NOVEL INORGANIC MATERIALS: ION EXCHANGE

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Introduction

The modification of open-structured solids by ion exchange is a versatile and powerful synthetic route to new compounds. These may be either novel inorganic phases that cannot be prepared directly using high temperature ceramic routes, or composite systems incorporating an additional organic or inorganic component. In both cases the methods used are part of *chimie douce*, a rare example of a scientific French term that has penetrated into common international usage.

From both a conceptual and a practical point of view, it is useful to distinguish those solids that, by the arrangement of their constituent atoms in space, form a rigid, open-structured network and that readily undergo ion exchange reactions only to within the limit of the size constraint of the window openings of the structure, and those in which the framework is made up of two-dimensional layers that may be prised apart if sufficient energy can be provided to overcome the van der Waals or hydrogen bonding interactions. Typical examples of the former are provided by microporous zeolites, such as zeolite A, while smectite clays, such as montmorillonite, exemplify the latter. Here, as in layered oxides, phosphates and other classes of bidimensional solids, the structure adapts itself depending on the incoming molecule, and the variable parameter represented by the interlayer spacing allows an enormous variety of species to be ion exchanged or intercalated. While more classically, ion exchange or intercalation was a single-step process, much recent work is characterized by the development and use of pre-expansion or exfoliation techniques, and reprecipitation of the dispersed layers in the presence of the desired intercalant ion, molecule or polymer. These methods have significantly broadened the range of new nanocomposite materials that can be prepared, which display properties including second harmonic generation (in the case of intercalation of dyes), chiral recognition, electronic conductivity (in the case of ion exchange of electroactive molecules or polymers), protonic conductivity, micro- and meso-porosity for catalysis and sorption, etc.

The term ‘intercalation’ will be used in its strictest sense here, to mean the topotactic and reversible insertion of a guest species into a host layered compound; this term has been more generally applied to host matrices of any dimensionality.

Host-Structures for Ion Exchange Reactions

To a first approximation, solids of fixed pore size are three-dimensional structures. In zeolites, and zeotypes with ultralarge pores and having alumino- or gallo-phosphate framework compositions, the window frames to the pores are composed of tetrahedrally coordinated atoms, the number of which defines the size of the entry aperture. Zeolite and zeotype molecular sieves are characterized by their high crystallinity and narrow pore size distribution dominantly in the micropore range, i.e. pore diameter below 2 nm, but more recently extending up into the low mesopore region. Charge imbalance created, in the simplest cases, by inclusion of aluminium in a silica framework, is counterbalanced by intrapore cations, and the Si/Al ratio therefore defines the number of exchangeable ions, or ion exchange capacity, usually expressed as the number of milliequivalents (of exchangeable ion) per gram (of ion exchanger). While the modification of zeolites and zeotypes is a starting point for new inorganic syntheses, zeolite ion exchange properties have long been exploited for water softening in detergents and their Brønsted acidity has been used by the petroleum industry in fluid catalytic cracking and other processes.

This enormous historical use and the economical necessity to crack progressively heavier fractions provided the impetus for the synthesis of ion exchanging materials having a pore size reaching more firmly into the mesopore range, and the plethora of activity associated with all aspects of surfactant-assisted syntheses of mesoporous solids attests to the significance of the discovery of this liquid crystal templating, or cooperative nucleation approach. If the surface acidity has since proved to be disappointing, the narrow and controllable mesopore distribution readily attainable using these routes represents a major advance with applications in many fields. Of the hexagonal, cubic and lamellar phases known, only the ion exchange capacity and unidimensional channels of the first have been used in the synthesis of composite new materials. Potential host structures for modification by ion exchange include the macroporous silicates or alumino- (zircono, titano-, etc.) silicates formed, for example, by sol-gel routes. However, these are generally amorphous compounds, and this article will be restricted to crystalline host matrices.

Compounds that crystallize in a layered arrangement have no permanent porosity, and the structures adapt in at least one dimension – that perpendicular to the stacking axis of the layers – on ion exchange or intercalation. Layer-structured crystals can be divided into those having neutral layers, which have no ion exchange properties and in which the driving force for any intercalation reaction is an electron transfer process, and those with either positively or negatively charged layers, which are anion and cation exchangers, respectively. The best-known anion exchangers are the layered double hydroxides $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[X^{m-}_{x/m}\cdot nH_2O]^{x-}$ and hydroxy double salts $M^{II}M'^{II}(OH)_3X$, where X is an exchangeable anion, such as OAc^-, Br^-, $CO_3{}^{2-}$, etc. In the first of these, charge imbalance in the parent brucite, $Mg(OH)_2$, crystal structure is induced by partial substitution of M^{II} by M^{III} and X occupies the interlayer region. The situation is different in the series based on the botallackite structure $Cu_2(OH)_3Br$, as the anion forms part of the coordination sphere of the metal atoms, and its replacement may involve a dissolution–reprecipitation mechanism. Layered silicates (e.g. smectite clays), layered niobate or titanate perovskite structures, layered silicic acids (magadiite, kenyaite, etc.), layered sulfates and phosphates are all known cation exchangers. These may be prepared directly in their hydrogen form, as is the case with α-metal(IV) hydrogen phosphates, or in a form containing an interlayer alkali metal ion, readily exchanged for the proton in acidic solutions. These are solid acids and may display, in addition to the catalytic properties already referred to above in the context of zeolite host matrices, high, water-assisted protonic conductivity. Indeed, ion exchange with inorganic layered matrices can be perceived in the more general framework of ion transfer/transport and ionic mobility.

