Reviews

Preparation and Properties of Two-Dimensional Microporous Pillared Interlayered Solids

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Received October 7, 1996. Revised Manuscript Received July 2, 1997⊗

There have been significant developments in the pillaring of lamellar ionic materials, and the resulting zeolite-like pillared derivatives have built a large family of microporous materials. This review focuses on the host−guest reactions involved in the preparative procedures. Furthermore, approaches to the modification of the low-dimensional porous network structure are discussed.

Introduction

Typical microporous materials are zeolites, which are hydrated crystalline aluminosilicates with regular pore shapes and sizes. They discriminate between molecules with high selectivity, being referred to as molecular sieves. Later, pure silica molecular sieves (e.g., silicalite) and phosphate-based molecular sieves (e.g., aluminophosphate ($AlPO_4$), and element-substituted aluminophosphates) have been synthesized. These zeolites and zeolite-related materials have pore sizes in the range of approximately 2−13 Å and pore systems of 1-D, 2-D, and 3-D.[1]

In the late 1970s, microporous clay intercalation compounds pillared with metal oxide clusters were prepared. These microporous materials were obtained by exchanging the interlayer cations of smectite clays with bulky inorganic cations followed by calcination. On heating, the intercalated cations are converted to metal oxide clusters, propping open the layers as pillars, generating interlayer space of molecular dimensions, i.e., a two-dimensional porous network. Consequently, bidimensional zeolite-like materials with high thermal stability and high surface areas were made, which are called pillared interlayered clays (PILC) or cross-linked clays (CLC). Subsequently, various host materials other than smectite clays have also been employed for this purpose.

The micropore structure is tailored by the nature of the host material and of the pillaring species, and may have pore sizes larger than those of zeolites and zeolite-related materials. Furthermore, intrinsic catalytic activity is induced to the pillared interlayered solids according to the nature of the pillar. Thus, the pillared derivatives have received widespread interest as a new type of microporous solid that can serve as shape-selective catalysts, separating agents, supports, sorbents, etc.[2]

There has been intensive research activity on the subject of pillared interlayered solids, and the preparative techniques have made remarkable progress. A variety of ionic layered materials have been pillared with a variety of metal oxides clusters, thus providing a large family of pillared interlayered solids with a wide spectrum of physicochemical properties and pore dimensions.

This paper reviews recent advances and problems in the pillared interlayered solids, specifically in the pore-space engineering including host−guest reactions and modifications of the low-dimensional pore structures. Catalytic properties of the pillared solids have been studied extensively, but they are omitted here because they are beyond the limited scope of this article.

Host Materials for Pillared Interlayered Solids

As mentioned above, pillared interlayered solids are generally obtained by the reaction of ionic lamellar materials with ionic precursor materials for metal oxides. Diverse classes of layered hosts can be utilized for pillared interlayered solids.

The most commonly used host materials are 2:1 clay minerals with cation-exchange properties, especially smectite clays. Smectite clays consist of negatively charged 2:1 layers that are compensated and bounded together by positively charged interlayer cations (Figure 1). A 2:1 layer contains two tetrahedral sublayers with a central octahedral sublayer. The cations in the tetrahedral layer are normally Si^{4+}. The cations in the octahedral layer are normally Al^{3+}, Fe^{3+}, Mg^{2+}, and Fe^{2+}. The interlayer cations, which are ion-exchangeable, are normally Na^+ and Ca^{2+}. The negative charge on the 2:1 layers (the negative layer charge) arises from the substitution of low valent elements for the tetrahedral cations (Si^{4+}) and/or octahedral cations (Al^{3+}, Fe^{3+}, Mg^{2+}) or from a deficiency in the tetrahedral layer and/or octahedral layer.

General formulas of some representative 2:1 clay host materials are shown in Table 1. 2:1 clay minerals are classified in terms of the magnitude of the layer charge: if the layer charge is from 0.2 to 0.6, the mineral belongs to the smectite group, while vermiculites have

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⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1997.

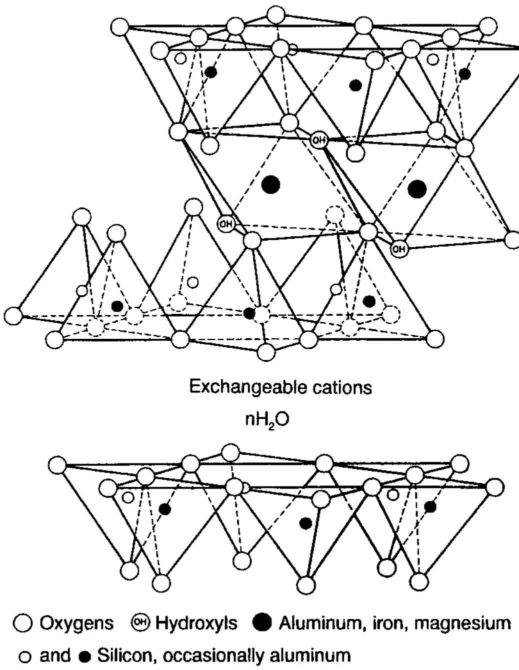

Figure 1. Structure of smectite (from ref 3).

layer charges from 0.6 to 0.9, micas have layer charge ~1, and brittle micas have layer charge ~2. Moreover, different names are given in each group according to the kind of predominant cations in the octahedral layer, and the position of substitution (namely, substitution in the tetrahedral layer or octahedral layer). In naturally occurring clays, considerable deviation from ideal constitutions is realized, and a great variety of substitution is possible. In particular, fluorine may substitute for hydroxyl groups in most species. The fluorine-substituted clays (fluoro clays) can be prepared artificially without hydrothermal treatment and have higher decomposition temperatures. Recently, rectorite, which is a regular interstratified clay mineral composed of expandable montmorillonite-like layers and nonexpandable mica-like layers, was employed as a host material.[4]

Clay host materials having cation-exchange properties other than 2:1 clay minerals involve layered polysilicates such as kanemite ($NaHSi_2O_5{\cdot}3H_2O$), makatite ($Na_2Si_4O_9{\cdot}5H_2O$), magadiite ($Na_2Si_{14}O_{29}{\cdot}xH_2O$), and kenyaite ($Na_2Si_{20}O_{41}{\cdot}xH_2O$), which are composed of silica tetrahedral layers and exchangeable interlayer cations.[5–7]

Host materials having cation-exchange properties other than clay minerals are layered acid salts having the general formula of $M^{IV}(HXO_4)_2{\cdot}nH_2O$ (M^{IV} = Zr, Ti, Sn, Ge; X = P, As) such as metal(IV) hydrogen phosphates (Figure 2) and metal(IV) hydrogen arsenate,[9] and layered oxygen acid salts having the general formula of $A_xM_yO_z$ (A = alkaline metal, alkaline earth metal, Ag; M = transition element (Ti, V, Nb, Mo, W, U)) including titanates, vanadates, niobates, molybdates, tungstates, and uranates.[10,11]

The above-mentioned host materials are laminar cation-exchangers. There are laminar anion-exchangers which may be used for pillared interlayered solids: hydrotalcite-type minerals. These layered double hydroxides (LDHs) are clay minerals having anion-exchange properties, which exist in nature and can be synthesized.[12,13] The structures are based on positively charged brucite-like layers $[R_{1-x}^{2+}, R_x^{3+} (OH)_2]^{x+}$ (R^{2+} = Mg^{2+}, Ni^{2+}, ...; R^{3+} = Al^{3+}, Fe^{3+}, ...) and negatively charged interlayers of anions and molecular water $[X_{x/n}^{-n}{\cdot}yH_2O]^{x-}$ (X = CO_3^{2-}, SO_4^{2-}, NO_3^-, ...).

