Intercalation Systems as Nanostructured Functional Materials

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The host/guest chemistry of intercalation systems provides a highly variable potential for synthesis strategies aiming at the controlled preparation of complex organized structures in the nanoscale regime at low temperatures. Specific aspects of actual progress are considered concerning the synthesis and functional modification of rigid-pore and flexible pore host lattices, intracrystalline processes, colloid systems, host/guest interaction, and electron-transfer processes.

Introduction

The term "nano" refers to a length scale based category that has been used in recent years to characterize a large variety of materials and associated phenomena, e.g., nanophase materials, nanophysics, nanochemistry, nanoporous solids, etc. With respect to physics the interest is largely concentrated on specific functional properties, e.g., quantum confined systems, while chemists are focusing strongly on particular aspects of synthesis and reactivity. There are several synthesis strategies to arrive at nanostructural materials. One line is to use the aggregation of small particles (atoms, molecules) for the preparation of nanoscale systems (e.g., metal clusters, supramolecular compounds by selforganization principles, etc.). The inverse line is to start from three-dimensional systems and to use microstructuring techniques to obtain objects with nanosize dimensions, e.g., quantum wires, quantum dots. Another approach is the sequential physical, chemical, or electrochemical deposition of homogeneous or heterogeneous multilayer materials with a single-layer thickness in the nanometer range.

A particular category in terms of materials definition are those phases which are characterized by intrinsic *open-pore systems* with nanoscale pore dimensions. Among these the so-called *intercalation compounds* represent a well-defined class of compounds characterized by their *functional* properties. They can be described by a crystalline rigid host matrix with a regular percolation pore system of nanometer dimensions that is able to take up reversibly atomic or molecular guest species with appropriate dimensions into the structure by bulk diffusion at ambient temperature. In terms of kinetics this topotactic process requires low activation energy for long-range diffusion pathways; the materials obtained by this process are usually metastable and cannot be prepared by conventional thermal synthesis techniques. With respect to pore architecture and pore properties we can differentiate between two classes of intercalation systems. The first class is characterized by *rigid pores* with constant pore volume, e.g., parallel isolated lattice channels or interconnected channel networks. The uptake of guest species is limited by the minimal channel cross section which results in guest shape selective intercalation behavior ("molecular sieves"). The second class is represented by low-dimensional host lattices, i.e., layer and chain type structures. They provide "*flexible pores*", since the pore dimensions can adapt to the dimensions of the guest species; in layered systems regular basal spacings up to 50 Å have been observed. With respect to the electronic properties of the host lattice we can again define two qualitatively different types. For insulator host lattices such as zeolites, layered aluminosilicates, or metal phosphates the basic physical properties of the lattice matrix are not affected by intercalation of deintercalation. Their behavior is characterized predominantly by acid/base and exchange properties. Host lattices with electronic conductivity (semiconductors, metals) may undergo redox reactions by electron/ion transfer processes resulting in a strong perturbation of the physical properties of the host matrix. General models and characteristics of intercalation systems have been treated in several reviews.[1−11]

In terms of nanostructural aspects intercalation chemistry provides a most versatile potential for synthesis strategies aiming at complex organized structures via the combination of the large variety of host lattices available with different structural dimensionality, the broad selection of guest species, and the clear underlying basic concepts for reaction mechanisms which allow a rational synthesis approach. We will consider in the following paragraphs several specific actual aspects of development in this domain of solid-state chemistry concerning new host lattices and guest compounds, complex systems, intracrystalline reactions, interaction host/guest, and electronic properties.

Rigid-Pore Systems

Although lattice architecture and chemical composition are highly variable for framework host compounds providing rigid-pore systems for the reversible topotactic insertion of guest species, we observe an interesting distinction with respect to pore dimensions that is correlated with synthesis conditions and electronic properties. *Large-pore* systems are characterized (i) by low electronic conductivity (insulators or wide-gap

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semiconductors) and (ii) by low-temperature synthesis conditions, e.g., zeolite type phases with main-group matrix cations (Al, Si, P, etc.) with lower coordination numbers. Framework hosts exhibiting high electronic conductivity, e.g., metallic compounds such as Chevrel phases $A_xMo_6X_8$ and chalcogen spinels $CuCr_2X_4$ with interconnected channels or Nb_3S_4 and $Tl_xV_6S_8$ with isolated parallel lattice channels provide diffusion pathways with rather narrow dimensions accessible only by atomic guest species and are obtained usually by synthesis at high temperatures.[11] This difference originates from the fact that a dense host matrix with higher connectivity of constituent elements and high coordination numbers of matrix ions as well as redox-active transition metals are required for high electronic conductivity.

The current trend in the *synthesis of new host systems* is clearly the search for wide-pore systems based primarily on the isolation of *kinetic* products in low-temperature windows from hydrothermal fluid phases. A most successful route is the use of "templates" as structure-controlling constituents. We can distinguish here two lines of approach: (i) the application of large molecular template units and (ii) the use of self-assembled supramolecular aggregates as template base. The matrix of molecular sieves obtained in this way are mainly aluminosilicates and related phases with replacement of Al/Si by Be, B, Ga, Ge, Zn, and P. Although the template process is not completely understood, it appears that the space filling effect is a major point in the reaction mechanism via structure-directing phenomena depending on size, morphology, and charge of the template agent avoiding kinetically the formation of more dense structures favored by thermodynamics. The first line represents a synthesis way which has been applied earlier already; recently, however, it was found possible to prepare wide-pore materials with pore sizes larger than those of conventional molecular sieves. The template ions used are aliphatic or cyclic quaternary to primary amines, e.g., the $C_{18}H_{36}N^+$ which is specific for the synthesis of the zeolite ZSM-18;[12] conventional systems with well-defined crystalline structures are in the range of 3−13 Å for pore width. Particularly large pore sizes obtained so far with this technique were observed for the gallophosphate "cloverite" with cage diameters of 30 Å and a critical pore size of 13 Å and JDF-20 with a pore opening of ca. 14 Å.[13,27] Large-pore zeolite type structures have also been observed for molybdenum and vanadium phosphates containing transition metal ions with coordination numbers higher than 4 (Figure 1).[14−17]

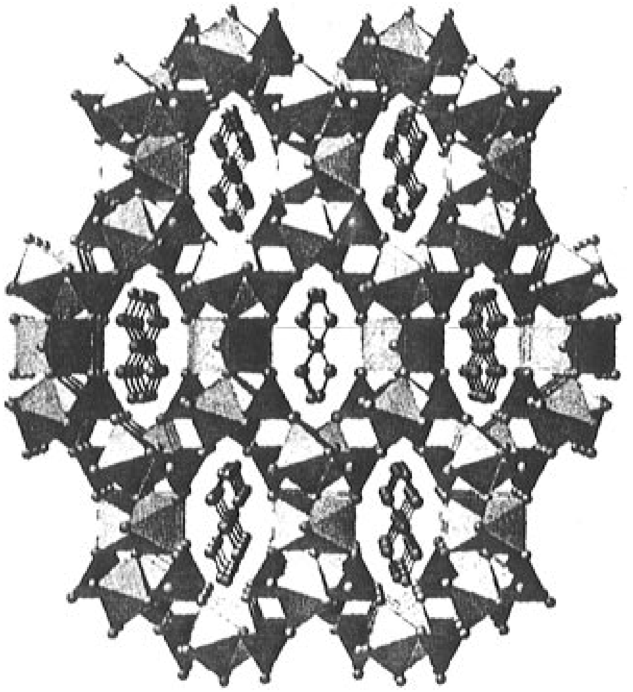

Figure 1. Structure scheme of an open-framework vanadium phosphate; channels filled with propane diammonium cations.[17a]

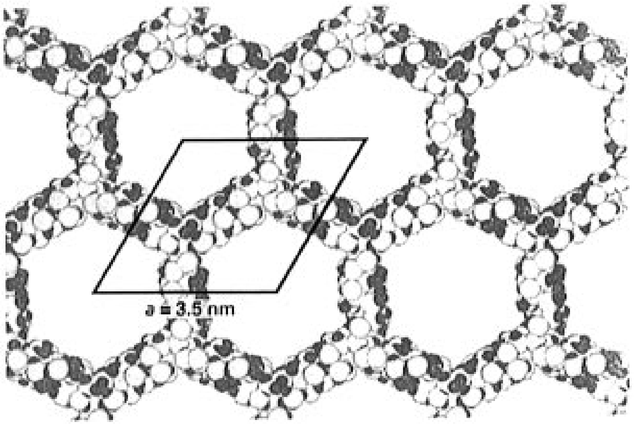

Figure 2. Structure scheme of a MCM-41 type phase with hexagonal pores and a pore width of 35 Å.[18c]

A major step ahead on the way to open pore framework structures is the second line of approach first used in the recent synthesis of MCM-41 type zeolites which gives access to the tailoring of mesoporous systems with adjustable pore widths in the range of 16−100 Å (Figure 2).[18] The concept concerns the use of a selfassembled molecular array template instead of isolated molecular units. The basic units are long chain quaternary *n*-alkylammonium ions of the type $n\text{-}C_nH_{2n+1}(CH_3)_3N^+$ which are known to form columnar micelles in aqueous solution by aggregation with paraffin type structural order. By cooperative formation of organic/inorganic interfaces with silicate oligomers in solution mesopore systems are formed with defined pore sizes and hexagonal cross section. The pores can be adjusted within the limit of 16−100 Å with a high degree of long-range order; the silicate matrix exhibits high thermal and hydrolytic stability but no long-range order. A model for the processes taking place in the course of the synthesis has been proposed that includes (i) the multidentate binding of silicate oligomers to the cationic surfactant, (ii) the preferential polymerization of silicate oligomers at the interface region, and (iii) a charge density matching between the micelle interface and the silicate phase (Figure 3).[19] Similar approaches with the use of neutral and nonionic surfactants have been reported.[20,21] The potential of the concept was demonstrated recently by the controlled preparation of mesostructural transition metal oxides (W/O, Te/O, Pb/O, etc.) via an interface-controlled condensation process using cationic as well as anionic surfactants.[22,23] Mesoporous vanadium oxide has been prepared similarly from ethanol solutions of cetyltrimethylammonium vanadate.[24] The possibility of an extension of template-based synthesis of mesostructured solids from oxide matrix materials to chalcogenide frameworks was dem-