This section would not be complete without mentioning two additional important classes of ion exchanging materials, which find their place quite naturally between those two extremes of three- and two-dimensionality described above. In one class a permanently porous structure is formed from a layered structure by pillaring, in which process some of the initial ion exchange capacity is retained, and in the other, a layered solid is formed from an initially three-dimensional framework by the clustering of structural defects induced by ion exchange. These two classes will be discussed in greater detail below.

Synthesis of Metastable Microporous Layered or Framework Materials

The classical approach to the synthesis of many solid state compounds is to mix individual elements or simple solid compounds together and fire them at elevated temperature. Here, the diffusion of atomic/ionic species through reactants and products controls product formation. Nonclassical routes to the preparation of inorganic solids, including the full range of solution chemistry, sol-gel chemistry, insertion and intercalation chemistry techniques of synthesis, have gained increasing importance because they offer alternative means by which both classical materials and novel compositions may be prepared. Of particular interest in the present context is the use of topochemical pathways whereby a solid prepared by high temperature ceramic methods is the precursor for a thermodynamically unstable but kinetically stable phase. This usually involves the extraction or insertion of a mobile species from/into a rigid framework, either by ion exchange or a redox process.

Often, the mobile species is an alkali metal ion. The material takes on industrial importance in the particular case of lithium, with the potential and actual use of lithium insertion compounds as electrodes in lithium batteries, in particular for portable electronic devices and for electric vehicles. For example, the spinel form of manganese dioxide known as λ-MnO_2 cannot be obtained directly by classical methods, nor is it stable at high temperatures, but it is prepared by extraction of lithium either chemically or electrochemically from its lithiated congener $LiMn_2O_4$. Generally, in order to maintain charge balance, this process occurs with oxidation of Mn^{III} in the mixed valence (Mn^{III}/Mn^{IV}) precursor to give λ-$Mn^{IV}O_2$. This oxidative extraction can provide cell voltages of *c.* 4 V. X-ray absorption spectroscopy (near-edge and fine structure) have provided much information on the changes in oxidation state and accompanying local structural modifications induced by the loss of the Jahn–Teller ion Mn^{III} and resulting increase in local symmetry. Lithium-rich spinel manganates $Li_{1+x}Mn_{2-x}O_4$, with $0 < x < 0.33$, are also known. In these materials lithium occupies octahedral sites left vacant by the lower manganese content and electrical neutrality is achieved by an increase of the average oxidation state from 3.5 in $LiMn_2O_4$ to 4 in $Li_{1.33}Mn_{1.67}O_4$. Oxidative removal is no longer possible, and ion exchange with protons occurs when lithium is removed chemically in acid solution. The octahedral sites vacated by manganese, and not occupied by lithium in the acid exchanged samples, result in lamellar-type lattice defects in the spinel structure in which weakly bound water could be trapped. There is no direct synthetic route to either protonated or nonprotonated λ-MnO_2.

Indeed, for obvious reasons, high temperature routes often preclude the formation of hydroxylated or hydrated inorganic compounds. Amongst others, protonated dicalcium triniobate $HCa_2Nb_3O_{10}$ and the trititanate $H_2Ti_3O_7$ are simply prepared in acid solution by ion exchange of potassium and lithium, respectively. The materials formed are solid acids, with important implications for eventual proton conductivity or catalytic activity; other modifications may be imposed depending on the dimensionality of the solid. Thus $HCa_2Nb_3O_{10}$ can be further derivatized by acid–base reaction with alkylamines, and by pillaring. These last aspects will be further developed below. The so-called γ-form of zirconium phosphate, γ-$ZrPO_4(H_2PO_4)\cdot 2H_2O$($\gamma$-ZrP), is metastable with respect to the α-form, α-$Zr(HPO_4)_2\cdot H_2O$, and protonated γ-ZrP can only be obtained via ion exchange in acid solution of sodium or ammonium ions in the corresponding precursor prepared at 80–180°C from zirconyl chloride, sodium or ammonium hydrogen phosphates, and phosphoric or hydrochloric acid.