Synthesis of Pillared Interlayered Solids

Microporous organo clays had been known earlier that were synthesized by exchanging the interlayer cations of smectite clays with bulky organic ions (tetraalkylammonium ions), which separated the clay layers as molecular props and created microporosity between the pillars.[14] These porous solids functioned as molecular sieves[15,16] but lacked thermal stability because of the organic pillars.

In the late 1970s, thermally stable porous pillared smectites were prepared by replacing organic pillars by inorganic ones.[17–20] Since then, tremendous progress has been made in the pillaring techniques, which include (1) the direct intercalation method, (2) the indirect (stepwise) intercalation method, (3) the template-synthesis method, and (4) preparative methods for anion-exchangers.

Direct Intercalation

In general, preparation of porous pillared materials consists of a direct exchange of the interlayer cations of smectite clays by cationic precursors to stable metal oxide pillars, i.e., bulky positively charged species: (1) polynuclear metal hydroxo or oxo complex ions, (2) polynuclear metal hydroxo complex ions bearing organic ligands, (3) metal chelate complex ions, (4) metal cluster complex ions, and (5) positively charged colloidal particles. On heating, these intercalated species are converted to metal oxide pillars, propping open the smectite layers (Figure 3).

(1) Polynuclear Metal Hydroxo or Oxo Complex Ions. These are the most commonly used pillaring agents that are usually obtained by the base hydrolysis of metal salts, although the number of metals that form poly- or oligomeric cations upon hydrolysis is limited. To date, several metal oxide pillared clays have been considered that include aluminum oxide, zirconium oxide, chromium oxide, titanium oxide, iron oxide, and gallium oxide.

The most extensively studied and best understood materials are aluminum oxide pillared clays, which are stable in both oxidizing and reducing atmosphere and offer high thermal stability and high surface areas. Here we describe aluminum oxide-pillared clays in detail and show that what kind of preparative steps and which nature of host materials influence the properties of the pillared derivatives. Most of these factors are equally important in influencing the properties of other pillared interlayered solids.

Aluminum Oxide-Pillared Clays. Al_2O_3-pillared clays have been obtained by the reaction of smectite clays with aluminum polynuclear ionic species formed in partially hydrolyzed solutions of aluminum salt solutions.[17–19,21] These pillared clays have interlayer free spacings (designated as *IS*) of 7–8 Å and Langmuir specific surface areas (designated as *SA*) of ~300 m^2/g after heat treatment of 500 °C.

Usually the intercalation is achieved with hydrolyzed aluminum salt solutions having OH/Al molar ratios of ~1.8–2.2. Investigations of the hydrolysis of aqueous

Table 1. General Formulas of Some Important Clay Host Materials

name of mineral	interlayer cation	cation in the octahedral layer	cation in the tetrahedral layer	anion
⟨smectite group[a]⟩				
montmorillonite	M_x[b]	$(Al^{III}_{2-x}Mg^{II}_x)$	(Si^{IV}_4)	$O_{10}(OH)_2$
beidellite	M_x	(Al_2)	$(Si_{4-x}Al_x)$	$O_{10}(OH)_2$
nontronite	M_x	(Fe^{III}_2)	$(Si_{4-x}Al_x)$	$O_{10}(OH)_2$
saponite	M_x	(Mg_3)	$(Si_{4-x}Al_x)$	$O_{10}(OH)_2$
hectorite (laponite)[c]	M_x	$(Mg_{3-x}Li^I_x)$	(Si_4)	$O_{10}(OH)_2$
⟨vermiculite group[d]⟩				
vermiculite	M_x[e]	(Mg_3)	$(Si_{4-x}Al_x)$	$O_{10}(OH)_2$
⟨mica group[f]⟩				
Na-taeniolite	Na_1	(Mg_2Li_1)	(Si_4)	$O_{10}(F)_2$
Na-tetrasilicic fluoro mica	Na_1	$(Mg_{2.5})$	(Si_4)	$O_{10}(F)_2$
⟨others⟩				
rectorite[g]		interstratified clay mineral		

[a] Layer charge is from 0.2 to 0.6. [b] Interlayer cations are usually sodium, but other species may also be found, notably calcium. [c] Laponite is synthetic hectorite. [d] Layer charge is from 0.6 to 0.9. [e] Interlayer cations are usually magnesium. [f] Layer charge is ~1.0. [g] Composed of expandable montmorillonite-like layers and nonexpandable mica-like layers.

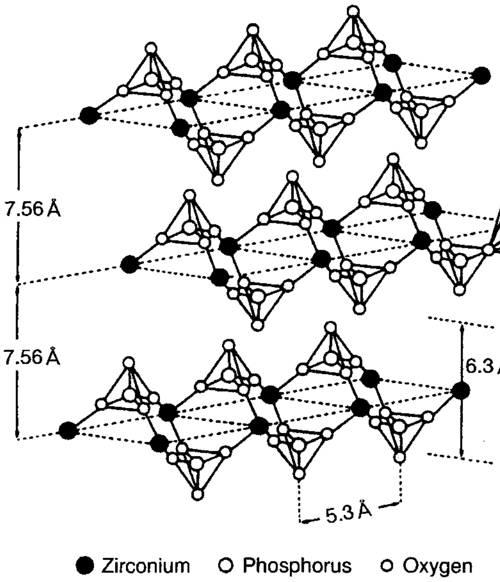

Figure 2. Structure of α-zirconium phosphate (from ref 8).

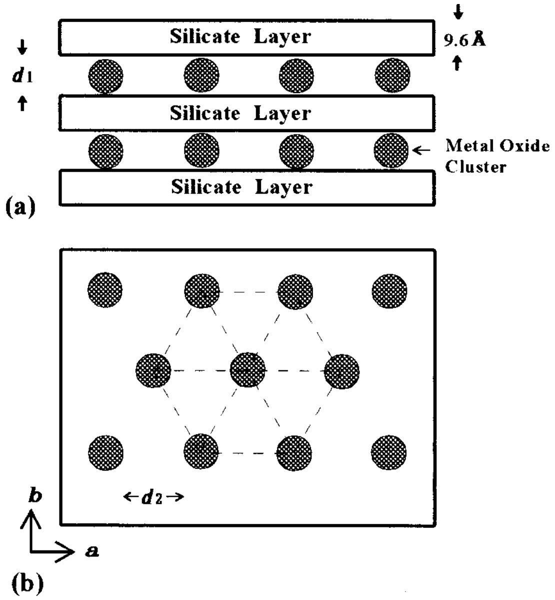

Figure 3. Schematic model of an ideal pillared interlayered smectite: (a) side view; (b) basal view. d_1 = interlayer spacing; d_2 = interpillar distance.