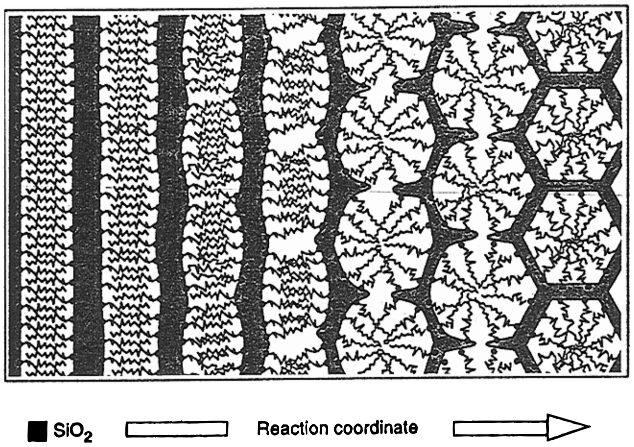

Figure 3. Scheme of the mechanism proposed for the transformation of a surfactant–silicate system to the hexagonal mesophase.[19]

onstrated by the synthesis of tin, germanium, and antimony sulfides; the structure of $Sn_3S_7[N(CH_3)_4]_2{\cdot}H_2O$ has been solved. It consists of a framework with the composition $[Sn_3S_7]^{2-}$ with exchangeable quaternary ammonium ions on the cavity sites.[25]

The template-based synthesis of porous structures is presently in a phase of rapid development and appears to provide more interesting results in the next future. The concepts for the formation mechanism are a reasonable base for controlled synthesis strategies. A further efficient way for the preparation of framework open-pore systems is the transformation of layered materials by irreversible chemical reactions into three-dimensional systems; we will discuss this aspect later on along with layered phases.

Intracrystalline Chemistry of Framework Hosts

In terms of application zeolite type porous framework systems are of considerable importance as ion exchangers, as sorbents for separation and purification of gases and as acid catalysts for mineral oil cracking, shape-selective and asymmetric catalysis, and related processes;[26–28] the Brönsted activity of the interior surface is a significant property for most applications in catalysis.[29,30] Zeolite thin-film nanostructures with a molecular sieve function tunable via ion exchange can be used as sensors when assembled on a piezoelectric quartz crystal balance.[31]

In recent years an increasing trend can be observed to profit from the well-defined pore system of zeolite type materials as constrained space matrix for the construction of supramolecular systems, molecular recognition, the inclusion of chromophores and semiconductor or metal cluster aggregates to achieve specific optical and electronic properties as well as for intracrystalline chemical reactions concerning polymerization, redox behavior, and enzyme models.[32,33] The guest species range from small molecules, clusters of extended solids, e.g., CdS up to large molecular species such as fullerene C_{60} and polymeric units synthesized via in situ processes.[34] The location, concentration and spatial distribution of guests is affected by the topology and by the chemical nature and reactivity of the internal host surface which can be used for the functionalization of the host matrix.

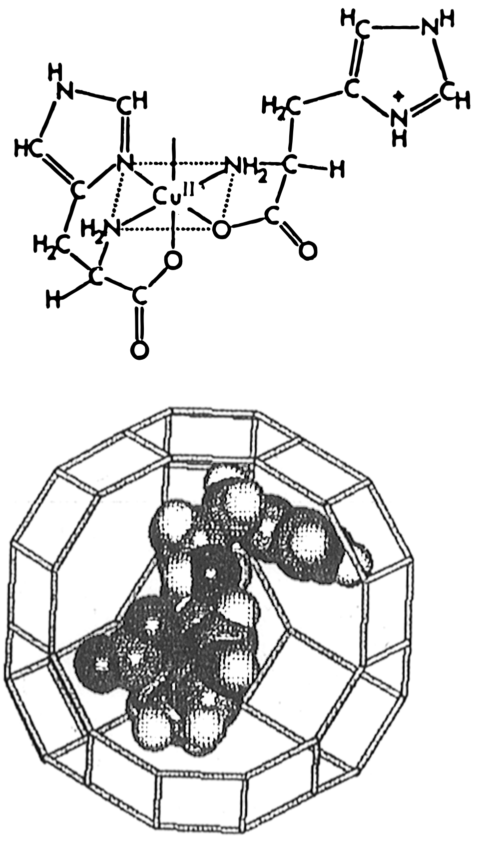

Figure 4. Copper/histidine complex $[Cu(His)_2]^+$ enclosed in a supercage of zeolite Y.[38]

Interesting recent examples for the stabilization of unusual species in molecular sieves are the formation of Ni(I) species in MCM-41 via hydrogen reduction or by radiation[35] and the characterization of substituted allyl cations within monodirectional acid zeolites, the first proof of the generally accepted model that carbenium-like species are intermediates in the conversion of hydrocarbons by zeolites.[36]

Room-temperature reversible binding of O_2 has been achieved by in situ synthesis of trapped cobalt cyanide ions inside zeolite Y;[37] similarly, immobilized copper histidine complexes in zeolite Y have been shown to be useful as model systems for natural copper enzymes (Figure 4).[38] The decomposition of tungsten hexacarbonyl in faujasite type zeolites by photooxidation results in the formation of tungsten oxide clusters WO_{3-x} which exhibit facile reduction and oxidation behavior and whose properties can be modified by the type of exchangeable charge-balancing cations.[33,39] The use of zeolites as templating agents for self-assembled systems able to undergo light-induced electron transfer has been demonstrated. It is based on acceptor molecules incorporated in the zeolite voids with donor molecules anchored at the external surface of the crystallites. Appropriately designed composites of this kind can drive redox reactions and may serve as models for natural photosynthesis processes.[40]

A large variety of organic guest compounds and dye molecules have been inserted into porous hosts with the intention to obtain specific optical properties in particular nonlinear behavior.[32,33] The recent demonstration that molecular sieve/chromophore composites can be aligned in electric fields provides the opportunity to line up collectively hyperpolarizable molecules (e.g.,

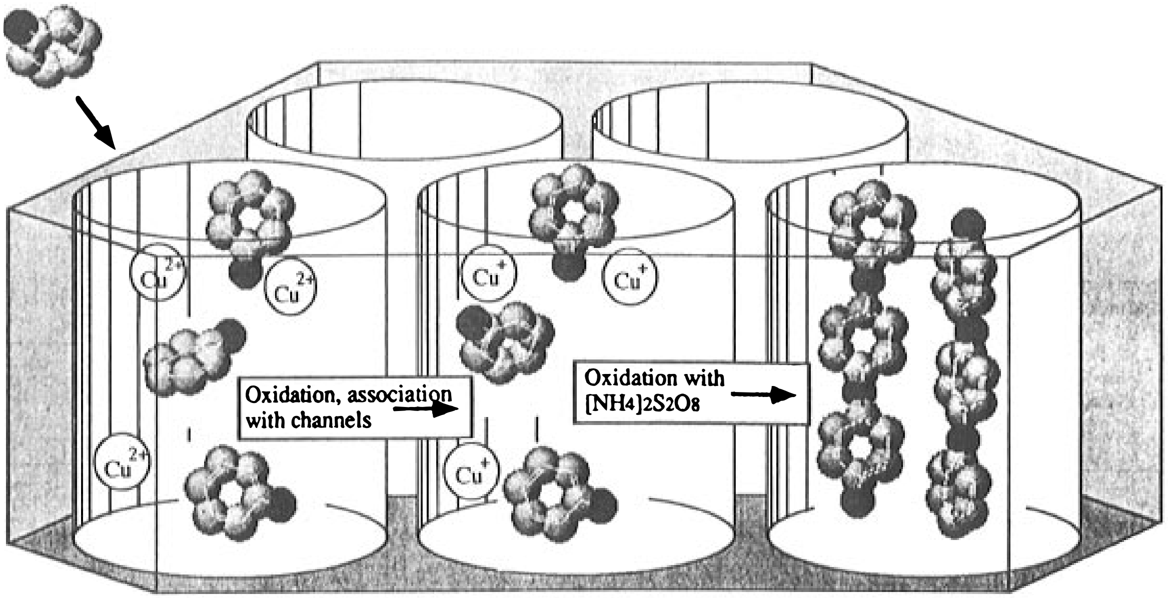

Figure 5. Scheme of encapsulation of polyaniline in MCM type channels.[45]

p-nitroaniline) in molecular sieve crystallites and to tune the materials optical properties (second hormonic generations).[41,42]

A most interesting type of intracrystalline reactions is the insertion of monomer molecules with subsequent controlled internal transformation into oligomer and polymer products. Conducting polymers such as polyaniline, polythiophene, polypyrrole, and polyacrylonitrile have been synthesized in zeolites.[43] Linear graphite-like structures can be obtained by a subsequent pyrolysis step with intercalated polyacrylonitrile.[44] The use of large-pore materials of the MCM-41 type with 30 Å channel diameter was shown to permit the encapsulation of parallel polyaniline chains; the resulting filament chains exhibit microwave conductivity (Figure 5).[45]

The loading of acid zeolites with transition-metal nanoclusters has been studied intensively as a consequence of the importance of these systems as bifunctional catalysts.[46] Investigations on Pt-, Pd-, and Rh-charged zeolites showed that the so-called "electron deficiency" of the metal clusters is related to the proton concentration of the zeolite.[47] Recent spectroscopic results suggest now the interesting existence of metal proton adducts.[48,49] In these complexes the positive charge of the proton is shared with the metal cluster; in zeolites with high proton concentration metal clusters may be limited to more than one proton in the same cage leading to species of the type $(M_n{-}H_x)^{x+}$.[49,50] The formation of "alloy clusters" in bimetallic zeolite catalysts can be controlled by reoxidation of one metal component by zeolite protons at higher temperatures.