Other possibilities are opened up when the topotactic step is followed by dehydroxylation–condensation. An interesting example is provided by a particular form of titanium dioxide that can be prepared from potassium tetratitanate, $K_2Ti_4O_9$. The latter is formed at 950°C, but is hygroscopic and sensitive to acid hydrolysis. In water, potassium ions are eliminated:

$$K_2Ti_4O_9 + (n + x)H_2O \rightarrow K_{2-x}(H_2O)_nTi_4O_{9-x}(OH)_x + x(OH)^- + xK^+$$

and, when $x = 2$, thermolysis at 500°C yields TiO_2(B), where the index B indicates the structural relationship to the bronze Na_xTiO_2 (Wadsley bronze). When $x = 1$, then the octatitanate is formed, $K_2Ti_8O_{17}$. The structure of this is identical to that of the potassium richer phase $K_3Ti_8O_{17}$ (Watts bronze), which can be prepared by a classical high temperature route. This is illustrated in **Figure 1**.

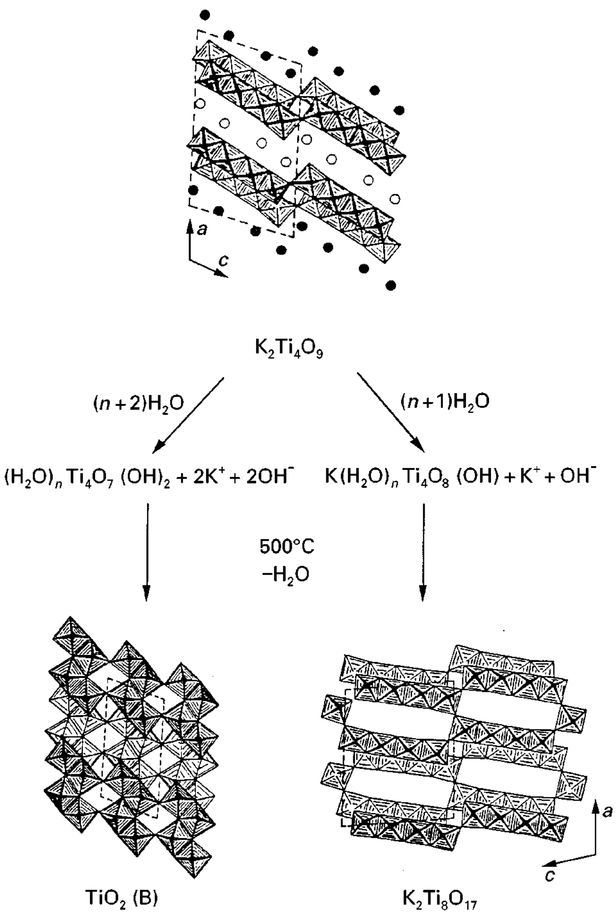


Figure 1 Soft chemical route from dipotassium tetratitanate to a form of titania [TiO_2(B)] and dipotassium octatitanate.

Rather than extraction, a starting compound can also be modified by further insertion of a mobile species. Thus, in addition to the removal of lithium from $LiMn_2O_4$ described above, lithium may be further reversibly inserted with reduction of Mn^{IV} to give $Li_2Mn_2O_4$. This intercalation can be performed electrochemically, at an average voltage of 3 V, or chemically, using butyllithium or lithium iodide. From a structural point of view, the local distortions around Jahn–Teller Mn^{III} ions in octahedral sites are no longer suppressed by the presence of non–Jahn–Teller Mn^{IV}, and the unit cell becomes increasingly tetragonally distorted due to cooperative elongation of the J–T $Mn^{3+}O_6$ octahedra along the *c*-axis of the crystal. Although the tetragonal structure is crystallographically different from the precursor cubic structure, they are related in that the linkage of edge-sharing MnO_6 octahedra in the three-dimensional $[Mn_2O_4]$ spinel sublattice is conserved.

Use of Ion Exchange and Intercalation for the Synthesis of Materials with New Compositions

The modifications of open-structured two- or three-dimensional hosts by ion exchange with functionalized organic (monomeric, polymeric), inorganic (simple ions, inorganic complexes, polynuclear ions) or organometallic species to give nanocomposite solids of new composition and tailored structure is an increasingly powerful route to materials displaying a range of enhanced or induced physical (mechanical, optical, electrical, magnetic, textural) or chemical (catalytic, molecular or chiral recognition) properties. Of these, perhaps most attention has been given over recent years in two areas, that of the insertion, or formation *in situ*, of polymers or extended aggregates in the interlayer or intrapore regions of inorganic hosts, and that of the synthesis of pillared layered solids.

