}(OH)_4 + 3H^+ \rightarrow (Al_3)(Si_8)O_{20}(OH)_2$$
$$+ Al^{3+} + 2H_2O$$

$$\overset{\displaystyle 2H^+}{\underset{|}{}}$$
$$(Al_4)(Si_8)O_{20}(OH)_4 + 6H^+ \rightarrow (Al_2)(Si_8)O_{20}(OH)_2$$
$$+ 2Al^{3+} + 4H_2O$$

Layer Double Hydroxides (LDH)

Natural layer double hydroxides (or hydrotalcite-like compounds as they are sometimes called) are, unlike clay minerals, relatively rare. Where they occur they are associated with metamorphic rock formations or saline deposits. The structure of LDHs is very similar to that of brucite, $Mg(OH)_2$, in which magnesium is octahedrally surrounded by six oxygen atoms in the form of hydroxide with the octahedral units extending to form infinite sheets through edge sharing. If some of the magnesium in the sheets is isomorphously substituted by a higher charge cation such as Al^{3+}, the resulting Mg^{2+}–Al^{3+}–OH layer gains a positive charge. Sorption of an equivalent amount of hydrated anions occurs so as to maintain electrical neutrality; in nature the charge-balancing hydrated anion is usually carbonate. The OH groups of the positively charged brucite-like sheet are linked to the CO_3^{2-} groups either directly (via OH–CO₃–HO linkages) or via intermediate water (i.e. OH–H₂O–CO₃–HO). The interlayer carbonate anions adopt an orientation parallel to the layers, i.e. they lie flat surrounded by loosely bound water (**Figure 7**). The resulting natural LDH may exist in either of two dimorphic forms, i.e. as a rhombohedral hydrotalcite or a hexagonal manasseite.

LDHs may be described by the general formula

$$[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[X^{m-}]_{x/m}\cdot nH_2O$$
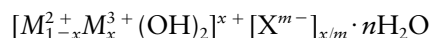
where M represents a metal cation and X represents an anion. M^{2+} may be Mg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and M^{3+} may be Al^{3+}, Cr^{3+} or Fe^{3+}. M^{2+}/M^{3+} ratios between 1 and 5 are possible but are typically $0.25 \leq x \leq 0.33$ and $0 \leq n \leq 6$. Synthetically there is a wide range of variables such as: (i) different combinations of M^{2+} and M^{3+}; (ii) different charge balancing anions; (iii) different amounts of interlayer water; and (iv) crystal morphology and size. To form LDHs, the M^{2+} and M^{3+} cations must be of a size that can be contained in
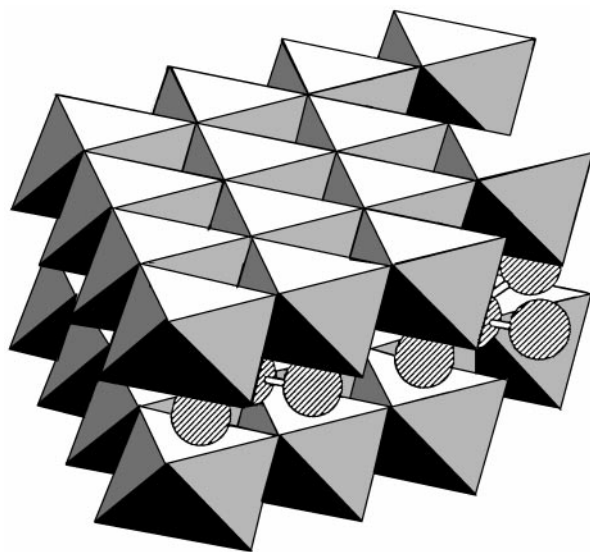
Figure 7 Illustration of the top view of LDH ($Mg_6Al(OH)_{16}CO_3 \cdot 4H_2O$) lattice.

the holes (octahedral sites) between the close-packed OH groups in the brucite-like layers. This limits the possibilities to cations of ionic size between 0.5 and 0.8 Å and, in the main, excludes cations such as Be^{2+} (0.35 Å), Ca^{2+} (0.99 Å) and Cd^{2+} (0.97 Å). The formation of LDHs is not, however, limited to M^{2+}/M^{3+} cations; it is, for example, possible to incorporate monovalent cations (M^+) such as Li^+ in a Li/Al material, or to have divalent/tetravalent materials such as Co/Ti.