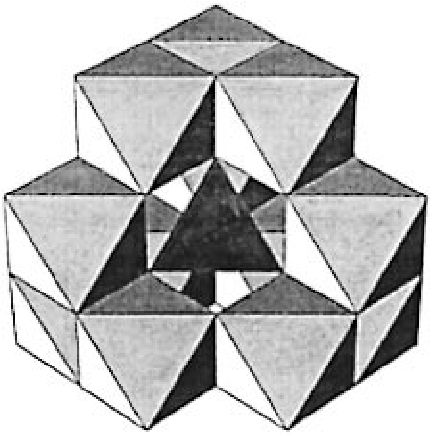

Figure 4. Structure of the Al_{13} complex (from ref 30).

aluminum salt solutions suggest that several kinds of aluminum complexes are present in the solutions, but the tridecameric cation $[Al_{13}O_4(OH)_{24}(HO)_{12}]^{7+}$ (abbreviated Al_{13}) is predominant for a hydrolysis ratio R (=OH/Al) of approximately 1.5−2.3.[22−25]

The pillaring species of the intercalates has been assumed to be the Al_{13} ion: ^{27}Al NMR studies demonstrated that Al_{13} is present in the interlamellar space of the intercalates as well as in hydrolyzed Al solutions;[26,27] moreover, the observed layer expansion (=interlayer spacing) is consistent with the size of the Al_{13} ion. The Al_{13} ion, which is one of the Keggin isomers, consists of 12 aluminum octahedra surrounding a central aluminum tetrahedron (Figure 4)[28−30] and is approximately 8.6 Å in diameter.[31]

The base hydrolysis of aluminum salt solutions is usually performed by sodium hydroxide but occasionally is carried out by amines instead of inorganic bases in order to avoid any competition of the alkali-metal ions with the Al_{13} ions in the subsequent ion-exchange process.[32−35]

Al_{13} pillaring solutions that contain mainly the Al_{13} species are also prepared by electrolytically dissolving aluminum metal in an aluminum chloride solution[36,37] or by reacting aluminum metal with hydrochloric acid solutions.[38] The former solution, commercially available, is referred to as aluminum chlorohydrate (ACH) solution.

The Al_{13} ions in these pillaring solutions were once considered to be selectively intercalated among several kinds of aluminum complex ions into the interlamellar region of clays, because the high-charge Al_{13} ions are predominant in these solutions. However, it has been revealed that the selectivity of aluminum complex ion taken up by the clay varies depending on the layer charge and other factors.[39−41]

Therefore, the use of solutions containing exclusively the Al_{13} ions is essential to obtain distinct and reproducible results on the pillared clays, although experiments have been rarely conducted with pure Al_{13} solutions.

The pure Al_{13} solution is prepared in the following way.[22,42] The Al_{13} cation can be crystallized as sulfates and selenates.[30,43] The Al_{13} cation is first precipitated as the aluminum sulfate, $[Al_{13}O_4(OH)_{25}(H_2O)_{11}](SO_4)_3 \cdot xH_2O$ by the addition of sulfate anions to an aluminum-hydrolyzed solution. Then the precipitate was filtered off and redissolved with $BaCl_2$ or $Ba(NO_3)_2$ by a displacement reaction. Subsequently solid $BaSO_4$ is filtered off and then the filtrate is the pure Al_{13} solution. The addition of the filtrate to acetone leads to the solid water-soluble Al_{13} chloride.

The intercalated Al_{13} ions further hydrolyze between the silicate layers[41,44] (namely, upon intercalation, the charge of the Al_{13} ions varies due to the polarization effect[45]), and the hydrolysis of Al_{13} in the atmosphere finally results in the destruction of the Al_{13}.[46] Therefore, the calcination of the intercalates with the Al_{13} ions must be performed soon after the intercalation and drying.

Upon calcining the intercalates with the Al_{13} ions, the Al_{13} ions dehydrate and convert to aluminum oxide pillars, and then a chemical reaction between the silicate layers and the pillars is induced for the smectites having substitution in the tetrahedral layer or the presence of F atoms.[26,27,47−51]

The atomic force microscope analysis revealed that the pillaring reaction of montmorillonite with alumina cluster leads to stretched clay silicate layers, while in alumina-pillared rectorite there is no stretching deformation of the silicate layers.[4,52]

Properties of Al-pillared clays are influenced by a number of other preparative steps such as the method of washing,[41,53] aging,[54,55] and drying.[56] Base-hydrolyzed aluminum salt solutions are occasionally aged at elevated temperatures to produce pillared clays with higher thermal stability.[54,55] However, aging of the Al_{13} solution gradually generates a dimer of Al_{13}, which is formed by the condensation of two Al_{13} ions.[22,57] Freeze-drying favors the formation of delaminated clays and a house-of-cards structure, leading to a broad pore size distribution.[56,58]

The choice of host materials greatly influences the properties of pillared clays. As mentioned above, upon calcining clays with the Al_{13} ions, a chemical reaction between the host material and the pillaring agent occurs when smectites with tetrahedral substitution (e.g., beidellite, saponite) or smectites containing F atoms (e.g., fluorohectorite) are employed. In contrast, there is no reaction for smectites without tetrahedral substitution (e.g., montmorillonite, hectoite, laponite).

Clays have their own intrinsic acidic properties. For example, montmorillonite contains both weak Brönsted and Lewis acid sites; saponite has Lewis acid sites, but no Brönsted acid sites;[59] Na−tetrasilicic fluoro mica has no acid sites.[60]

Since the fluorine-substituted clays (fluoro clays) have high decomposition temperatures, pillared clays derived from these clays exhibit high thermal stability.[61] Rectorite pillared with alumina clusters showed zeolite-like high hydrothermal stability, which is attributed to the presence of nonswellable mica-like layers in the pillared structure.[4]

The magnitude of layer charge is responsible for pillar density, namely, pore structure, surface area, and thermal stability. The crystallinity of clays plays a vital role on the thermal stability and homogeneity of the corresponding pillared solids.

Gallium Oxide-Pillared Clays. Smectites have been pillared with partially hydrolyzed solutions of gallium and gallium−aluminum.[62−67] These pillaring precursors are the $Ga_{13}([GaO_4Ga_{12}(OH)_{24})(H_2O_{12})]^{7+})$ and the $GaAl_{12}([GaO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+})$ cations, which have similar structure to the Al_{13} ion. Ga_{13}- and $GaAl_{12}$-pillared clays have an *IS* of 8 Å and BET *SA*s of ~300 m^2/g after 500 °C; the thermal stability of the $GaAl_{12}$ pillars is greater than those of Al_{13} pillars and Ga_{13} pillars.

Iron Oxide-Pillared Clays. Fe_{13} ($[Fe_{13}O_4(OH)_{24}(HO)_{12}]^{7+}$), an ionic species that is structurally analogous to the Al_{13} ion, is suggested to be formed upon base hydrolysis of iron(III) aqueous solutions.[68] This Fe_{13} ion is extremely labile and quickly decomposes, but the addition of iron(II) stabilizes the Fe_{13} ion. The *IS* of the smectite intercalated with the Fe_{13} ion is ca. 9.7 Å, which is identical with the spacing of the smectite intercalated with the Ga_{13} ion.