Molecular Recognition

The separation of enantiomers on a preparative, rather than analytical, scale is an increasingly important objective, in particular for the pharmaceutical industry. Ion exchanging, microporous solids represent one route currently being explored for the separation of chiral molecules, either making use of a chiral inorganic solid or by modifying the host structure by ion exchange in a first stage such that it recognizes, and becomes specific for, the uptake of one enantiomer from a racemic solution. This is an exciting area of study that deserves to receive much attention in the future.

Intercalated Polymers and Extended Aggregates

During the 1990s considerable interest has focused on the association of ion exchanging host matrices and polymers (or extended aggregates), inspired from both fundamental and more applied viewpoints. As well as being considered to be model systems for interface studies, such constrained environments are expected to enforce a higher degree of polymer ordering, and be conducive to the isolation of polymer chains. Polymer–inorganic host nanocomposites can be discussed, *inter alia*, in relation to the nature of the property induced or enhanced. Currently, two important areas can be distinguished corresponding to materials displaying either mechanical or electrical (ionic, electronic) properties. For example, unprecedented mechanical properties of nylon–clay nanocomposites have been observed, involving a doubling of the tensile modulus and strength, and an increase of the heat distortion temperature by up to 100°C. On intercalation of polymer electrolytes, typically poly(ethylene oxide) (PEO), into a host structure, the oxyethylene units replace water in the coordination sphere of interlayer Li^+ or Na^+ ions and the normally soluble polymer is heterogenized and protected from chemical aggression. Thermal stability is improved, and the materials display good ionic conductivity over a broader temperature range than PEO–salt electrolytes. The association of host matrices with electroactive polyaniline, polypyrrole and organic metals such as tetrathiafulvalene provide an original source of electronically conducting materials and has inspired research directed at building devices from molecular assemblies. In addition, it can be predicted that in the future, matrices occluding chromophore aggregates will play a role in the field of second harmonic generation; however, as yet the number of examples of nanocomposite solids displaying nonlinear optical properties is limited.

Inorganic host structure–polymer (or aggregate) nanocomposites can also be discussed in relation to the synthetic method used to intercalate or form the polymer *in situ*. From a conceptual point of view the simplest, direct ion exchange, has been used to insert hydrophilic polymers such as PEO, poly(ethylene–imine) (PEI), poly(ethylene glycol) (PEG), poly(phosphazene), gelatin, lysozyme and protamine from solution into layered solids including montmorillonite, fluorohectorite, divanadium pentoxide, transition metal phosphorus trichalcogenides and zirconium phosphate. This strategy requires a compatible polymer–host solvent system. An alternative related method lies in the use of direct intercalation from polymer melts in which the solid polymer (polystyrene, polyamides, polyesters, polycarbonate) and the inorganic matrix are heated to above the softening point of the polymer. The hydrophobicity of the polymer and of the interlayer environment is a key experimental factor, and the latter can be modified prior to intercalation from the melt, e.g. by ion exchange of interlayer Na^+, etc., for surfactant ions. The intercalated organic–inorganic hybrids formed have an interlayer separation of 1–3 nm, but another, rarer, situation exists when the miscibility of the inorganic and organic systems is high, in which the layered host is exfoliated and individual layers are separated by 10–15 nm. Third, in the absence of any exchange reaction with the host solid, a phase-separated composite is formed, where packets of nonmodified host matrix are embedded in a polymer matrix (**Figure 2**).

Other synthetic routes make use of ion exchange with a monomer and *in situ* polymerization in the interlayer or intrapore region. Here, distinction can be made between the polymerization of assembled monomers and a redox intercalative polymerization. In the former, monomer species bearing reactive groups that might be, for example, acetylenic, nitrile, functionalized aromatic molecules or condensable moieties, are ion exchanged in a first stage into the inorganic host. In the case of a layered host structure, the charged surface leads to a particular orientation of the monomer units that may favour a given polymerization pathway in the subsequent polymerization