The number of exchangeable anions in LDHs depends on the charge density on the host layers. However there are no particular restrictions on the nature of the anion. Inorganic charge-balancing anions include Cl^-, OH^-, NO_3^-, ClO_4^- and SO_4^{2-}. Organic acids such as adipic, succinic, oxalic, malonic, sebacic and terephthalic may also serve as charge-balancing species. However, as mentioned above, nature favours the carbonate ion which is tenaciously held in the interlayer region due to its relatively high polarizability and synthesis of pure LDHs with other anions requires special preparation procedures (see below). LDHs may undergo swelling in a manner not unlike that of silicate clays. For example sulfate-containing LDH may be solvated with glycol or glycerol. In general swelling of LDHs depends on the nature of the interlayer anion (charge, mass, structure), nature of the solvent (polarity, molecular dimensions) and of course the layer charge.

Pillared Layer Double Hydroxides

Pillared LDHs which possess empty interlayer/interpillar space are desirable but unlike pillared clays

are difficult to prepare. The difficulty is largely due to the affinity of the layers for the carbonate anion; if CO_2 is present during synthesis, the carbonate is preferentially incorporated and once in the interlayer it is held tenaciously and not easily replaced. Most of the pillaring strategies employ a CO_2-free environment and make use of the fact that Cl^- or NO_3^- anions are easier to displace. Thus the Cl^- or NO_3^- LDH is prepared, usually under nitrogen, and these anions are then replaced with larger polyoxometalate anions such as, for example, $V_{10}O_{28}^{6-}$, $Ta_6O_{18}OH^{7-}$, $Nb_6O_{18}OH^{7-}$. Another approach has relied on the use of LDH initially synthesized with large intercalated organic anions, for example the terephthalate dianion (**Figure 8**) as the interlayer species. The organic anion is then displaced by the polyoxometalate species. As in clays, the pillaring of LDHs results in an increase in surface area and pore volume. The increases are however lower than in pillared clays. This is due to the high layer charge in LDHs which leads to a high pillar density which in some cases yields materials in which the pillars are 'stuffed' into the LDH and do not exist as isolated discrete pillars. An example is polyvanadate-intercalated LDH which has a surface area of *ca.* 35 $m^2 g^{-1}$ compared to 25 $m^2 g^{-1}$ for the unpillared material. True pillaring does occur as in the case of $Zn_2Al[\alpha-SiV_3W_9O_{40}]$ which exhibits a surface area of 155 $m^2 g^{-1}$.

Applications of Pillared (or Intercalated) Layered Solids

The applications of expanded layered solids (LDHs or clays) are largely due to their large surface area and variation in their chemical and physical properties. These properties may be enhanced by the ability to
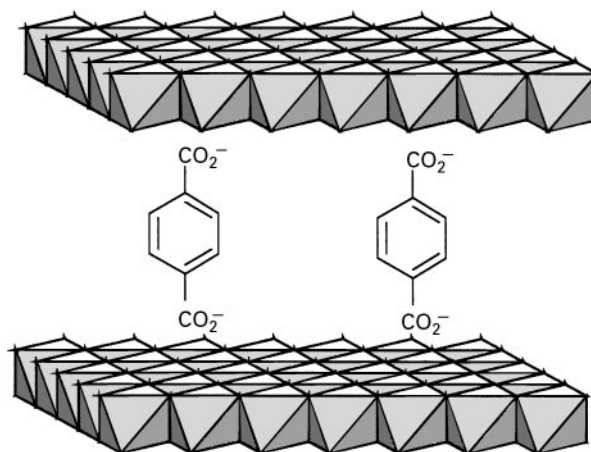

Figure 8 Illustration of terephthalate intercalated LDH.