Furthermore, iron-pillared clays with large gallery heights ($IS = 13-18$ Å after 350 °C) were obtained by cation exchange of smectite with base-hydrolyzed solutions of iron(III) salts.[69] The Fe-pillared clays were unstable even under ambient conditions.

Chromium Oxide-Pillared Clays. A variety of oligomeric and polymeric chromium(III) species (dimer, trimer, tetramer, and higher polymers) are formed during the base hydrolysis of chromium(III) in aqueous solution;[70−74] the existence of the Cr_{13} species analogous to the tridecameric aluminum(III) and gallium(III) ions (Al_{13} and Ga_{13}) has been suggested.[75] Several kinds of Cr-pillared clays,[76−79] including one with a high interlayer spacing of 18 Å at 25 °C,[80] were obtained. However, these pillared clays are unstable at elevated temperatures in air due to oxidation.

Zirconium Oxide-Pillared Clays. ZrO_2-pillared clays are of particular interest, because they are stable at high temperatures, having high surface areas and large interlayer spacings of over 10 Å.[19,81,82] In the synthesis of ZrO_2-pillared clays, zirconium oxychloride solutions are commonly employed as the pillaring solution. The predominant species in aqueous zirconium oxychloride solutions at room temperature is the zirconium tetrameric cation, $[Zr_4(OH)_8(H_2O)_{16}X_z]^{(8-z)+}$ (X = Cl, Br),[83−85] and the formation of an intercalate with the zirconium tetramer was reported by the reaction of smectite with a zirconium oxychloride solution at room temperature.[20]

Addition of a base to zirconium oxychloride solutions or heating or other aging of the solutions brings about hydrolytic polymerization of the zirconium tetramer in the solutions;[86−88] Zr-pillared clays with large layer spacings were obtained by the reaction of clays with hydrolyzed zirconium oxychloride solutions.[19,81,82,89−91]

It was postulated that two higher polymerized species are generated by the hydrolytic polymerization of the

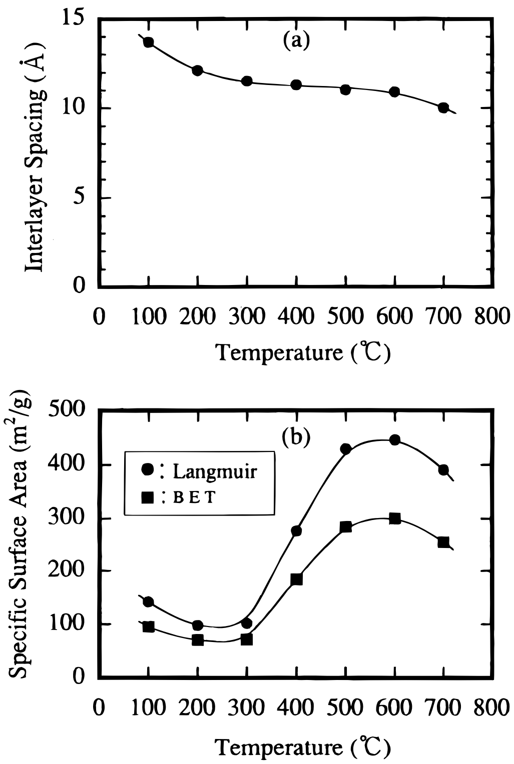

Figure 5. Changes in (a) interlayer spacings and (b) specific surface areas by the Langmuir and the BET models with heating temperature for a Zr-pillared clay with a 14 Å interlayer spacing (from ref 82).

zirconium tetramer, providing intercalates with 12 and 14 Å interlayer spacings.[82] These two polymeric species are composed of three-dimensionally polymerized clusters based upon the tetramer. The Zr-pillared clay with a 14 Å interlayer spacing has a regular structure and homogeneous pore structure, showing a high thermal stability up to 700 °C. The product after calcination at 500 °C has an *IS* of 11 Å and a Langmuir *SA* of 420 m²/g (Figure 5).

Titanium Oxide-Pillared Clays. Titanium oxide pillars were inserted into the smectite layers using polymeric Ti cations obtained by hydrolysis of titanium(IV) tetrachloride in hydrochloric acid or sulfuric acid,[92−94] and by hydrolysis of titanium(IV) sulfate solutions.[95] These TiO_2-pillared clays have *IS*s of ~18 Å and BET *SA*s of ~270 m²/g after 500 °C.

Other Pillared Clays. Rare earth-aluminum oxide pillared smectites with an *IS* of 17 Å were prepared by the reaction of smectite with hydrothermally treated mixtures of aluminum chlorohydrate (ACH) and chlorides of La, Ce, Pr, Nd. Large polymeric rare-earth-bearing aluminum cations are believed to be formed during the hydrothermal treatment.[96,97]

(2) Polynuclear Metal Hydroxo Complex Ions Bearing Organic Ligands. Polynuclear metal hydroxo complex ions bearing organic ligands have been prepared from the hydrolysis of organic molecules and replaced with the interlayer cations of smectites. The intercalated metal oxide clusters are silicon oxide, iron oxide, titanium oxide, chromium oxide, tantalum, and niobium oxide.

Silicon oxide-pillared clays were synthesized by the in situ hydrolysis of tris(acetylacetonate)silicon(IV) cations between the smectite layers.[98,99] Furthermore, smectite clays were intercalated with three-dimensional cationic silicon complexes (oligosilasesquioxanes) which were derived from the hydrolysis of organosilanes.[100,101] The latter SiO_2-pillared clays after heating at 500 °C exhibited an *IS* of 9.6 Å and a BET *SA* of 400 m²/g.[100]

Iron oxide-pillared clays with an *IS* of 7 Å were obtained from the reaction of trinuclear (acetatohyroxo)iron(III) complex ions with smectite followed by calcination at 500 °C.[102,103] However, high-resolution transmission electron microscopy revealed the existence of isolated large iron(III) oxide particles along with the Fe_2O_3-pillared clays.[104]

Titanium oxide-pillared clays were prepared from trinuclear (acetatochlorohydroxo)titanium(III) complex ions[105] and from polynuclear titanium cations obtained by (hydrochloric acid)/(titanium alkoxide) solutions.[106]

Chromium oxide-pillared smectites with an *IS* of 6 Å after calcination under ammonia at 500 °C were obtained by the intercalation of (acetatohydroxo)chromium(III) complex ions.[107]

Zirconium oxide-pillared clays with a large gallery height were prepared using a zirconyl acetate solution as the pillaring solution.[108] The resulting solid after heating to 400 °C had an *IS* of 11 Å and a *SA* of 300 m²/g.