Research continues on alkali-metal clusters $M_n^{(n-x)+}$ (Na_4^{3+}, Na_6^{5+}, K_4^{3+}, Rb_6^{4+}, etc.) in zeolite matrixes which can be prepared, e.g., by treatment of the alkali-exchanged zeolites with the appropriate alkali-metal vapor or with solutions of alkali metals in aprotic solvents.[51] They are of interest as electron acceptors toward a variety of substrates. The effects of the zeolite Si/Al ratio and of electron-scavenging transition metal ions has been investigated recently.[52] A single-crystal study on sodium zeolite X confirmed that the Na_5^{4+} clusters found in the sodalite cavities represent centered tetrahedra with the full site symmetry T_d.[53] In zeolite A Na_3^{2+} clusters were found to be located on the cage site.[54] Combined neutron diffraction and ESR studies on K zeolite L suggest the possibility to achieve charge transport along the channels in these compounds via quantum wire type connections.[55] Investigations on potassium zeolite A saturated with potassium metal showed the existence of a zeolite-directed potassium superlattice with ca. 5 valence electrons for 17 cations. A spontaneous segregation into electron-rich and predominantly cation-rich zones is interpreted as an incipient insulator/metal transition that may be electronically or structurally driven.[56] Single-crystal X-ray structure studies on reduced cesium and rubidium zeolites yield detailed information now on the location of the heavy cation species in the Si/Al matrix.[57]

The chemistry of silver clusters in zeolites has been reviewed recently;[58] investigations on sodalite type narrow pore zeolites showed that silver halogeno sodalites can be used to synthesize phases with organized arrays of $(Ag_4X)^{3+}$ silver/halogen clusters.[59,60] The optical properties of these compounds are of interest for photocatalytic splitting of water and light-write/light-erase materials. Silver zeolite modified electrodes may be applied in electrocatalysis and for chemical sensors.[61]

The silver/halogen cluster compounds mentioned above represent the link to a different approach, i.e., the aim to synthesize organized semiconductor clusters with nanometer size inside the pores of molecular sieves. Quantum size effects and electronic and optical properties dominate the interest in this class of materials. Extensive investigations have been devoted to the formation of cadmium chalcogenide clusters in wide-pore zeolites of the faujasite type.[62,63] The traditional synthesis by using Cd-exchanged zeolites and subsequent H_2S treatment has been extended by a stepwise synthesis via the MOCVD technique, i.e., the deposition of metal chalcogenides inside the zeolite pores by reaction with metal organic precursors.[64] Among the cluster types identified are $(Cd_6S_4)^{4+}$, $(Cd_6Se_4)^{4+}$, $(Zn_6S_4)^{4+}$, and $(Zn_6Se_4)^{4+}$.[65] Mixed ZnSe/GaP semiconductor species have been synthesized in a sodalite oxoborate framework.[66]

Flexible-Pore Systems

In contrast with the framework hosts discussed above, intercalation systems based on host lattices with lower dimensionality are characterized by intracrystalline voids on the nanometer scale for the uptake of guest species which are variable with respect to volume and adapt to the size and morphology of the guests. The most important group in terms of chemical reactivity and application are layered compounds,[7,8,11] while few studies have been devoted to crystalline one-dimensional and zero-dimensional systems under these aspects.[8]

Layered compounds provide a wide variety in terms of composition ranging from graphite—the only element host lattice known[67]—over metal oxides, phosphates, oxyhalides, halides, and chalcogenides. They can be classified by electronic conductivity. Layered materials with insulator or wide-gap semiconductor properties are of commercial importance with respect to the application as heterogeneous catalysts. Layered phases with appropriate band structure and electronic conductivity exhibit redox properties, i.e., the physical properties of the guest matrix can be modified by the intercalation process, when the latter is associated with electron/ion transfer reactions.[4,6] They are of interest as electrode materials for batteries, as electrochromic systems, sensor materials etc.[68] An important consequence of the adaptive behavior of layered systems is the large variety of guest species that can be intercalated ranging from protons and metal atoms up to large molecular species and polymers; the interlayer space height may range up to ca. 50 Å. The layer thickness itself varies from ca. 5 to 22 Å in perovskite type layered oxides.[69] The properties of these systems are obviously particularly favorable to the approach of supramolecular synthesis.

Layered host lattices may undergo specific changes upon intercalation by rearrangement of the two-dimensional matrix elements which are not found for framework systems.[11] These concern reversible stacking transition of the layer units relative to each other (depending upon guest type, guest concentration, layer excess charge density) and staging phenomena, i.e., modulated periodic sequences of intercalated and vacant interlayer spaces for phases with low guest concentrations. Depending upon the equilibrium conditions mono- and multilayers of guest molecules can be observed. Redox processes can be associated with a change of host matrix metal atom positions; acid/base reactions may lead to irreversible chemical modifications of the layer surface.

The interlayer chemistry of two-dimensional host lattices has become a broad field in various terms. Clay minerals are of interest in industrial catalytic processes as well as for laboratory-scale reactions in organic chemistry.[70,71] Clay type aluminosilicates intercalated with long-chain quaternary alkylammonium ions are potent catalysts for three-phase reactions.[72] A theoretical approach has been made for the understanding of two-dimensional molecular organization (chiral recognition) of $[Ru(bipyridine)_3]^{2+}$ ions confined between clay mineral layers by lattice minimization techniques.[73] The presence of stable organic radicals in the interlayer space of low charge density clays has been shown.[74] In the large field of metal phosphates, arsenates, and vanadates the hydrothermal synthesis of new host lattices is in rapid progress.[75] Shape-selective intercalation reactions, chiral molecular recognition, and preparative-scale separation of enantiomers has been demonstrated for layered metal phosphate and phosphonate host lattices.[76] A novel host synthesis approach is the use of self-assembly and Langmuir–Blodgett techniques for the controlled preparation of multilayers of organic metal phosphates and phosphonates including the construction of acentric multilayered phases and self-assembling electron-transport chains.[77–79] The use of layered zirconium phosphates and phosphonates as potentiometric and amperometric gas sensors—based on protonic conduction—has been demonstrated.[80] Secondary low-temperature modification of lamellar iron oxychloride FeOCl presents a new route to the preparation of layered iron phosphates.[81]

The few examples given may provide an impression on the rapid growth of interest in layered systems in recent years, in particular with respect to the synthesis of combined inorganic/organic layered systems with specific properties. In the following we will consider some selected actual developments and aspects of the chemistry of layered materials.

Intercalation of Polymers in Layered Systems

Considerable interest has focused in recent years upon the synthesis of inorganic/organic multilayer composites by insertion of macromolecules into layered host lattices. The constrained environment is expected to lead to a higher degree of polymer ordering and to useful optical and mechanical properties. Intercalation of conducting polymers—which themselves exhibit a most interesting intercalation chemistry[82]—may confer redox properties to insulator host lattices or result in redox competitive host/guest systems in the case of host lattices with electronic conductivity with a potential for application, e.g., as reversible battery electrodes.

There are several principal synthesis strategies:

(i) The intercalation of monomer molecules with subsequent chemical, thermal, or photoinduced in situ polymerization as a two-step process; this approach is possible when suitable monomers are available.

(ii) The direct intercalation of extended polymer chains into the host lattice; a disadvantage are slow kinetics for the transport of macromolecules in the interlayer space.

(iii) The transformation of the host lattice with counterions of high solvation energy into a colloid system in appropriate solvents by delamination, the addition of the polymer and subsequent reprecipitation of one-dimensionally disordered intercalates; we will discuss this point later on together with colloid systems.

Extended studies have been performed with iron oxychloride, metal phosphates, layered silicates, and transition-metal dichalcogenides. Examples of polymers that have been inserted into layered host lattices are polyaniline, polypyrrole, polyfuran, polycaprolactane, and poly(ethylene oxide).