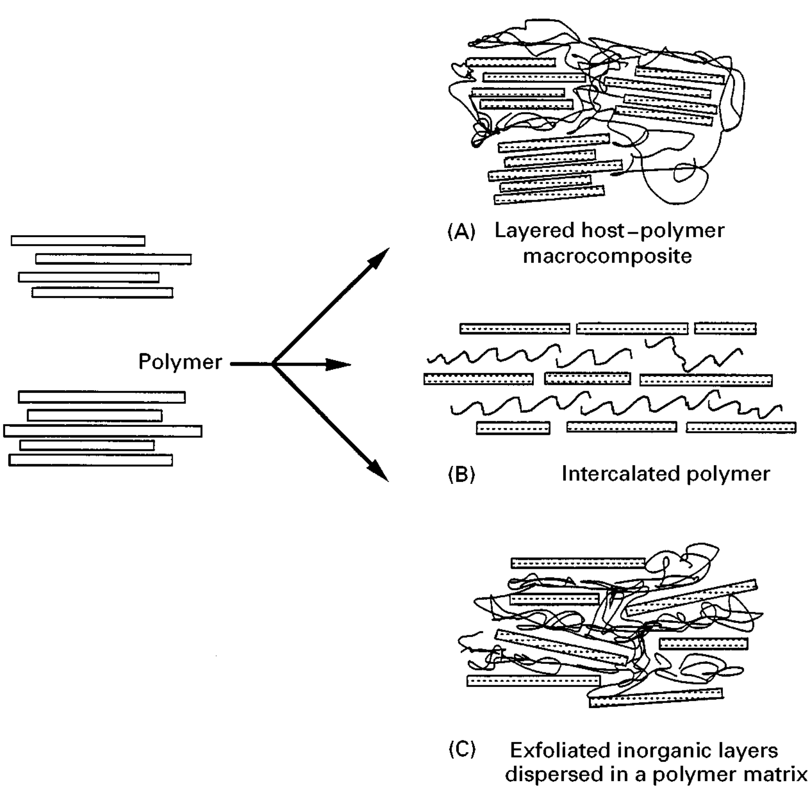


Figure 2 Schematic representation of the continuum in inorganic layered host structures and polymer arrangements between (A) phase-separated regime; (B) intercalated polymer; and (C) polymer dispersion of exfoliated inorganic layers.

step induced thermally, radiatively or chemically. Thus cation exchange of aminocaproic acid into montmorillonite or zirconium phosphate, or anion exchange from acrylic acid into layered double hydroxides, lead to nylon-6 and to polyacrylate, respectively, as the monomers are condensed and water is split off when the temperature is raised to *c.* 200°C. Propargylamine ($HC{\equiv}CCH_2NH_2$) and dipropargylamine $[HC{\equiv}CCH_2(NH)]_2$ readily intercalate with proton transfer into metal(IV) phosphates, and γ-radiation or thermal treatment under inert atmosphere produces polymers of polyacetylenic character. ^{13}C NMR is of particular utility, as a probe spectroscopic technique for the interlayer region, in following the loss of monomer and identifying the nature of the polymer formed. An interesting example is provided by ion exchange of *p*-xylylene-α-dimethylsulfoxonium for Li^+ or Na^+ in M_xMoO_3. On thermal treatment at 100–250°C, dimethylsulfide is eliminated and interlayer poly(*p*-phenylenevinylene) generated. Chemical oxidation (atmospheric oxygen, ammonium peroxide, etc.) has also been used to initiate the polymerization process, e.g. of anilinium in zeolite-Y, mordenite and ordered mesoporous aluminosilicate MCM-41, and of methyl methacrylate in montmorillonite.

The polymer intercalate may also serve as a precursor phase; a potentially important development lies in the use of clay–polymer intercalation nanocomposites as precursors for graphite films. Such template carbonization uses the inorganic matrix to orient the organic species as it evolves from the ion exchanged monomer to a polymer to a carbon. Destruction of the template and subsequent heat treatment leads to flexible graphite films.

Intercalative polymerization can occur when the matrix has electron transfer properties. These may be inherent to the host solid, as in FeOCl, V_2O_5, etc., or may be conferred on a redox-inactive matrix by ion exchange with appropriate transition metal ions. Thus following ion exchange of Cu^{2+} or Fe^{3+} into mordenite, zeolite-Y, montmorillonite, zirconium phosphate, ordered mesoporous aluminosilicate MCM-41, etc., electron donor molecules such as aniline (**Figure 3**) and pyrrole are oxidized, ion exchanged and undergo polymerization concomitantly, and the metal ion is reduced and, in some cases, eliminated as electrically neutral colloidal particles. Electroactive molecules such as tetrathiafulvalene (TTF) have also been assembled in γ-zirconium phosphate using this same approach.

TTF provides an example of an electron donor molecule that can only be inserted in an ion