A niobium oxide-pillared clay was prepared by the reaction of smectite with niobium(IV) polymeric complex species obtained by the hydrolysis of $Nb_4O_7Cl_7(OC_2H_5)_2(dipyridyl)_2 \cdot 2H_2O$.[109]

(3) Metal Chelate Complex Ions. Incorporation of metal chelate cations $M(chel)_3^{2+}$ (M = Fe, Ni; chel = phen, bpy) into smectite clays and subsequent calcination provided iron oxide- and nickel oxide-pillared materials.[110] Moreover, pillared smectites with a double oxide ($LaNiO_x$) were prepared by intercalation of a heterobinuclear cationic chelate complex of the form $NiLa(fsaen)^+$ (H_4fsaen = *N,N′*-3-hydroxysalicylidene-ethylenediamine) into smectite followed by calcination.[111] The products after 500 °C calcination had an *IS* of 3.8 Å and a BET *SA* of 220 m²/g.

(4) Metal Cluster Complex Ions. Pillaring of smectite with niobium and tantalum oxides was achieved with the cation exchange and subsequent oxidation of niobium and tantalum cluster cations of the type $M_6Cl_{12}^{n+}$ (n = 2,3; M = Nb, Ta, Mo). The niobium oxide- and tantalum oxide-pillared clays after calcination at 325 °C exhibited an *IS* of 9 Å and BET *SA*s of 60−70 m²/g.[112]

(5) Positively Charged Colloidal Particles. Positively charged metal oxide sols may be intercalated into the interlayer of clays by cation-exchange reactions, providing pillared materials after calcination. Although pillared materials with super galleries were made, the pore structure is not homogeneous, and the pore size distribution occurs over a broad range because the interlamellar region is stuffed with flocculated sol particles of different sizes. Using this pillaring technique, TiO_2-pillared smectites (*IS* = 13 Å; BET *SA* = 300 m²/g after 300 °C),[113] (SiO_2-TiO_2)-pillared smectites,[114] Al_2O_3-pillared smectites,[115,116] and SiO_2-pillared smectites[117] were obtained. Moreover, pillared clays with mesopores were obtained from (SiO_2-TiO_2) pillared clays by modification of the surfactant.[118]

Supercritical drying of smectites intercalated with colloidal particles leads to the formation of a card-house structure, generating much larger pore volume including meso- and macropore than air-dried samples.[119,120]

Monodispersed sol particles having the same diameter may be produced by the homogeneous precipitation method.[121] Here one must devise a technique of introducing the monodispersed particles without flocculation into the interlayer of clays.

Indirect (Stepwise) Intercalation[122]

Smectite clays can swell in aqueous solutions and, consequently, can react directly with large pillaring species in aqueous solutions. However, other layered host materials possess generally high charge densities, showing limited swellability in aqueous solutions. Hence, they usually cannot exchange directly with such species, and preswelling of the layered substance by amine is performed prior to the insertion of pillaring species. Amines readily intercalate into these hosts to form alkylammonium-intercalated derivatives, and the expanded layers permit the subsequent ion-exchange reaction of the interlayer alkylammonium ions with large cationic pillar precursors.

Most of the preparative steps (e.g., preparative method of pillaring agents, method of aging and drying, etc.) that influenced the properties of pillared clays prepared from the direct intercalation method similarly influence the properties of the pillared materials obtained from this indirect intercalation method.

There are successful stepwise syntheses of Al_2O_3-pillared titaniumphosphate,[123] Al_2O_3-pillared tetratitanate,[124] Al_2O_3-pillared α-tin phosphate,[125] Al_2O_3-pillared buserite,[126] Al_2O_3-pillared magadiites,[35] Al_2O_3-pillared titanate,[32] Cr_2O_3-pillared α-tin phosphate,[127] Cr_2O_3-pillared α-zirconium phosphate,[128] and mixed ($Al_2O_3-Cr_2O_3$)-pillared α-zirconium phosphate.[129] These chromium oxide-pillared solids were obtained from the reaction of acetatohydroxochromium(III) complex ions with alkylammonium-intercalated layered phosphates and subsequent calcining of the products.

In the synthesis of these aluminum oxide-pillared solids, the Al_{13} ions were used as the cationic pillar precursor. Upon pillaring phosphates with an alumina cluster, strong bonds (Al−O−P) between the pillars and the phosphate layer are formed.[130,131] This seems to be responsible for the fact that the *IS*s (5−6 Å) of alumina pillared phosphates are always smaller than those (~9 Å) in smectite clays.[130] Recently, alumina pillared α-zirconium phosphates with an *IS* of 14.8 Å (at 25 °C) were obtained using a dimer of Al_{13} and intercalating under reflux and hydrothermal treatment in the presence of F^-.[131]

SiO_2-pillared metal(IV) phosphates (ZrP and SnP) were produced from indirect intercalation of oligosilasesquioxanes formed by the hydrolytical polymerization of organosilanes.[8,132−134]

Sodium trititanate ($Na_2Ti_3O_7$) was, however, pillared with the Al_{13} by direct intercalation under certain conditions.[135]

Template Synthesis

This method provides a means of manipulating pillared solids with super galleries.

Aluminum oxide-pillared clays with large interlayer spacings were afforded by pillaring smectites with the Al_{13} oligomers in the presence of poly(vinyl alcohol) (PVA).[136−140] Al_{13} pillaring solutions were added to the suspension of PVA−smectite complexes with expanded gallery space and then aged at 60 °C. PVA was considered to act as a template, and condensation of Al oligomers occur in the interlamellar region. Removal of the PVA by calcination at 500 °C created pillared solids with an *IS* of 14 Å and BET *SA*s of about 310 m^2/g. The pore size is controlled through the choice of concentrations of PVA or the Al_{13} in solution.

Table 2. Properties of Silica-Pillared Sodium Titanates with Varying *d* Spacings after Calcination at 538 °C (after Landis et al.[141])

preswelling agent	surface area, m^2/g	increase in *d* spacing,[a] Å	cyclohexane adsorption, wt %
starting material $Na_2Ti_3O_7$	<5	<1	<1
propylammonium	50	2−3	<3
hexylammonium	200	9	6
octylammonium	280	12	9
dodecylammonium	470	21	16

[a] The increase in *d* spacing is calculated by the formula d_{001} (pillared) − d_{001} (layered phase), where d_{001} (layered phase) = 8.4 Å.

Silicon oxide-pillared products of kenyaite,[141] magadiite,[142] alkali titanates,[143] and smectite[144] were produced as follows: The layered metal oxides were first preswelled by the intercalation of alkylammonium ion, and then an organic pillar precursor such as tetraethyl orthosilicate (TEOS) was absorbed into the organophilic interlayer region, where alkylammonium is a templating surfactant and siloxane polymer was formed by hydrolytic polymerization of the metal alkoxide. Calcining the derivatives removes the organogroups and completes the dehydroxylation of the siloxane polymer. The pore structure of the products can be tailored by varying the chain length of the alkylammonium or the concentration of TEOS (Table 2). The template-synthesis approach seems to be a promising route for tuning of the pore structure with the same pillar species, whereas the pore structure has not been elucidated and a problem of residual carbon after calcination remains.

Pillared Solids from Anion-Exchangers (LDHs)

Layered double hydroxides (LDHs) are anion exchangers. As they usually have high charge densities, they do not swell in water, encountering some difficulty in ion-exchange reactions such as lamellar cation exchangers with high charge densities. Pillaring of LDHs with bulky polyoxometalate anions (POMs) has been attained by four different routes: (1) direct anion exchange, (2) indirect anion exchange, (3) reconstruction method, and (4) coprecipitation method. The structure of a polyoxovanadate species (decavanadate $V_{10}O_{28}{}^{6-}$) is illustrated in Figure 6.