In situ intercalation of monomers with subsequent oxidative polymerization can be achieved by taking layered host materials with high oxidation potential or by using molecular oxygen as the electron acceptor in the presence of redox active host ions acting as electron transfer catalysts (e.g., Fe^{3+}, Cu^{2+}); this process has been termed “redox-intercalative polymerization”.[83] Iron oxychloride (FeOCl) has been shown to be a suitable host lattice for the oxidative polymerization of aniline inserted from aprotic organic solvents to yield $(aniline)_{0.28}FeOCl$.[84] It was possible to obtain single crystals of this phase with reasonable quality. X-ray diffraction studies lead to a model that involves emeraldine type polymer units stacked side by side in the interlayer space with the axes of the zigzag chains running along the [101] direction of the host crystal and hydrogen bonding of the NH groups to chlorine atoms of the host lattice layers. The polymer chains are commensurate with the FeOCl lattice;[85] molecular weight studies after removal of the host layers by dissolution in aqueous acid yielded a value of $M_w = 6100$ with a narrow chain length distribution. Mössbauer studies suggest a mixed valence state with a ratio $Fe^{2+}/Fe^{3+} \sim 1:9$. The polymer intercalate behaves as a p-type semiconductor, the conductivity measured on single crystals is 1.5×10^{-2} S/cm. Upon oxidation of the material in air for extended time a mixture of polyaniline and β-FeOOH is obtained. The formation of protonated emeraldine/MoO_3 by intercalation of aniline into molybdenum(VI) oxide with subsequent oxidation by $(NH_4)_2S_2O_8$ has been reported.[86]

Oxidative polymerization of aniline, pyrrole, and thiophene monomers intercalated in layered aluminosilicates by molecular oxygen yield highly oriented multilayers host/guest. The reactions proceed by the catalytic action of Cu^{2+} cations which had been preinserted into the pristine host lattice via ion exchange.[87-89]

The postintercalative polymerization of aniline and of aniline derivatives in the layered metal phosphates $Ti(HOPO_3)_2 \cdot H_2O$, $Zr(HOPO_3)_2 \cdot H_2O$, and $HUO_2PO_4 \cdot (H_2O)_4$ has been reported; the polymerization of the inserted monomer molecules was achieved by heating to 130 °C in air. The compounds obtained turned out to be insulators.[90] Formation of polyaniline intercalation compounds from monomer precursors have also been obtained from layered zirconium copper hydrogen phosphates.[91] An example for the direct intercalation of a polymer is the formation of poly(ethylene oxide) in mica type sheet silicates by reaction of the polymer melt with Na^+ or alkylammonium exchanged host lattices.[92]

Colloid Systems

One particular property of low-dimensional host lattices is their ability to disintegrate into their nanoscale building blocks under appropriate reaction conditions. Among the oldest examples for this behavior are smectite clays with negatively charged layers and hydrated interlayer cations; complete delamination (exfoliation) to colloid suspensions is achieved, e.g., with counterions of higher hydration energy in electrolyte-free aqueous suspension. The colloid and rheological properties of these clay materials are of importance, e.g., in soil chemistry and as drilling fluid components in mineral oil winning. In recent years a series of other layered materials have been found which are similarly able to form colloid solutions provided the particle size is small and the layer charge density low, e.g., colloid vanadium oxide and reduced layered dichalcogenides such as MoS_2 or TaS_2. An interesting aspect of colloid formation is the possibility to insert large molecular weight species and polymers with reasonable kinetics by reaction of the guest species with the colloid solution and subsequent precipitation of intercalated systems by removal of the solvent phase or increasing the electrolyte ion concentration.

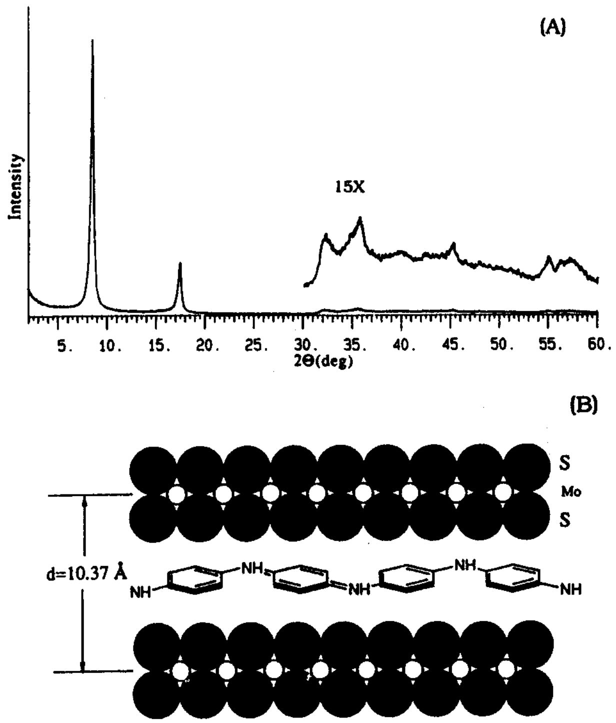

Figure 6. X-ray powder diffraction pattern and structure scheme of polyaniline/MoS_2.[83]

The mechanism of clay tactoid exfoliation in epoxy–clay nanocomposites has been described recently;[93] the materials exhibit improved mechanical properties. The polymer uptake is assisted by introducing long-chain *n*-alkylammonium ions via ion exchange into the precursor host lattice.

The formation of colloid solutions of layered transition-metal dichalcogenides has been reported originally for hydrated NbS_2 phases in aqueous electrolytes[94] and for TaS_2 compounds in organic solvents.[95] By exfoliation of dichalcogenide layer systems, addition of the dissolved guest species and subsequent restacking in random mode by coagulation large-dye molecules such as cyanine, substituted ferrocenes, or hydrocarbons (e.g., decahydronaphthalene) can be intercalated.[95,96] X-ray investigations on colloid MoS_2 layers prepared by exfoliation of lithium-intercalated molybdenum disulfide in polar solvents[97] showed that the single MoS_2 layers exhibit distorted octahedral coordination with a (2×1) superlattice;[98] nuclear quadrupole interaction measurements revealed coordinatively unsaturated Mo sites (sulfur vacancies) at the prismatic sites of the MoS_2 slabs.[99]

The direct intercalation of polyaniline via colloid suspensions into MoS_2 has been reported (Figure 6).[83] Recently it was shown that in situ formation of polypyrrole/MoS_2 can be achieved via an oxidative encapsulation reaction and polymer growth under kinetically restricted conditions. The product is a p-type conductor; the electronic conductivity is 3 orders of magnitude higher as compared to pristine MoS_2.[100] The intercalation of poly(ethylene oxide) has been performed with delaminated suspensions of MoS_2 and TiS_2.[101] Metal chalcogenides with more complex layer units, e.g., the misfit layer compounds $PbNb_2S_5$ and $SmNb_2S_4$ can similarly be exfoliated and intercalated subsequently.[102] A further way to profit from colloid systems of layered phases is the preparation of simple ternary metastable compounds which cannot be obtained by thermal reactions. The electronic structure of MoS_2 does not allow the direct synthesis of ternary compounds T_xMoS_2 with transition-metal atoms T. By application of the colloid route it was possible, however, to insert iron ions between the MoS_2 layers; Mössbauer studies indicated two oxidation states (+2) and (+3) for the iron ions intercalated.[103]

Redox intercalation of organic monomers such as aniline, pyrrole or 2,2′-bithiophene with $V_2O_5{\cdot}(H_2O)_m$ colloid xerogels yield layered intercalates containing conductive polymers in the interlayer space which exhibit high electronic conductivity; the oxidative polymerization proceeds via partial reduction of V^{5+} to V^{4+}.[104] No redox reaction is associated with the direct intercalation of polyethylene oxide in $V_2O_5(H_2O)_n$ xerogels;[105] the interlayer space height of the restacked material of 4.5 Å suggests a straight-chain conformation rather than coiled (helical) conformation observed for poly(ethylene oxide) in layered silicates.

Among one-dimensional host systems Chevrel type phases AMo_3Se_3 (A = Li,Na) have been found to form colloid solutions with negatively charged monodispersed (Mo_3Se_3) condensed cluster chains in polar solvents;[106,107] in NMF they display liquid-crystalline behavior.[108] These systems should be of interest for the synthesis of composite materials with larger molecular species; it should also be possible to prepare combined (1D + 2D) systems by mixing colloid solutions of Mo_3Se_3 with layered colloids followed by precipitation.

2D → 3D Transformations

The development of systems with *rigid* pores in the nanometer regime is of considerable current interest in shape-selective catalysis, absorption, ion exchange, and the design of new structural and functional composites. One actual fruitful approach discussed above is the use of templates to direct the crystallization of framework structures. A conceptionally complementary synthesis strategy for the design of rigid nanoporous solids is based on a transformation of *layered* systems into porous framework materials. In principle this approach can be described as a specific type of modification of layered hosts by (mostly irreversible) intercalation processes.

One disadvantage of layered intercalation systems is the collapse of the interlayer voids, when the guest species responsible for the layer separation are removed. If large rigid guest species—anchored to the neighboring sheet units—are introduced as a kind of "pillars" into the interlayer space, then it is possible to prevent a layer collapse. There are several criteria to be met for obtaining nanoporous systems by this approach: (i) the pillaring species must be sufficiently rigid and exhibit uniform distribution, (ii) their lateral spacing and effective height have to be large enough to provide pores of the desired size, (iii) the host layer units must provide sufficient rigidity in order to avoid layer bending which would affect the accessible pore space and geometry (Figure 7). Due to the existence of a large number of host lattices with layered structure types and of a large variety of guest species with adequate properties flexible synthesis routes for rigid nanoporous materials with chemical functionality are available.[109−111]

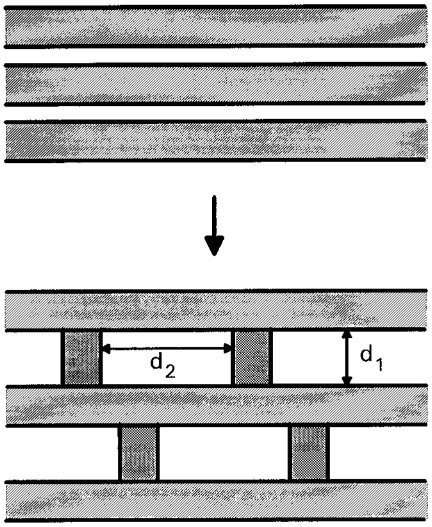

Figure 7. Scheme for conversion of layered materials into nanoporous framework systems by "pillaring".