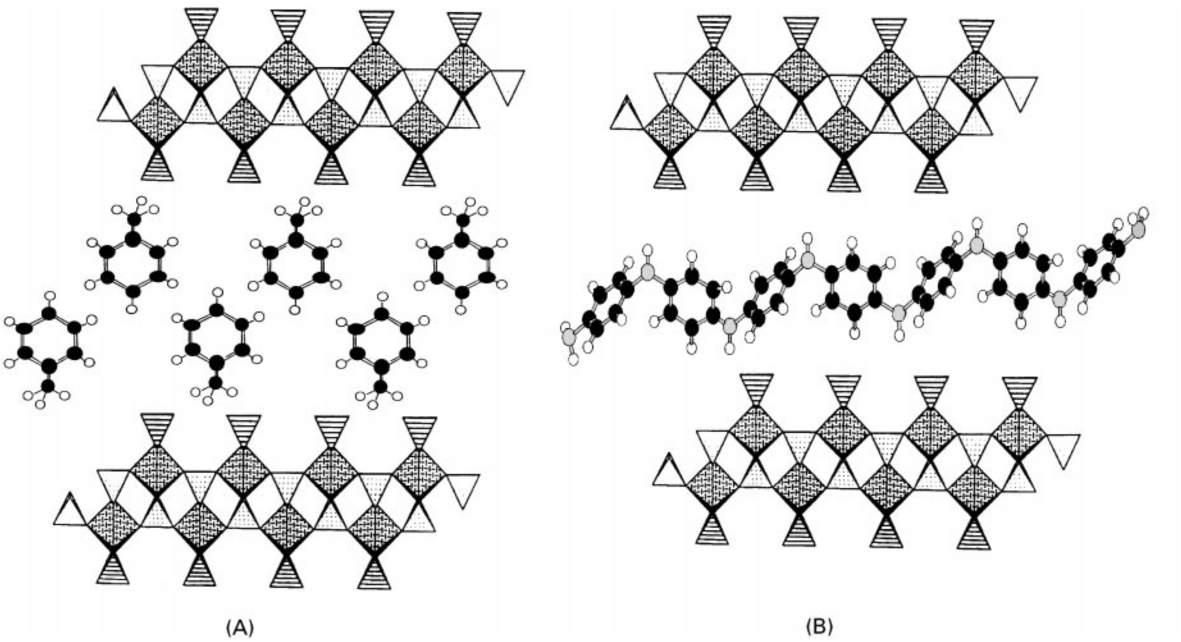


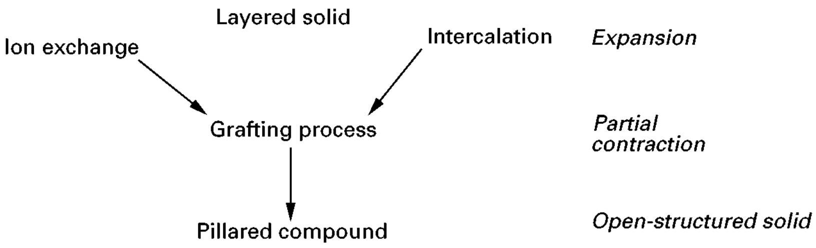
Figure 3 Schematic diagram showing layers of (A) γ-$ZrPO_4 \cdot HPO_4 \cdot$(anilinium), (B) γ-$ZrPO_4 \cdot HPO_4 \cdot$(PANI).

exchanging matrix if oxidized. Indeed, from the point of view of associated electrical properties, partial oxidation of TTF is required. These two conditions have been combined recently by oxidizing TTF with bromine to $TTF^{0.72+}$, which can then be ion exchanged with species used to pre-expand the interlayer region in host α- and γ-ZrP. The TTF units do not lie parallel to the plane of the phosphate layers and, although not a polymer system, they are nevertheless stacked into extended aggregates and provide the π-orbital overlap necessary for conduction.

Pillared Layered Solids

Reference was made above to the requirement by the petroleum industry during the 1970s for acid catalysts of pore size in the mesopore region, distinctly greater than that of the zeolites available at that time. Although templated routes to larger pore zeolites had not yet been successful, the modification of preformed layered solids by 'pillaring' was to give rise to a new area of chemistry and a new type of porous solid. The calculated surface area of a two-dimensional solid is high, $960\,m^2\,g^{-1}$ for example for α-zirconium phosphate, although nitrogen BET (Brunauer, Emmett, Teller) measurements indicate a surface area of *c.* $5\,m^2\,g^{-1}$ only. To render at least part of the surface area accessible, the layers must be permanently separated using inorganic spacers introduced by ion exchange or intercalation. To consolidate the structure and liberate interlayer regions occupied by organic moieties, hydroxyl groups or water, the expanded phase is then treated thermally or chemically (**Scheme 1** and **Figure 4**).

The presence of inorganic species acting as pillars and interacting strongly with the layers gives rise to thermally stable materials of high surface area (BET surface areas typically between 150 and $400\,m^2\,g^{-1}$) and pore volume accessible for adsorption and separation, catalysis and ion exchange. An important area



Scheme 1 Formation of a pillared compound from a layered solid.