POM species have a complex equilibrium in solution, and the distribution of these species depends on the pH and concentration of POM anions. Hence, optimization of pH and concentration of POM anions is of great importance during the synthetic procedure of POM−LHD intercalates.[145] During pillaring reactions in solutions, hydrolysis of the LDHs or POMs may occur because LDHs are basic, whereas most POM ions are acidic.[146] Furthermore, defects may be generated in the LDH layers owing to strong interactions between the basic LDH layers and acidic POM ions.[147]

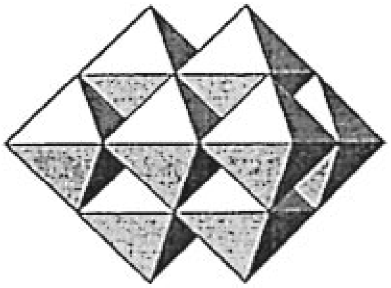

Figure 6. Structure of decavanadate ion ($V_{10}O_{28}^{6-}$) (from ref 145).

Pillared LHDs with POMs have generally low thermal stability, because LDHs dehydrate below 500 °C. Furthermore, even gentle thermal treatment of a POM ($V_{10}O_{28}^{6-}$)–LDH intercalate causes a chemical transformation of the intercalated species.[148]

(1) Direct Anion Exchange. Anion exchange of polyoxometalate ions with interlayer anions was performed using the Cl^- and NO^{3-} forms of LDHs, which undergo relatively facile displacement reaction in solutions.[149,150] $V_{10}O_{28}^{6-}$ POMs yielded pillared derivatives with an *IS* of 7.1 Å.[149] α-$[H_2W_{12}O_{40}]^{6-}$ and α-$[SiV_3W_9O_{40}]^{7-}$ POMs with Keggin structures yielded pillared derivatives with an *IS* of 9.8 Å and BET *SA*s of 63 and 155 m^2/g after 130 °C, respectively. The exchange reaction depended upon both the charge and geometry of the POM anions.[150] However, completely wet and swollen NO^{3-} forms of LHD were intercalated with $PW_{12}O_{40}^{3-}$, $PV_2W_{10}O_{40}^{5-}$, $PV_3W_9O_{40}^{6-}$, and $PV_4W_8O_{40}^{7-}$ ions, and it was found that the ease of the exchange reaction is almost independent of the anion charge, provided that the LDH is thoroughly wet.[147]

(2) Indirect Anion Exchange. LDHs were first intercalated with large organic anions prior to polyoxometalate exchange. The intermediate swelling of LDHs then facilitated ion exchange of POMs ($Mo_7O_{24}^{6-}$ ion[148,151] and $V_{10}O_{28}^{6-}$ ion,[145,148,151] $H_2W_{12}O_{40}^{6-}$ and $SiW_{11}O_{39}^{8-}$ ions[146]) for the organic species. Normally, these exchange reactions occur immediately and competing hydrolysis of the POM anions is depressed. Well-ordered LDH intercalates with organic anions result in the production of homogeneous pillared derivatives. They were obtained by the reaction of an organic acid with LDHs having interlamellar hydroxyl ion in the presence of glycerol as a swelling agent.[146]

The thermal decomposition process of a $V_{10}O_{28}^{6-}$-intercalated LDH (magnesium–aluminum hydroxide framework) was revealed as follows.[148] The intercalated decavanadate ions ($V_{10}O_{28}^{6-}$) transform into cyclic and chainlike metavanadate species between 160 and 350 °C. Above 350 °C, the LHDs layer structure begins to collapse. At temperatures over 450 °C, reaction between the metal oxide (dehydroxylated collapsed LHD layer) and the metavanadate species takes place to form magnesium vanadates.

(3) Reconstruction by Hydration of Calcined LDHs. Calcined materials of LDHs adsorb various anions to regenerate the LDH structure. Intercalation of POMs ($Mo_7O_{24}^{6-}$ and $V_{10}O_{28}^{6-}$ ions) was effected by exposure of calcined LHDs to POM solutions.[152]

(4) Coprecipitation Method. α-$SiW_{11}O_{39}^{8-}$ pillared LDH (zinc–aluminum hydroxide matrix) was prepared by the coprecipitation reaction of Zn^{2+} and Al^{3+} ions in the presence of α-$SiW_{11}O_{39}^{8-}$ ions.[153] In this procedure, pH compatibility is important between the LDH and the POM ions.

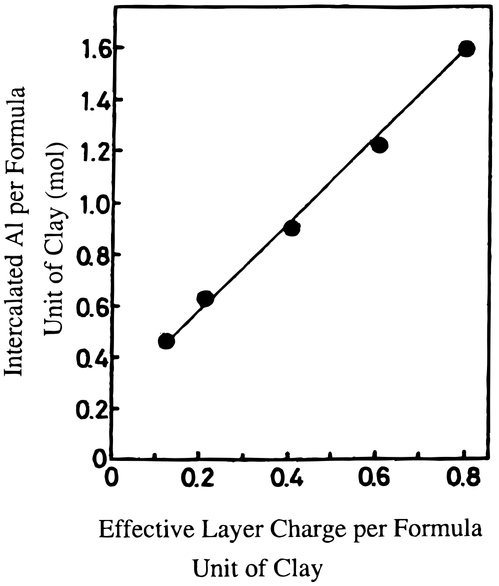

Figure 7. Intercalated Al content against effective layer charge of reduced-charge fluoro clays (modified from ref 40).

Modification of Pillared Interlayered Solids

(1) Control of Lateral Pore Opening through Varied Pillar Density. A series of pillared derivatives differing only in pillar concentration, namely, a series of pillared derivatives having different lateral pore openings, are prepared using reduced-charge host materials. There are two paths for preparing reduced-charge cationic 2:1 clay minerals: (1) synthesis of clays by isomorphous substitution[39,154] and (2) heat treatment of clays.[155–161]

Fluoro clays having different layer charges, $Na_xMg_{3-x}Li_xSi_4O_{10}F_2$ ($x = 0.4-1.0$) were synthesized by isomorphous substitution, and the Li ion-exchanged forms of them showed good swellability and ion-exchange ability.[39]

Heat treatment induces a charge reduction in cationic 2:1 clay minerals: during the thermal treatment, small interlayer cations migrate toward the vacant octahedral sites (Hofmann–Klemen effect[155]). In addition, large interlayer cations are fixed in the hexagonal holes, resulting in a decrease of their exchange capacity. Thus, the production of pillared layered materials of varied and controlled pillar density is attained.[156–161]

A series of Al_2O_3-pillared clays obtained from pure Al_{13} solution and fluoro clays having different layer charges showed that the amount of alumina taken up by the clay increased with increasing charge density (Figure 7).[40] However, the control of the lateral pore size was restricted to an appropriate layer-charge range because the amount of pillar fixed by smectite influences the thermal stability of pillared clays. Pillared clays with low pillar density have low thermal stability and are inclined to have irregular micropores on heating.