A considerable fraction of the interest in pillared systems has focused on smectite type clay materials with low negative layer charge density. One way to achieve rigid porous systems is cation exchange with large isometric organic or metal complex cations, e.g., quaternary ammonium ions and related species; the pore dimensions can be varied via the host layer charge density (i.e., the lateral separation of pillar units) of the pristine clay. A disadvantage of these materials is their low-temperature stability. A different approach is the use of polyoxycations of aluminium, zirconium, chromium, titanium, etc. Subsequent thermal dehydration/dehydroxylation of the intercalated species converts the guest ions into small metal oxide like particles in the interlayer space. This process may lead to coordinatively unsaturated metal ions on the pillar surface which are of interest for catalytic properties; these composites exhibit high thermal stability. The shape-selective performance of these materials appears to be competitive now with that of zeolite catalysts in current commercial use.[110]

Transparent oriented microporous films of tetramethylammonium-pillared saponite have been prepared for the application of photoactive species.[112] Mo_6Cl_8 type clusters and lanthanum/nickel organic complexes were used for the design of controlled architecture of pillared systems;[113,114] zirconia-pillared tetrasilicic fluoromica exhibits high crystallinity and a high surface area of 300 m^2/g.[115] A recent report demonstrates that highly ordered mesoporous materials with a hexagonal array of uniform channels can be synthesized from layered polysilicates by exchange with *n*-alkyltrimethylammonium ions followed by calcination (Figure 8).[116]

Layered double hydroxides of the hydrotalcite type $[M^{II}_{1-x}M^{III}_x(OH)_2][A^{n-}]_{x/n}$ are complementary to layered aluminosilicates with respect to the reversed layer excess charge which requires *anionic* species as interlayer ions for charge balance; a large number of compositions is accessible by varying the matrix ions M. Oxovanadate anions $[V_{10}O_{28}]^{6-}$ and heteropolyanions such as $[H_2W_{12}O_{40}]^{6-}$ and $[SiV_3W_9O_{40}]^{7-}$ were shown to be useful pillaring units.[117] Zn/Al layered double hydroxides pillared with cobalt(II) phthalocyanine tetra-

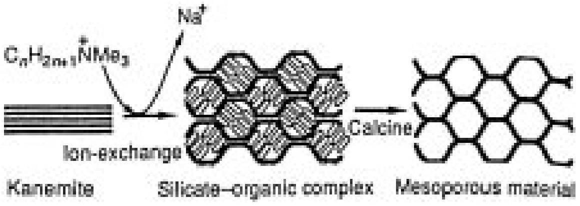

Figure 8. Model for the formation of mesoporous materials from layered polysilicates.[116]

sulfonate are able to catalyze the oxidation of mercaptides to disulfides with O_2 at ambient temperature.[118] Other layered host materials that can be modified by pillaring are, e.g., metal phosphates and phosphonates,[119] niobates,[120] molybdenum(VI) oxide and tantalum disulfide TaS_2.[121] It is obvious that the transformation of two-dimensional structures into three-dimensional hosts has become a useful flexible approach to the synthesis of new nanoporous systems.

Electron/Ion Transfer Reactions

In intercalation reactions with insulator host lattices the host matrix is usually not accessible for redox processes (which can take place only via guest species). Host lattices which exhibit electronic conductivity and an appropriate band structure can be directly involved in redox intercalation reactions, however, by electron/ion transfer processes which in turn may significantly perturb the physical properties of the host matrix.[4,6,11] They are therefore useful functional materials for electrodes in secondary batteries, electrochromic systems, electrocatalysis, etc.[1,68] Their chemistry provides interesting aspects in terms of charge-transfer mechanisms; we will discuss here a few selected points and our progress in understanding of these phenomena in the following:

Neutral Molecular Guest Species. A wide range of molecular neutral species with Lewis base character (e.g., NH_3, amines, pyridine, acid amides) can be intercalated into layered host lattices with neutral layer units and electronic conductivity which has induced studies on the nature of the host/guest interaction responsible for the spontaneous intercalation and the reaction free energy. Investigations on single guest molecules like NH_3 and pyridine with high ionization energy have demonstrated that the intercalation process is associated with a partial irreversible transformation of the guest species which yields electrons that are transferred to the host matrix acceptor and ionic guest species for charge balance.[1,4,6,7,9,122] In those cases, where the ionization energy of the guest is rather low, a direct electron-transfer process to the host matrix without irreversible molecular reactions should be possible, e.g., with low potential metal complexes or tetrathiofulvalene.

A large number of investigations on the intercalation of *metallocenes* into various host lattices have been performed in recent years[7,9] ranging from transition-metal dichalcogenides, metal phosphorous chalcogenides to oxides such as MoO_3 and V_2O_5 xerogels,[123] and misfit layer chalcogenides.[124] Semiconducting tin diselenide $SnSe_2$ was found to become superconducting upon intercalation of cobaltocene.[125] Metallocenes are nonspherical neutral guest molecules and their intralayer orientation—which has been under debate for some time—is of interest concerning the question of host/guest interaction. Combined X-ray diffraction, neutron diffraction, and NMR measurements on polycrystalline and single-crystal material led to the surprising conclusion that in most cases the unsubstituted metallocene molecules are located in the interlayer space with their C_5 axes parallel to the host layer planes.[126] The guest molecules may adapt an ordered superlattice with single orientation of the principal molecular axes; at higher temperatures reorientation around the normal to the layer phases is observed.[127]

Metallocenes are intercalated under retention of the molecular integrity of the guest species. As concerns the interaction host lattice/guest species, a model has been proposed earlier that involves the electron affinity of the host and the ionization energy of the guest and predicts the possibility of a mixed valence state $(R_2T^+)_x(R_2T)_y[MX_2]^{x-}$ (R = organic ligand, T = transition metal).[5,122] In principle the following competitive electron-transfer scheme is conceivable (not considering potential kinetic restrictions) based on relative electron affinities E_A of host lattice (Z) and metallocene guest R_2T:

$$E_A(R_2T) > E_A[Z] \qquad (R_2T)_n[Z] \qquad \text{(a)}$$

$$E_A(R_2T) \sim E_A[Z] \qquad (R_2T^+)_n(R_2T)_m[Z]^{n+} \qquad \text{(b)}$$

$$E_A(R_2T) < E_A[Z] \qquad (R_2T^+)_n[Z]^{n+} \qquad \text{(c)}$$

While no evidence exists for case (a) with neutral hosts and neutral guest layers, case (c) is found when the relative electron affinity of the host is large and the ionization energy of the neutral metallocene is low, e.g., $(Cp_2Co^+)_{0.25}[TaS_2]^{0.25-}$; metallocenes with higher ionization energy, e.g., ferrocene Cp_2Fe can be intercalated only into host lattices with rather high electron affinity, e.g., $RuCl_3$ or FeOCl. The intermediate case (b) can be assumed when the electron affinities of host and guest are comparable, i.e., a *competitive electron transfer* situation. In a localized valence model the intercalate structure should then correspond to the coexistence of uncharged *and* ionized metallocene species; the time window for electron delocalization between both species may depend upon the temperature. Evidence for case (c) has been observed recently. Solid-state ^2H NMR studies on single-crystal samples of $CdPS_3[Co(n\text{-}C_5D_5)_2]_{0.4}$ showed that the guest molecules reside in ordered domains with the coexistence of both neutral and ionized species.[128] Similar results have been obtained by infrared spectroscopic investigations on this phase.[129]

Electron/Anion Transfer and Anion Mixed Valence. Graphite is the only host lattice known to be able to undergo intercalation reactions by electron/cation transfer as well as by electron/anion transfer due to the specific band structure which allows the uptake of excess electrons into the conduction band as well as the formation of band holes upon oxidation with the formation of negative excess charges on the graphene layer units and compensation of these charges by intercalation of anionic guest species.[67,130,131] Recently it has been demonstrated that redox reactions with layer charge sign conversion of the type

$$[Z]^{x-} \rightleftarrows [Z]^{x+}$$

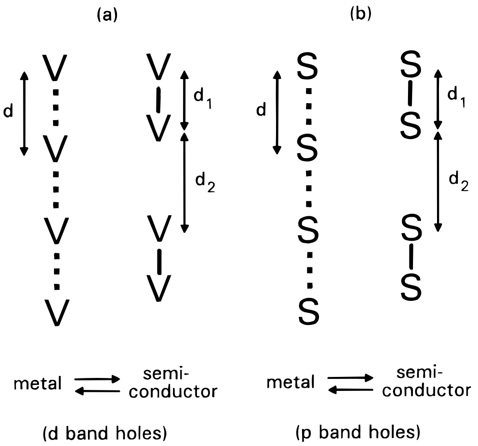

Figure 9. Scheme for reversible electronic transitions metal/semiconductor in systems with (a) cation d-band holes (VO_2, rutile type) and (b) anion p-band holes (hypothetical case for a metal sulfide).

can also be observed for layered oxometallates.[11,132,133] This reaction represents an interesting example for the correlation between electronic charge-transfer and intracrystalline protolysis equilibria. A redox/protolysis model has been proposed that involves deprotonated layers at high average oxidation state, while below a threshold average oxidation state of the layer matrix spontaneous collective protonation takes place which results in a change of the layer excess charge sign as a consequence of the change in M−(OH) acidity with the oxidation state of the intralayer redox-active cation M.