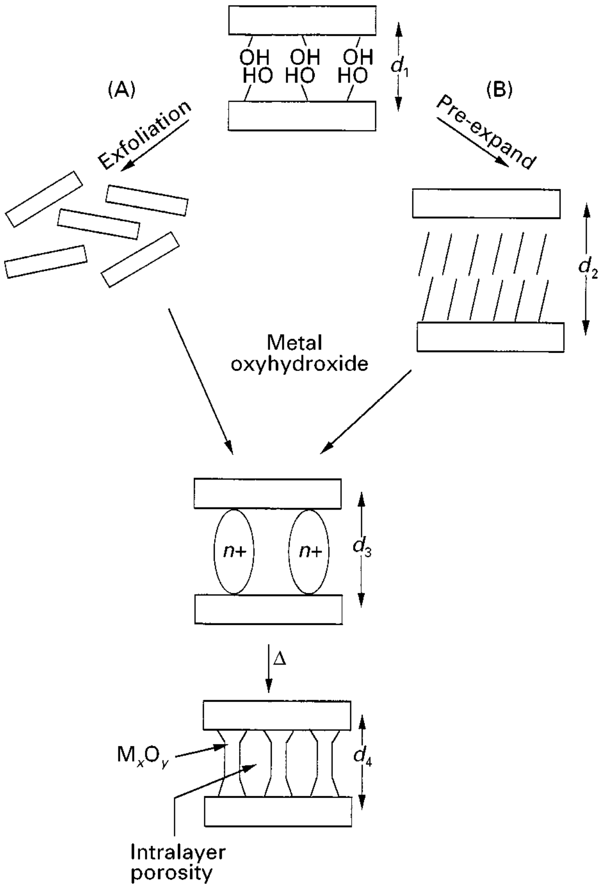


Figure 4 Synthesis of pillared layered structures by ion exchange and grafting from (A) swelling matrices and (B) host structures of high layer charge density.

represented by metal phosphonates is beyond the scope of this article by virtue of the synthetic routes to this class of pillared solid.

The extent of uptake of the pillar precursor species, a direct result of the ion exchange capacity of the host matrix, is a key parameter influencing the ultimate textural properties of the pillared solid, since it controls the lateral spacing of the pillars. Indeed, the synthesis of porous solids from higher layer charge density solids was only achieved some 15 years after the first results published on smectite clays. In addition, the layer charge density of smectite clays is sufficiently low that they swell spontaneously in water and the ion exchange of generally bulky, polynuclear inorganic ions still occurs readily. In contrast, for non-clay substrates of higher layer charge density a pre-expansion or exfoliation step is the general rule. This is summarized in **Table 1**.

A further requirement is that the pillaring species should be regularly arranged in the interlayer region, in order to generate a solid of narrow pore size distribution. While this regular distribution is achieved at the precursor stage by the registry between host and guest ions, sintering of the metal oxide particle on thermal treatment and degradation of the host structure itself both contribute to producing a broader – and frequently bimodal (spanning the micro- and small meso-pore range) – pore size distribution than is characteristic, say, of zeolites. Additional criteria for the matrix are therefore that it must be sufficiently rigid that it does not collapse in regions between the pillars on dehydration and that the layer charges must be uniformly distributed. In this respect, synthetic clays and non-clay substrates have received particular attention recently since, in addition, these provide the possibility of varying the layer charge density, e.g. by changing the Si/Al ratio or by partially replacing sites for ion exchange with nonexchangeable groups. Nevertheless, when the host matrix has small platelet diameter or when it undergoes an exfoliation stage in the synthesis, reassembly of the layers following ion exchange with the pillaring solution can lead to the situation where edge-to-face stacking predominates (‘house-of-cards’ arrangement), which has more developed mesoporosity (**Figure 5**).

Most of the two-dimensional matrices mentioned above have been used as a starting point for pillared

Table 1 Comparison of properties of smectite clays and nonswelling host lattices and consquences on the formation of porous, and not just cross-linked, layered solids

Smectite clays	*Non-clay substrates*
Low layer charge density	High layer charge density
Spontaneously swell in water	No spontaneous swelling in water; exfoliation (infrequent) under defined conditions not necessarily compatible with existence of polynuclear inorganic species
Pillaring by direct ion exchange with aqueous solution of polynuclear inorganic pillaring species	No direct intercalation → must pre-expand and then ion-exchange, e.g. butylamine/Al_{13}^{7+}
Inserted species are well spaced	Crowded interlayer