LDHs have the chemical formula of $[R_{1-x}^{2+}, R_x^{3+}(OH)_2]^{x+}[X_{x/n}^{n-}\cdot yH_2O]^{x-}$, and the structures can exist for values of x between 0.1 and 0.5. Hence, one may think that LDHs are a good candidate for the production of pillared solids having varied pillar density.

However, in general, pure hydrotalcite-like compounds are obtained only for $0.2 \le x \le 0.33$.[13]

Establishment of the tuning of the pore structure of pillared solids with the same host and guest materials remains to be explored.

(2) Control of Acidity. Pillared interlayered clays contain usually both Brönsted and Lewis acid sites.[162] Apparently, these acidic properties are associated with the kind and the amount of interlayer pillars as well as the nature of the parent clays. Generally, the main source of the Lewis acidity stems from the pillars, while the Brönsted acidity mainly results from proton attack on the clay sheets.[59] The protons are generated by dehydroxylation of pillaring cationic species upon calcining the intercalates. For example, protons are released from the Al_{13} ions as follows:[21]

$$2[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+} \rightarrow 13Al_2O_3 + 14H^+ + 41H_2O$$

Al_2O_3-pillared smectites with Brönsted and Lewis acid sites were found to exhibit acidity predominantly of the Lewis type at high temperatures (over ~300 °C under vacuum).[162-164] These Lewis acid sites at high temperatures are believed to promote coke formation and deactivate the pillared clays quickly in most hydrocarbon reactions.[163] In contrast, in HY zeolites both Brönsted and Lewis acid sites remain at high temperatures, and the ratio of Brönsted to Lewis acid sites is >1.[163,164] The strong Lewis acid sites of Al_2O_3-pillared smectites at high temperatures were found to decrease in a H_2 stream using Pd-loaded Al_2O_3-pillared smectite.[164]

To improve the acidity and catalytic activity of pillared clays, silicate host materials have been modified through cation fixation (Ca^{2+}, La^{2+}, etc.)[54,165-167] and alumina pillars modified by silica,[48] zirconia,[168] boron,[168] Cr^{3+},[169] Fe^{3+},[170] and phosphorus.[171] Zirconia pillars have been modified with sulfate[172] and iron oxide pillars converted into ironsulfide.[173,174]

Problems and Future Issues

Twenty years have passed since the first announcement of a pillared interlyered clay. The preparative techniques have progressed remarkably with a wide variety of pillared solids being made. Adsorption studies revealed that pillared solids exhibit selective adsorption,[21,80,82,175] and studies with HPLC proved that they perform separations of aromatic isomers (Figure 8).[176-178] Furthermore, gas separation was carried out conveniently using pillared clays.[81,179] Extensive studies have shown the potential use of pillared derivatives in catalysis, which is summarized elsewhere.[180-182]

However, there have not been any actual commercial uses for pillared solids yet. The reasons are in part due to the facts that (1) the problem of reproducibility remains and (2) structure–property relationships have not been established.

(1) Reliable and Reproducible Procedures. The properties of pillared materials are influenced by the nature of the host and guest materials as well as the preparative steps. Concerning the host materials, synthesis of layered solids is required with high crystallinity, homogeneous structure, and composition and as well as a series of similar compounds with varied charge density. Natural solids, usually containing impurities, have wide diversity in their nature (composition, structure, etc.) even when they belong to the same kind of minerals.

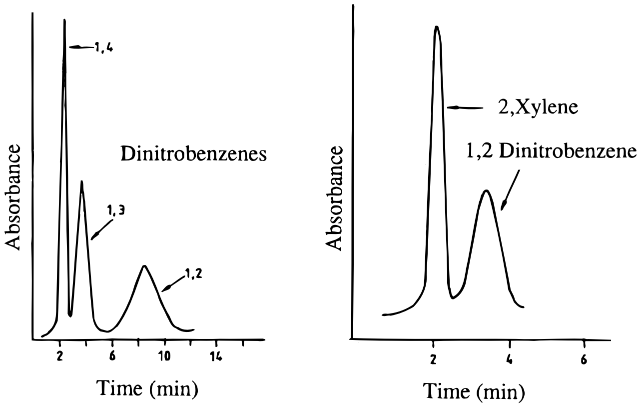

Figure 8. Separation of aromatic isomers on a zirconium oxide-pillared smectite column; eluent = methanol; flow rate = 1 mL min^{-1}; temperature = 70 °C (from ref 176).

Upon intercalation, positively charged guest species formed by the hydrolysis of metal salts further hydrolyze within the interlayer of the host, and the degree of this hydrolysis depends on the layer charge. Upon calcining the intercalates, chemical reactions between the host material and the pillaring agent occur depending on the nature of the host materials. The magnitude of the layer charge is associated with pillar density, namely, pore structure, surface area, and thermal stability. The composition and structure of the host materials are responsible for the thermal stability of the corresponding pillared solids. Pillared clays derived from fluoro clays and rectorite exhibit high thermal stability. The crystallinity of the host materials plays a vital role not only in the thermal stability but also in the homogeneity of the pillared derivatives. Furthermore, host materials have their own intrinsic acidic properties.

As guest species, the use of stable, well-identified and characterized, pure species is recommended. The most commonly used pillaring agents obtained by the hydrolysis of metal salts contain several kinds of minor constituents, which sometimes cannot be bypassed during ion-exchange reactions due to ion selectivity. The selectivity of the ionic species fixed by the host materials varies depending on the layer charge. Therefore, the use of solutions containing exclusively one species is essential to obtain reproducible results.

Besides, preparative steps such as the method of drying (air-drying; freeze-drying; supercritical drying), aging, etc., all have effects on the properties of the pillared solids.

In POM-pillared LDHs, there is intrinsically the problem of alternation of acidic POM ions and basic LDH layers. Moreover, even upon mild heat-treatment, intercalated POM anions ($V_{10}O_{28}^{6-}$) transform into other species.

(2) Pore Structure. The assessment of pore structure is indispensable for the application of pillared solids. Pore sizes in pillared clays are characterized in terms of both longitudinal and lateral pore size. The longitudinal pore size (=interlayer distance; interlayer spacing; interlayer separation; gallery height) is calcu-

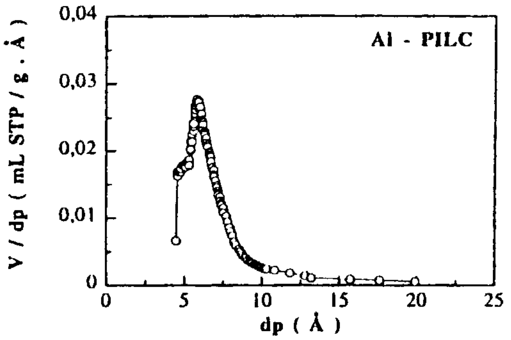

Figure 9. Micropore size distribution graph for Al_{13}-pillared montmorillonite (dried at 120 °C) obtained by the Horvath−Kawazoe model (from ref 183).

lated by subtracting the layer thickness of the host materials from the value of observed X-ray basal spacing. The lateral pore size (interpillar distance) is estimated by molecular probing,[21,80,82,175] and gas adsorption−desorption isotherm analysis.[81,179,183]