tailor them for specific uses. In general these materials have found use as catalysts, ion exchangers and adsorbents and are also useful in gas and liquid separation processes (where they exhibit molecular sieving properties similar to those of zeolites). Some examples are:

1. Organoclays containing molecules such as $(CH_3)_4N^+$ are especially suited for certain separation processes due to their hydrophobic nature and high affinity for certain organic compounds.
2. Clays and their oxide-pillared derivatives have found use as: (i) scavengers for hazardous organics (especially from effluent streams); (ii) selective adsorbents of heavy metals from effluent streams; and (iii) purifiers for edible oils where the clays adsorb compounds such as carotenoids and chlorophyll to give the oil its clear look and taste. Indeed acid activated clays are the industry standard for the decolorizing of oil.
3. LDHs have found use as excellent acid residue scavengers.

Greater use of layered materials in separation processes can be achieved when the materials are used in the form of membranes where they act as ionic and molecular filters or sieves.

See also: **II/Ion Exchange:** Historical Development; Novel Layered Materials: Phosphates; Organic Ion Exchangers; Organic Membranes.

Further Reading

Barrer RM (1978) *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*. London: Academic Press.

Bein T (ed.) (1992) *Supramolecular Architecture: Synthetic Control in Thin Films and Solids*. ACS Symposia Series, vol. 499.

Dresselhaus MS (ed.) (1986) *Intercalation in Layered Materials*. New York: Plenum Press.

Dresselhaus MS, Dresselhaus G, Fischer JE and Moran MJ (eds) (1983) *Intercalated Graphite*. MRS Symposia Proceedings, vol. 20.

Lévy F (ed.) (1976) *Crystallography and Crystal Chemistry of Materials with Layered Structures*. Dordrecht: Reidel.

Lévy F (ed.) (1976) *Structural Chemistry of Layer-type Phases*. Dordrecht: Reidel.

Lévy FA (ed.) (1979) *Intercalated Layered Materials*. Dordrecht: Reidel.

Lieth RMA (ed.) (1977) *Preparation and Crystal Growth of Materials with Layered Structures*. Dordrecht: Reidel.

Mitchell IV (ed.) (1990) *Pillared Layered Structures: Current Trends and Applications*. London: Elsevier.

Newman ACD (ed.) (1990) *Chemistry of Clays and Clay Minerals*, 2nd edn. London: Longman and Mineralogical Society.

Birch R (1988) Pillared clays. *Catalysis Today* 2.

Sequeira CAC and Hudson MJ (eds) (1992) *Multifunctional Mesoporous Inorganic Solids*. Dordrecht: Kluwer.

Whittingham MS and Jacobson AJ (eds) (1982) *Intercalation Chemistry*. London: Academic Press.

Yamagishi A, Amarita A and Taniguchi M (eds) (1998) *The Latest Frontiers of the Clay Chemistry*. Sendai: Smectite Forum of Japan.

Organic Ion Exchangers

C. Luca, 'Petra Poni' Institute of Macromolecular Chemistry, Lasi, Romania

Abstract

The definition and some characteristic concepts regarding organic ion exchangers are pointed out. The development of these ion exchangers, beginning with chemically modified natural products and continuing with the synthetic ones, is further presented. A classification of organic ion exchangers is proposed according to several criteria, such as the synthesis method, morphology of the three-dimensional network, their physical shape and the nature of their functional groups.

Of the general characteristics of organic ion exchangers only the exchange capacity and selectivity are briefly discussed.

Preparation and structure – chemical property relationships, and some applications with reference to strong and weak cation and anion exchangers, as well as to chelating ion exchangers – are described in more depth.

Definition

An ion exchanger generally is a solid, insoluble material that contains groups which ionize in aqueous medium.

Organic ion exchangers are three-dimensional covalent networks that contain exchangeable ions associated with fixed acid or basic groups. The term 'ion exchange resins' is also used to describe organic ion exchangers.

The ion exchangers that have fixed acid groups and carry exchangeable cations (usually H^+ or Na^+) are cation exchangers described as in the H form and Na