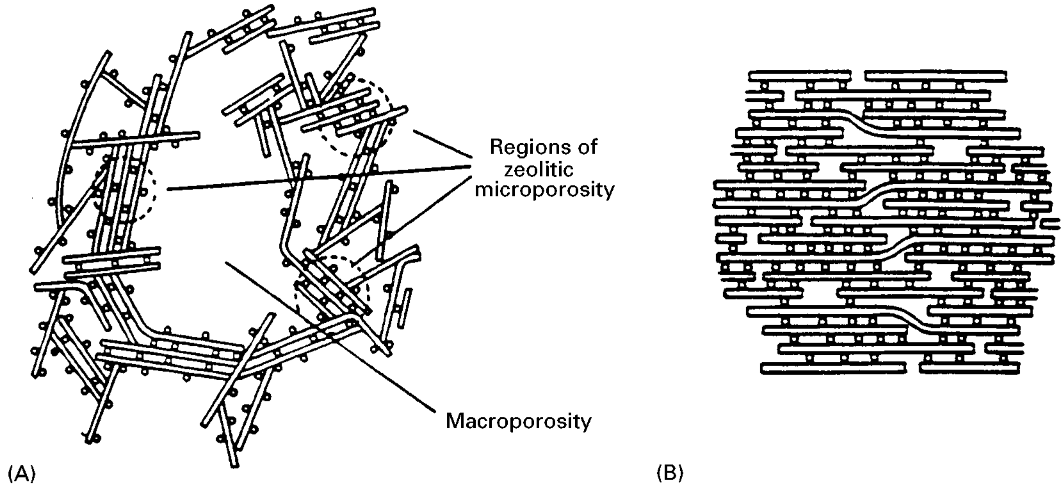


Figure 5 (A) House-of-cards arrangement of the layers of a pillared solid where flocculation after delamination has led to predominant edge-to-face stacking. (B) regular pillared solid with predominant edge-to-edge stacking morphology.

layered structures. A broad spectrum of pillaring species exists based on polynuclear metal hydroxo or oxo complex ions obtained by the hydrolysis of metal salts, such as the aluminium Keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, their gallium and iron anlogues, and heteronuclear combinations. These include aluminium Keggin ion modified by the addition of rare earth ions, $[Cr_3(OH)_4(H_2O)_9]^{5+}$, $[Zr(OH)_8(H_2O)]^{8+}$, metal chloride cluster ions $[M_6Cl_{12}]^{2+}$, M = Nb, Ta, organometallic oligomers, e.g. $[H_2N(CH_2)_3Si_{1.5}]_8$, silicon tris(acetylacetonate), positively charged colloidal particles of titania or silica and, in the case of cationic layers, polyoxometallate ions. The variety of pillaring ions and layered hosts available provides enormous flexibility for creating numerous chemical combinations. This opprotunity arises precisely because the route to pillared solids in via ion exchange, which allows variety in framework chemical and atom concentrations not yet attainable in other porous solids, in particular in the family of M41S mesoporous silicates. However, in large part because of the low degree of crystallinity of pillared layered solids, little direct structural information is available using X-ray diffraction and the relationship between structure and properties remains to be explored. Furthermore, in the case of complex polynuclear ions, the dominant species in solution may not be the same as that stabilized in the interlayer region. Local structural information around the metal atoms of the layer and the pillaring species can be obtained using magic angle spinning nuclear magnetic resonance (MAS-NMR) and X-ray absorption spectroscopies.

Some of the ion exchange capacity used in assembling the pillaring species is regenerated during the calcination stage. This retained ion exchange capacity is important, since it provides the opportunity for a Brønsted acidity additional to the Lewis acidity generally conferred by the inorganic oxide particles forming the pillars. It can be exploited to further modify the chemical composition of the solids, and so tailor them for a particular application, in particular in catalysis. In addition, pillared layered solids can be seen as a new type of confining matrix for the organization and quantization of polymers and metal clusters or sulfides, and pillared materials derivatized in this way have been termed nano/nanocomposites.

Finally, mention should be made of a new development in a related area making use of sol-gel and intercalation chemistry, and surfactant-directed synthesis. Porous clay heterostructures are formed by reacting cationic surfactant exchanged fluorohectorite, vermiculite or rectorite with neutral amine/tetraethoxysilane to give a structure in which silica-lined cavities impact permanent porosity to the interlayer region.

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.

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THE NUCLEAR INDUSTRY: ION EXCHANGE

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Introduction

Ion exchange is used in nearly all phases of the nuclear fuel cycle beginning in the early stages of uranium ore treatment where ion exchange is one of the major processes used: uranium is removed from ore leach liquors using anion exchange resins.

At nuclear power plants, ordinary organic ion exchange resins are mainly used for the removal of ionic and particulate contaminants from the primary circuit, condensate and fuel storage pond waters. Ion exchange resins are also used for the solidification of low- and medium-activity nuclear waste solutions. The number of applications of selective inorganic ion exchangers in the separation of radionuclides from nuclear waste solutions has been increasing since the mid-1980s.

In nuclear fuel reprocessing plants, the main separation method is solvent extraction. Ion exchange is, however, used for the solidification of low- and medium-activity waste solutions, as well as for the partitioning of radioactive elements for further use.

This article reviews all the most important areas of the utilization of ion exchangers in the nuclear power industry. Special attention is paid to ion exchange processes, which involve radionuclide removal functions, and to new developments in selective ion exchange materials.

Ion Exchange Materials Used in the Nuclear Industry

Nuclear Grade Ion Exchange Resins

Organic ion exchangers used at nuclear power plants are based on conventional poly(styrene–divinylbenzene) resins with sulfonic acid ($-SO_3^-$) and quaternary ammonium ($-N(CH_3)_3^+$) functional groups for cations and anions, respectively. Nuclear grade resins,