Molecular probe studies, that is the measurements of adsorption of molecules of different molecular dimensions, give effective lateral pore size, although probe molecules with large kinetic diameter are limited.[184]

Gas adsorption−desorption isotherm analysis gives physical pore size including pore-size distribution and the degree of homogeneity of the pore structure. Several models concerning this analysis have been proposed.[185] The BJH and CI models using Kelvin equation are not applicable to micropore analysis. The Horvath−Kawazoe model based on a slit-pore model and the Saito−Foley model based on a cylindrical-pore model are applied to pillared interlayered solids (Figure 9).[179,183,186] There are uncertainties as to which model works better for pillared materials and how to interpret the pore distribution curves because bimodal pore size distribution (=the presence of two micropore sizes) is common for pillared solids.[183,186] The Dubinin−Radushkevich formula is used to describe the energetic heterogeneity of microporous solids, which seems to reflect a nonuniform microporous structure in pillared interlayered solids.[183]

Structure−property relationship of pillared solids can be established only when the pore structure of the pillared solids as well as the composition and structure of the host and guest are clarified.

(3) Other Issues. *(i) Deactivation of the Acid Sites on the External Surfaces of Pillared Solids.* Host materials have ion-exchange properties on the external surfaces as well as on the internal surfaces. Consequently, guest clusters exist not only on the internal surfaces but also on the external surfaces, whereas the external area of pillared solids is small in comparison to the internal area. Therefore, when diffusion limitations in the two-dimensional pore system become significant, external active sites (external pillar agents) must be deactivated so that they do not contribute to the shape-selective catalytic reaction. Deactivation of the exterior acid sites is effected by organic bases that are too large to penetrate into the pores.[187]

Diffusion phenomena is associated with both the pore structure of the pillared derivatives and the diffusion substances. Diffusion studies of organic molecules in pillared clays have been performed;[188−190] diffusivities of C_6−C_{10} *n*-paraffins in a smectite pillared with aluminum oxide showed that these molecules were allowed to transport easier than 5A, Y, and T zeolites.[188] Further studies are required to elucidate the nature of the diffusion phenomenon.[189]

(ii) Metal-Loaded Pillared Solids. Incorporation of transition metals into the two-dimensional nano cavities opens a way to versatile potential applications of pillared materials in catalysis and in molecular devices.[191] Some approaches have been carried out,[192] but loading of a large amount of metal solely on the intracrystalline walls has not been achieved yet.

(iii) Application. A range of potential applications of pillared interlayered solids has been discussed in terms of their pore structure and physicochemical properties: adsorbents, separating agents, catalysts, and so on. New applications need to be explored besides these classical uses. The voids of pillared solids offer a cosseted environment to encapsulate readily degraded substances, volatile materials, etc. which are not easy to handle in air; the voids act as templates for low-dimensional material synthesis. Moreover, new kinds of molecular devices (molecular electronics/optics) and molecular functional materials will be provided by organizing semiconductor materials, conductive polymers, and metal clusters in the nanometer-dimension cavity of pillared solids: for example, optical devices using quantum size effect of semiconductor interpillars, functional materials for photochemical reactions using the photoelectric effect of semiconductor interpillars, and so on.

Other Porous Materials

Different types of micro- and mesoporous materials have been prepared by different approaches. Microporous amorphous metal oxides with pore diameters between 6.5 and 7.7 Å and with a narrow pore size distribution were synthesized by a sol−gel process.[193]

A new family of molecular sieves denoted M41S has been reported recently, which is composed of aluminosilicate with regular arrangements of mesopores.[194−196] These M41S type materials, including the hexagonal phase (MCM-41), the cubic phase (MCM-48), and a lamellar phase, have been prepared by aluminosilicate gels in the presence of surfactants through a templating mechanism.

MCM-41 has regular arrays of one-dimensional hexagonally ordered channels such as honeycomb structure; the pore diameter can be varied in the range of approximately 15−100 Å by varying the alkyl chain length of the surfactant or by adding an auxilliary organic molecule to the synthesis. However, the pore size distribution for MCM-41 materials is not narrow. A MCM-41 sample with a pore size of ~40 Å exhibits the half width of 4 Å at the ~40 Å peak in the pore-size distribution curve (Figure 10).[196]

The templating approach has been extended and generalized as a route for preparing mesoporous materials.[197−199] A lot of potential catalytic and separation applications for the M41S family have been suggested,[200] but they are in a rather early stage. The M41S family differs from pillared interlayered solids in pore size range, pore system, structure, composition, and so on. The pore sizes of M41S materials are approximately in the mesopore range (mesopore: $20\ Å \le$ pore diameter < 500 Å); on the other hand, those of

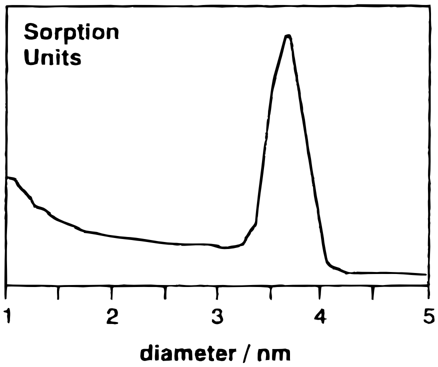

Figure 10. Mesopore size distribution graph for a MCM-41 sample (calcined at 540 °C) obtained by the Horvath−Kawazoe model (from ref 196).

pillared interlayered materials are approximately micropore range (micropore: pore diameter < 20 Å). The attractive M41S materials, having a short history of study, have a number of issues (e.g., control of pore size; control of elemental composition, etc.) to be applied for industrial uses.

Mesoporous materials similar to MCM-41 have been prepared by ion exchange of layered polysilicate kanemite with alkylammonium ions followed by calcination.[201−203] The products possess one-dimensional channels with pore about 20−40 Å in diameter, being formed through the folded sheets mechanism.

Concluding Remarks

Considerable success has been achieved in terms of preparative procedures for pillared interlayered solids since the synthesis of microporous pillared smectite clay was published in the late 1970s. The host materials have included not only traditional lamellar cation exchangers such as smectite clays but also a large number of other ionic lamellar solids such as metal hydrogen phosphates, hydrotalcite-like minerals, etc. Concerning the pillaring techniques, the indirect intercalation method, template-synthesis method, etc., have been developed besides the direct intercalation method.

However, a number of issues remain to be explored. Reliable and reproducible preparative techniques must be established. The properties of pillared interlayered solids greatly depend not only on the nature of the host and guest materials but also on the preparative steps. In combination with the preparative techniques, characterization for the resulting pillared solids, in particular, characterization of pore structure is essential to develop applications for the pillared solids. In the next stage, general principles regarding the relationship between the properties and the structure of pillared solids need to be established.

Pillared layered solids have versatile potential applications, but the study in fields other than catalysis and separation has been scarcely examined. Development of new kinds of molecular devices and molecular functional elements from pillared solids is the next fascinating field to explore.

Acknowledgment. The author thanks Yasuo Kuroda of Central Research Institute for his help and encouragement in this work, and also Mitsubishi Materials Corporation for its support.

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CM9605227