As concerns the redox active centers involved on the side of the matrix units, all cases discussed above (with the exception of graphite) are based on metal *cation redox reactions* and *cation mixed valence* states. Only recently several examples of intercalation processes have been described which are based upon host matrix *anion redox reactions* and *anion mixed valence states*.[11] These concern mainly chalcogenide systems, e.g., copper chromium spinels $CuCr_2X_4$,[134,135] KCu_4S_3,[136] Li_2FeS_2,[137] transition-metal trichalcogenides,[138] and the rhenium cluster sulfide Re_6S_{12}.[139] They rely on chalcogen mixed valence states X^{2-}/X^- (p-band holes, X = S, Se, Te) of the matrix anions and formal redox processes of the type

$$X^{2-} \rightleftarrows X^- + e^-$$

with constant valency of the matrix metal ions. Valence delocalization is proved by the metallic properties, e.g., of the $CuCr_2X_4$ spinels. Similar to the corresponding compounds with cation mixed valence (e.g., VO_2) one should expect to observe cases with temperature-dependent metal/semiconductor transitions and correlated structural distortion and electron localization (Figure 9) also for anion mixed valence compounds; so far no example has been reported for an electronic transition of this type, however.

Conclusions

As mentioned above intercalation chemistry belongs to the oldest known examples of functional chemical systems providing the opportunity to modify materials on the nanoscale level. Qualitative models for the chemical reactivity are available based on topological aspects, electronic properties, acid−base, and exchange phenomena which enable a rational synthesis approach for given types of host lattices and guest species. The actual literature demonstrates the increasing tendency to profit from the opportunities provided by intercalation systems for designing the microstructural architecture of metastable complex composite materials at low temperatures.

References

(1) Whittingham, M. S., Jacobson, A. J., Eds. *Intercalation Chemistry*; Academic Press: New York, 1982. Thomas, J. M. *Ibid*., p 55. Thomas, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 913.
(2) Müller-Warmuth, W., Schöllhorn, R., Eds. *Progress in Intercalation Research*; Kluwer: Dordrecht, 1994.
(3) Lévy, F., Ed. *Intercalated Layered Materials*; D. Reidel: Dordrecht, 1979.
(4) Schöllhorn, R. In: *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 1, p 249.
(5) Schöllhorn, R. In: *Intercalation Chemistry*; Whittingham, M. S., Jacobson, A. J., Eds.; Academic Press: New York, 1982; p 315.
(6) Schöllhorn, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 983.
(7) Jacobson, A. J. In: *Solid State Chemistry Compounds*; Cheetham, A. K., Day, P., Eds.; Clarendon Press: Oxford, 1992; p 183.
(8) Rouxel, J. *Inorg. Chem.* **1979**, *1*, 245. Rouxel, J. In: *Advances in the Synthesis and Reactivity of Solids*; Mallouk, Th. E., Ed.; JAI Press: London, 1994; Vol. 2, p 27.
(9) O'Hare, D. In: *Inorganic Materials*; Bruce, D. W., O'Hare, D., Eds.; Wiley and Sons: New York, 1992; p 165.
(10) Murphy, D. W. In: *Advances in the Synthesis and Reactivity of Solids*; Mallouk, Th. E., Ed.; JAI Press: London, 1991; Vol. 1, p 237.
(11) Schöllhorn, R. In: *Progress in Intercalation Research*; Müller-Warmuth, W., Schöllhorn, R., Eds.; Kluwer: Dordrecht, 1994; p 1.
(12) Lanston, S. L.; Rohrbough, W. J. *Science* **1990**, *247*, 1319.
(13) Estermann, M.; Mc Cusker, L. B.; Baerlocher, C.; Merrouche, A.; Kessler, H. *Nature* **1991**, *352*, 320. Ru, X.; Jones, R. H.; Chen, J.; Thomas, J. M. *J. Chem. Soc., Chem. Commun.* **1992**, *12*, 875.
(14) Haushalter, R. C.; Strohmaier, K. G.; Lai, F. W. *Science* **1989**, *246*, 1289.
(15) Mundi, L. A.; Strohmaier, K. G.; Goshorn, D. P.; Haushalter, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 8182.
(16) Haushalter, R. C.; Wang, Z.; Thompson, M. E.; Zubieta, J. C. *Inorg. Chem.* **1993**, *32*, 3700. Soghomonian, V.; Chen, O.; Haushalter, R. C.; Zubieta, J. C.; O'Connor, C. J.; Lee, Y. S. *Chem. Mater.* **1993**, *5*, 1690.
(17) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J. C.; O'Connor, C. J.; Lee, Y. S. *Chem. Mater.* **1993**, *5*, 1690. Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J. C. *Angew. Chem.* **1993**, *105*, 601; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 610.
(18) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710. Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, C. T.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; Mc Cullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834. Behrens, P.; Stucky, G. D. *Angew. Chem.* **1993**, *105*, 729.
(19) Monnier, A.; Schüth, F.; Hugo, Q.; Kumar, D.; Margolese, D. I.; Maxwell, R. S.; Stucky, G. D.; Krishnamurty, M.; Petroff, P. M.; Fironzi, A.; Janicke, M.; Chmelka, B. F. *Science* **1993**, *261*, 1299.
(20) Taner, P. T.; Pinnavaia, Th. J. *Science* **1995**, *267*, 865.
(21) Hard, G. S. A.; Glyde, J. C.; Göltner, C. G. *Nature* **1995**, *378*, 366.
(22) Huo, G.; Margolese, D.; Ciesla, U.; Fen, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.
(23) Ciesla, U.; Demuth, D.; Leon, R.; Petroff, P. M.; Stucky, G. D.; Unger, K.; Schüth, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1387.
(24) Luca, V.; Mac Lachlan, D. J.; Hook, J. M.; Withers, R. *Chem. Mater.* **1995**, *7*, 2220.
(25) Parise, J. B.; Ko, Y.; Rijsenbeek, J.; Nellis, D. M.; Tan, K.; Koch, S. *J. Chem. Soc., Chem. Commun.* **1994**, 527.
(26) Thomas, J. M. *Angew. Chem.* **1988**, *100*, 1735; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1673.
(27) Davies, M. E. *Acc. Chem. Res.* **1992**, *26*, 111.
(28) Corma, A.; Martinez, A. *Adv. Mater.* **1995**, *7*, 137.
(29) Van Santen, R. A.; Kramer, G. J. *Chem. Rev.* **1995**, *95*, 637.
(30) Farneth, W. E.; Gorte, R. J. *Chem. Rev.* **1995**, *95*, 615.
(31) Yan, Y.; Bein, Th. *J. Am. Chem. Soc.* **1995**, *117*, 9990.
(32) Stucky, G. D. In: *Progress in Inorganic Chemistry*; Lippard, J., Ed.; J. Wiley: New York, 1992; Vol. 40, p 99.
(33) Ozin, G. A. *Adv. Mater.* **1992**, *4*, 612. Ramamurthy, V. *J. Am. Chem. Soc.* **1994**, *116*, 1345.

(34) Anderson, M. W.; Shi, J.; Leigh, D. A.; Moody, A. E.; Wade, F. A.; Hamilton, B.; Carr, S. W. *J. Chem. Soc., Chem. Commun.* **1993**, 553. Gügel, A.; Müllen, K.; Schmidt, W.; Schön, G.; Schüth, F.; Spickermann, J.; Titman, J.; Unger, K. *Angew. Chem.* **1993**, *105*, 618; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 556.

(35) Hartmann, M.; Pöppl, A.; Kevan, L. *J. Phys. Chem.* **1995**, *99*, 17494.

(36) Cano, M. L.; Fornés, V.; Garcia, H.; Miranda, M. A.; Pérez-Prieto, J. *J. Chem. Soc., Chem. Commun.* **1995**, 2477.

(37) Taylor, R. J.; Drago, R. S.; Hage, J. P. *Inorg. Chem.* **1992**, *31*, 253.

(38) Weckhusen, B. M.; Verberckmoes, A.; Vannijvel, I. P.; Pelgrims, J. A.; Buskens, P. L.; Jacobs, P. A.; Schoonheydt, R. A. *Angew. Chem.* **1995**, *107*, 2868; *Angew. Chem. Int. Ed. Engl.* **1995**, 34.

(39) Ozin, G. A.; Özkar, S. *Adv. Mater.* **1992**, *4*, 11.

(40) Kim, Y. I.; Riley, R. L.; Yonemoto, E. H.; Rong, D.; Mallouk, Th. E. In: *Supramolecular Architecture*; ACS Symposium Series 499; Bein, Th., Ed.; American Chemical Society: Washington, DC, 1992; p 333. Krueger, J. S.; Lai, C.; Li, Z.; Mayer, J. E.; Mallouk, Th. E. In: *Inclusion Phenomena and Molecular Recognition*; Atwood, J. L., Ed.; Plenum Press: New York, 1990; p 365.

(41) Caro, J.; Finger, G.; Kornatowski, J.; Richter-Mendan, J.; Werner, L.; Zibrowius, B. *Adv. Mater.* **1992**, *4*, 273.

(42) Caro, J.; Marlow, F.; Wübbenhorst, M. *Adv. Mater.* **1994**, *6*, 413.

(43) Bein, Th. In: *Supramolecular Architecture*; ACS Symposium Series 499; Bein, Th., Ed.; American Chemical Society: Washington, DC, 1992; p 275. Enzel, P.; Bein, Th. *Chem. Mater.* **1992**, *4*, 819.

(44) Ozin, G. A.; Kupermann, A.; Stein, A. *Angew. Chem.* **1989**, *101*, 373; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 359.

(45) Wu, C. G.; Bein, Th. *Chem. Mater.* **1994**, *6*, 1109.

(46) Tonscheid, A.; Ryder, P. L.; Jaeger, N. I.; Schulz-Ekloff, G. *Surf. Sci.* **1993**, *281*, 51.

(47) Karpinski, Z.; Homeyer, S. T.; Sachtler, W. M. H. In: *Structure-Activity Relations in Heterogeneous Catalysis*; Grasselli, R. K., Sleight, A., Eds.; Elsevier: Amsterdam, 1991; Vol. 67 of Studies in Surface Science and Catalysis, p 203.

(48) Shen, L. L.; Knözinger, H.; Sachtler, W. M. H. *J. Am. Chem. Soc.* **1989**, *111*, 8125. Zhang, Z.; Wong, T. T.; Sachtler, W. M. H. *J. Catal.* **1991**, *128*, 13.

(49) Sachtler, W. M. H. *Acc. Chem. Res.* **1993**, *26*, 383.

(50) Stakheev, A. Y.; Sachtler, W. M. H. *Catal. Today* **1992**, *12*, 283.

(51) Edwards, P. P.; Anderson, P. A.; Thomas, J. M. *Acc. Chem. Res.* **1996**, *29*, 23. Yoon, K. B. *Chem. Rev.* **1993**, *93*, 321.

(52) Liu, X.; Iu, K. K.; Thomas, J. K. *J. Phys. Chem.* **1994**, *98*, 13720.

(53) Kim, Y.; Han, Y. W.; Seff, K. *J. Phys. Chem.* **1993**, *97*, 12663.

(54) Iu, K. K.; Liu, X.; Thomas, J. K. *J. Phys. Chem.* **1993**, *97*, 8165.

(55) Anderson, P. A.; Armstrong, R. A.; Edwards, P. P. *Angew. Chem.* **1994**, *106*, 669; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 641.

(56) Armstrong, R. A.; Anderson, P. A.; Edwards, P. P. *J. Chem. Soc., Chem. Commun.* **1994**, 473.

(57) Sun, T.; Seff, K.; Heo, N. H.; Petranovski, V. *J. Phys. Chem.* **1994**, *98*, 5768. Song, S. H.; Kim, U. S.; Kim, Y.; Seff, K. *J. Phys. Chem.* **1992**, *96*, 10937.

(58) Sun, T.; Seff, K. *Chem. Rev.* **1994**, *94*, 857.

(59) Stein, A.; Ozin, G. A.; Macdonald, P. M.; Stucky, G. D., Jalinek, R. *J. Am. Chem. Soc.* **1992**, *114*, 5171.

(60) Stein, A.; Ozin, G. A.; Stucky, G. D. *J. Am. Chem. Soc.* **1992**, *114*, 8119.

(61) Baker, M. D.; Senaratne, C.; Zhang, J. *J. Phys. Chem.* **1994**, *98*, 1668.

(62) Stucky, G. D. In: *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley and Sons: New York, 1992; Vol. 40, p 99.

(63) Ozin, G. A. *Adv. Mater.* **1992**, *4*, 612.

(64) Wang, Y.; Herron, N. *J. Phys. Chem.* **1987**, *91*, 257; **1988**, *92*, 4988. Herron, N.; Wang, Y.; Eddy, M.; Stucky, G. D., Cox, P. E.; Moller, K.; Bein, Th. *J. Am. Chem. Soc.* **1989**, *111*, 530.

(65) Ozin, G. A.; Steele, M.; Macdonald, P. M. *J. Am. Chem. Soc.* **1993**, *115*, 7285. Ozin, G. A.; Steele, M.; Holmes, A. J. *Chem. Mater.* **1994**, *6*, 999.

(66) Moran, K. L.; Gier, T. E.; Harrison, W. T. A.; Stucky, G. D.; Eckert, H.; Eichele, K.; Waylishen, R. E. *J. Am. Chem. Soc.* **1993**, *115*, 10553.

(67) Schlögl, R. In: *Progess in Intercalation Research*; Müller-Warmuth, W., Schöllhorn, R., Eds.; Kluwer: Dordrecht, 1994; p 83.

(68) Besenhard, J. O. In: *Progress in Intercalation Research*; Müller-Warmuth, W., Schöllhorn, R., Eds.; Kluwer: Dordrecht, 1994; p 457.

(69) Jacobson, A. J. In: *Chemical Physics of Intercalation*; Bernier, P., Fischer, J. E., Roth, S., Solin, S., Eds.; Plenum Press: New York, 1993; p 117.

(70) Thomas, J. M. *Angew. Chem.* **1988**, *100*, 1735; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1673.

(71) Balogh Plaszlo, M. In: *Organic Chemistry Using Clays*; Springer-Verlag: Heidelberg, 1993; Reactivity and Structure Concepts in Organic Chemistry, Vol. 29. Izumi, Y., Urabe, K., Onaka, M., Eds.; *Zeolites, Clay and Heteropolyacids in Organic Reactions*; VCH Verlagsgesellschaft: Weinheim, 1992.

(72) Carrado, K. A.; Thiyagarajan, P.; Winans, R. E.; Botto, R. E. *Inorg. Chem.* **1991**, *30*, 794. Carrado, K. A.; Anderson, K. B.; Grutoski, P. S. In: *Supramolecular Architecture*; Bein, Th., Ed.; American Chemical Society: Washington, DC, 1992; p 155.

(73) Breu, J.; Catlow, C. R. A. *Inorg. Chem.* **1995**, *34*, 4504.

(74) Fujita, W.; Awaga, K. *J. Chem. Soc., Chem. Commun.* **1995**, 739.

(75) Soghomonian, V.; Haushalter, R. C.; Chen, Q.; Zubieta, J. C. *Inorg. Chem.* **1994**, *33*, 1700. Zhang, Y.; Clearfield, A.; Haushalter, R. C. *J. Solid State Chem.* **1995**, *117*, 157. Liu, K. H.; Wu, L. S.; Gau, H. M. *Inorg. Chem.* **1993**, *32*, 4153. Haushalter, R. C.; Wang, Z.; Meyer, L. M.; Dhingra, S. S.; Thompson, M. E.; Zubieta, J. C. *Chem. Mater.* **1994**, *6*, 1463. Riou, D.; Férey, G. *J. Solid State Chem.* **1995**, *120*, 137. Marcos, M. D.; Amorós, P.; Beltrán, D.; Beltrán, A. *Inorg. Chem.* **1994**, *33*, 1220.

(76) Cao, G.; Mallouk, Th. E. *Inorg. Chem.* **1991**, *30*, 1434. Cao, G.; Garcia, M. E.; Alcalá, M.; Burgess, L. F.; Mallouk, Th. E. *J. Am. Chem. Soc.* **1992**, *114*, 7574. Garcia, M. E.; Naffin, J. L.; Deng, N.; Mallouk, Th. E. *Chem. Mater.* **1995**, *7*, 1968.

(77) Thompson, M. E. *Chem. Mater.* **1994**, *6*, 1168.

(78) Kim, Y. I.; Riley, R. L.; Yonemoto, E. H., Rong, D.; Mallouk, Th. E. In: *Supramolecular Architecture*; ACS Symposium Series 499; Bein, Th., Ed.; American Chemical Society: Washington, DC, 1992; p 333. Lee, H.; Kepley, L. J.; Hong, H. G.; Mallouk, Th. E. *J. Am. Chem. Soc.* **1988**, *110*, 618. Lee, H.; Kepley, L. J.; Hong, H. G.; Akhter, S.; Mallouk, Th. E. *J. Phys. Chem.* **1988**, *92*, 2597.

(79) Katz, H. E.; Scheller, G.; Putvinski, T. M.; Schilling, M. C.; Wilson, W. L.; Chidsey, C. E. D. *Science* **1991**, *254*, 1485.

(80) Alberti, G.; Cherubini, F.; Palombari, R. *Sensors Actuators* **1995**, *B24−25*, 270.

(81) Palvadeau, P.; Rouxel, J.; Queignac, M.; Bujoli, B. In: *Supramolecular Architecture*; ACS Symposium Series 499; Bein, Th., Ed.; American Chemical Society: Washington, DC, 1992; p 114.

(82) Billaud, D. In: *Progress in Intercalation Research*; Müller-Warmuth, W., Schöllhorn, R., Eds.; Kluwer: Dordrecht, 1994; p 273.

(83) Kanatzidis, M. G.; Bissessur, R.; De Groot, D. C.; Schindler, J. L.; Kannewurf, C. R. *Chem. Mater.* **1993**, *5*, 595.

(84) Kanatzidis, M. G.; Tonge, L. M.; Marks, T. J.; Marcy, H. O.; Kannewurf, C. R. *J. Am. Chem. Soc.* **1987**, *109*, 3797. Kanatzidis, M. G.; Marcy, H. O.; McCarthy, W. J.; Kannewurf, C. R.; Marks, T. J. *Solid State Ionics* **1989**, *32/33*, 594. Kanatzidis, M. G.; Hubbard, M.; Tonge, L. M., Marks, T. J., Marcy, H. O.; Kannewurf, C. R. *Synth. Met.* **1989**, *28*, C89. Kanatzidis, M. G., Wu, C. G.; Marcy, H. O.; Kannewurf, C. R.; Kostikas, K.; Papaefthymiou, V. *Adv. Mater.* **1990**, *2*, 364.

(85) Wu, C. G.; De Groot, D. C.; Marcy, H. O.; Schindler, J. L.; Kannewurf, C. R.; Bakas, T.; Papaefthymiou, V.; Hirpo, W.; Yesniowski, J. P.; Liu, Y. L.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 9229.

(86) Bissessur, R.; De Groot, D. C.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *J. Chem. Soc., Chem. Commun.* **1993**, 687.

(87) Mehrotra, V.; Giannelis, E. *Solid State Commun.* **1990**, *77*, 155.

(88) Mehrotra, V.; Giannelis, E. *Solid State Ionics* **1992**, *51*, 115.

(89) McCann, G. F.; Millar, G. J.; Bowmaker, G. A.; Cooney, R. P. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 4321.

(90) Liu, Y. J., Kanatzidis, M. G. *Chem. Mater.* **1995**, *7*, 1525; *Inorg. Chem.* **1993**, *32*, 2989.

(91) Jones, D. J., Mejjad, R. E., Rozière, J. In: *Supramolecular Architecture*; ACS Symp. Ser. 499; Bein, Th., Ed.; American Chemical Society: Washington, DC, 1992; p 220.

(92) Vaia, R. A.; Vasudevan, S.; Krawiec, W.; Scanlon, L. G.; Giannelis, E. P. *Adv. Mater.* **1995**, *7*, 154.

(93) Lan, T.; Kaviratna, P. D.; Pinnavaia, T. J. *Chem. Mater.* **1995**, *7*, 2144.

(94) Murphy, D. W.; Hull, G. W. *Chem. Phys.* **1975**, *62*, 973.

(95) Lerf, A.; Schöllhorn, R. *Inorg. Chem.* **1977**, *16*, 2950.

(96) Murphy, D. W.; Hull, G. W.; Waszczak, J. V.; Mayer, S. F.; Stewart, G. R.; Early, S.; Acrivos, J. V.; Geballe, T. H. J. *Chem. Phys.* **1975**, *62*, 976. Tagaya, H.; Hashimoto, T.; Karasu, M.; Izumi, T.; Chiba, K. *Chem. Lett.* **1991**, *12*, 2113. Divigalpitoya, W. M. R.; Frindt, R. F.; Morrison, S. R. *Science* **1989**, *246*, 369. Nazar, L. F.; Jacobson, A. J. *J. Chem. Soc., Chem. Commun.* **1986**, 570.

(97) Joensen, P.; Frindt, R. F.; Morrison, S. R. *Mater. Res. Bull.* **1986**, *21*, 457.

(98) Yong, D.; Frindt, R. F. *Mol. Cryst.* Liq. *Cryst.* **1994**, *244*, 335.

(99) Mottner, P.; Butz, T.; Lerf, A.; Ledezma, G.; Knözinger, H. *J. Phys. Chem.* **1995**, *99*, 8260.

(100) Wang, L.; Schindler, J. L.; Thomas, J. A.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1995**, *7*, 1753.

(101) Ruiz-Hitzky, E.; Jimenez, R.; Casal, B.; Manriquez, V.; Santa Ana, A.; Gonzalez, G. *Adv. Mater.* **1993**, *5*, 738. Lemmon, J. P.; Lerner, M. M. *Solid State Commun.* **1995**, *94*, 533.

(102) Bonneau, P.; Mansot, J. L.; Rouxel, J. *Mater. Res. Bull.* **1993**, *28*, 757.

(103) Danot, M.; Mansot, J. L.; Golub, A. S.; Protzenko, G. A.; Fabritchny, F. B.; Novikov, Y. N.; Rouxel, J. *Mater. Res. Bull.* **1994**, *29*, 833.

(104) Kanatzidis, M. G.; Wu, C. G.; Marcy, H. O.; Kannewurf, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 4139. Wu, C. G.; Kanatzidis, M. G.; Marcy, H. O.; De Groot, D. C.; Kannewurf, C. R. *Polym. Mater. Sci., Eng.* **1989**, *61*, 969. Kanatzidis, M. G.; Wu, C. G.; Marcy, H. O.; De Groot, D. C.; Kannewurf, C. R. *Chem. Mater.* **1990**, *2*, 222.

(105) Liu, Y. T.; De Groot, D. C.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1991**, *3*, 992.

(106) Tarascon, J. M.; Di Salvo, F. J.; Chen, C. H.; Carroll, P. J.; Walsh, M.; Rupp, L. *Solid State Chem.* **1985**, *58*, 290.

(107) Golden, J. H.; Di Salvo, F. J.; Fréchet, J. M. J. *Chem. Mater.* **1994**, *6*, 844.

(108) Davidson, P.; Gabriel, J. C.; Levelut, A. M.; Batail, P. *Europhys. Lett.* **1993**, *21*, 317.

(109) Mitchell, I. V., Ed.; *Pillared Layered Structures*; Elsevier Applied Science: London, 1990.

(110) Pinnavaia, T. J. In: *Materials Chemistry*, Adv. in Chem. Series 245; Interrante, L. V., Ed.; American Chemical Society: Washington, DC, 1995; p 283.

(111) Clearfield, A.; Kuchenmeister, M. In: *Supramolecular Architecture*; ACS Symposium Series 499; Bein, Th., Ed.; American Chemical Society: Washington, DC, 1992; p 128.

(112) Ogawa, M.; Takahashi, M.; Kato, C.; Kuroda, K. *Mater. Chem.* **1994**, *4*, 519.

(113) Christiano, S.; Pinnavaia, T. J. *Solid State Chem.* **1986**, *64*, 232.

(114) Skaribas, S. P.; Pomonis, P. J.; Grange, P.; Delmon, B. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 3217.

(115) Johnson, J. W.; Brody, J. F.; Alexander, R. M.; Yacullo, L. N.; Klein, C. F. *Chem. Mater.* **1993**, *5*, 36.

(116) Inagaki, S.; Fukushima, Y.; Kuroda, K. *J. Chem. Soc., Chem. Commun.* **1993**, 680.

(117) Drezdon, M. A. *Inorg. Chem.* **1988**, *27*, 4628. Kwon, R.; Tsigdinos, G. A.; Pinnavaia, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 3653. Kwon, T.; Pinnavaia, T. J. *Chem. Mater.* **1989**, *1*, 381.

(118) Perez, M. E.; Ruano, R.; Pinnavaia, T. J. *Catal. Lett.* **1991**, *11*, 51.

(119) Jones, D. J.; Rozière, J.; Maireles-Torres, P.; Jiménez-López, A.; Olivéra-Pastor, P.; Rodríguez-Castellon, E.; Tomlinson, A. G. *Inorg. Chem.* **1995**, *34*, 4611. Ferragina, C.; Massucci, M. A.; Tomlinson, A. G. *J. Chem. Soc., Dalton Trans.* **1990**, 1191. Alberti, G.; Murcia Mascarós, S.; Vivani, R. In: *Soft Chemistry Routes to New Materials*; Rouxel, J., Tourneaux, M., Brec, R., Eds.; Trans. Tech. Publ.: Switzerland, 1994; Materials Science Forum Vols. 152−153, p 87.

(120) Treacy, M. M.; Rice, S. B.; Jacobson, A. J.; Lewandowski, J. T. *Chem. Mater.* **1990**, *2*, 279.

(121) Lerf, A.; Lalik, E.; Kolodziejski, W.; Klinowski, J. *J. Phys. Chem.* **1992**, *96*, 7389.

(122) Schöllhorn, R. *Comments Inorg. Chem.* **1983**, *2*, 271.

(123) O'Hare, D.; Evans, J. S. O.; Turner, P. A.; Stephen, S. M.; Heyes, J.; Greenwood, J. *J. Mater. Chem.* **1995**, *5*, 1383.

(124) Hérnan, L.; Morales, J.; Sánchez, L.; Tirado, J. L. *Chem. Mater.* **1995**, *7*, 1576.

(125) O'Hare, D.; Wong, H. V.; Hazell, S.; Hodby, J. W. *Adv. Mater.* **1992**, *4*, 658.

(126) Wong, H. V.; Evans, J. S. O.; Barlow, S.; Mason, S. J.; O'Hare, D. *Inorg. Chem.* **1994**, *33*, 5512.

(127) Evans, J. S. O.; O'Hare, D. *Chem. Mater.* **1995**, *7*, 1668.

(128) Mason, S. J.; Heyes, S. J.; O'Hare, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1657.

(129) Clerc, D. G.; Cleary, D. A. In: *Chemical Physics of Intercalation*; Bernier, P., Fischer, J. E., Roth, S., Solin, S. S., Eds.; Plenum Press: New York, 1993; p 365.

(130) Okino, F.; Bartlett, N. *J. Chem. Soc., Dalton Trans.* **1993**, 2081.

(131) Doyen-Lang, S.; Charlier, A.; Lang, L.; Charlier, M. F. *Synth. Met.* **1993**, *58*, 95.

(132) Schöllhorn, R.; Otto, B. *J. Chem. Soc., Chem. Commun.* **1987**, 1559.

(133) Schöllhorn, R. *Solid State Ionics* **1989**, *32/33*, 23.

(134) Payer, A.; Schöllhorn, R.; Ritter, C.; Paulus, W. *J. Alloys Compounds* **1993**, *191*, 37. Payer, A.; Schmalz, M.; Paulus, W.; Schlögl, R.; Schöllhorn, R. *J. Solid State Chem.* **1992**, *98*, 71.

(135) Schöllhorn, R. *Angew. Chem.* **1988**, *100*, 1446; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1392.

(136) Viola, F.; Schöllhorn, R. *J. Chem. Soc., Chem. Commun.* **1992**, 907. Berger, R.; Bucur, R. V. *Mater. Res. Bull.* **1992**, *27*, 439.

(137) Brec, R.; Prouzet, E.; Ouvrard, G. *J. Power Sources* **1989**, *26*, 325.

(138) Sourisseau, G.; Gwet, S. P.; Gard, P.; Mathey, Y. *J. Solid State Chem.* **1988**, *72*, 257.

(139) Nemudry, A.; Schöllhorn, R. *J. Chem. Soc., Chem. Commun.* **1994**, 2617.

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