Mesostructured Aluminophosphates Synthesized with Supramolecular Structure Directors

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Over the past few years a growing number of scientists have dedicated their attention to the synthesis of mesostructured aluminophosphates following the concept of supramolecular structure direction. Their research has produced a large variety of synthetic approaches and yielded materials with various structural properties. Today a substantial number of publications have accumulated; this short review provides a general summary of the literature with the aim to display the opportunities for future work.

I. Introduction

I-1. The Concept of Structure-Directed Synthesis. The utilization of supramolecular arrays of organic amphiphiles as structure-directing species in the synthesis of mesostructured materials was introduced in 1992 by researchers of Mobil company.[1,2] Their work focused on the preparation of mesoporous silica or aluminosilicate materials (referred to as M41S materials), which are obtained in a two-step procedure: The initial synthesis leads to an inorganic/organic composite material, in which the organic component (the amphiphile) is periodically arranged within the amorphous inorganic (silica) matrix. In a second step the amphiphile is removed from the solid material (e.g., by calcination or solvent extraction), which leads to regularly arranged mesopores. For this purpose the inorganic part must be stable enough and consist of a three-dimensional network in order to maintain its mesostructure after removal of the organic component. After its introduction, this synthetic approach was applied to the preparation of numerous mesostructured materials, some of which were turned into mesoporous materials, including various silica-based materials,[3−4] metal oxides, or chalcogenides (see reviews[6−10] for details) as well as aluminophosphates; the latter shall be discussed here in detail (for references see the following sections).

Mesoporous materials are of great interest for numerous potential applications, for example as molecular sieves or size-selective catalysts or catalyst supports. However, all ordered mesostructured materials, including those which are not porous, have in common unique structural properties on the level of several nanometers, which suggest further potential applications such as novel conducting or semiconducting devices, photoactive materials, or host−guest compounds. Regardless of whether or not the organic part can be removed without collapse of the mesostructure, the synthesis of inorganic/organic mesostructured composite materials is always interesting for structural investigations or mechanistic studies.

I-2. Important Aspects in the Synthesis of Mesostructured Aluminophosphates. Crystalline microporous (zeolite-analogous) aluminophosphate- and silicoaluminophosphate-based materials ($AlPO_4$-*n*, SAPO-*n*)[11,12] have an immense significance in the field of heterogeneous catalysis. For example, aluminophosphates containing transition metals in their network (e.g., V, Cr, Mn, Co) can be used for various oxidation reactions of alkanes, cycloalkanes, or phenols; transition-metal-substituted silicoaluminophosphates are efficient catalysts for methanol conversion. A comprehensive review on this topic has been published by Hartmann and Kevan.[13]

Accordingly, there is an apparent interest in ordered mesoporous aluminophosphates which combine this catalytic potential with larger pores, giving way to the catalytic conversion of new (larger) substrates. Over the past few years such materials have been synthesized in a variety of mesostructures, including lamellar, hexagonal (i.e., analogous to MCM-41 silica[1,2]), or randomly ordered tubular (comparable to MSU-1[3] or KIT-1[5] silica materials). However, in the nonlamellar phases the degree of structural order is generally somewhat lower as compared to mesostructured silica materials. No mesostructured aluminophosphates with cubic symmetries (analogous to MCM-48[1,2] or SBA-1[4] silicas) have been reported so far. The reason for the poorer structural order and the lower symmetry may to some degree be attributed to the fact that the syntheses are carried out utilizing two inorganic reactants (i.e., two separate sources of Al and P) rather than just one, as in the case of silica materials. Another remarkable tendency in the synthesis of mesostructured aluminophosphates is that nonlamellar structures have almost never been obtained from utilizing surfactants with neutral or anionic headgroups; cationic surfactants are the most favorable ones.

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Table 1. Summary of Mesostructured Aluminophosphates Synthesized by the Utilization of Supramolecular Arrays of Amphiphiles as Structure-Directing Agents Reported in the Literature

surfactant	solvent	structure[a]	surface area[b]	Al/P[c]	authors	remarks
neutral:						
$C_nH_{2n+1}NH_2$ (n = 10, 11)	TEG, (H_2O)	lam		0.5	Oliver et al.[14−17]	
$C_nH_{2n+1}NH_2$ (n = 8, 10, 12)	H_2O	lam		0.5−2	Sayari et al.; Chenite et al.[20−22]	
$C_nH_{2n+1}NH_2$ (n = 6, 8, 10, 12)	EG,ROH, H_2O	lam		∼2	Gao et al.[23,24]	
$C_nH_{2n+1}NH_2$ (n = 12,14,16)	EtOH, (H_2O)	tub	690	1.1	Tiemann et al.[56]	
$C_nH_{2n+1}NH_2$ (n = 4, 6, 8)	H_2O	lam, tub		1[d]	Cheng et al.[39]	
$C_6H_{13}NH_2$	H_2O, (MeOH)	tub, lam	190[e]	0.5−1	Eswaramoorthy et al.[36]	
$H_2N(CH_2)_nNH_2$ (n = 8, 10, 12)	H_2O	lam		0.75[d]	Kraushaar-Czarnetzki et al.[37]	Co[f]
$H_2N(CH_2)_nNH_2$ (n = 9, 12)	EG	lam		0.72[d]	Feng et al.[38]	
cationic:						
CTABr	H_2O, (EtOH)	hex		1.18	Feng et al.[40]	
CTABr	H_2O	tub	480−650	1.3−6.7	Cabrera et al.[54]	
CTABr	H_2O, (EtOH)	hex	800	1.25	Kapoor and Raj[55]	Ti[f]
CTABr	H_2O	hex	900	∼1	Chakraborty et al.[49,50]	
CTABr	H_2O	lam, hex		1−1.35	Perez O. et al.[35]	
CTACl	H_2O	tub	700	>1	Zhao and Luan et al.[41−45]	Si, Mn, V[f]
CTACl[g])	H_2O, (MeOH)	hex, lam	>700	>1	Kimura et al.[32,33,46−48]	
CTACl	H_2O	lam, tub	990	0.6−1	Khimyak and Klinowski[29−31]	
$C_{16}H_{33}(CH_3)_3N^+OH^-$	H_2O	lam			Pophal et al.[34]	
anionic:						
$C_{12}H_{25}OPO(OH)_2$	H_2O	lam		0.8−4	Fröba and Tiemann;[25] Schulz et al.[26]	
$C_{12}H_{25}OPO(OH)_2$	EtOH, (H_2O)	lam, hex[h]	(not porous)	0.5−1.5	Tiemann and Fröba et al.[57,58]	
$C_nH_{2n+1}OPO(OH)_2$ (n = 6, 8, 10)	H_2O	lam		∼1	Tanaka and Chikazawa[27,28]	
SDS	H_2O	hex	630	1.3	Holland et al.; Kron et al.[51−53]	Ga[f]

[a] lam = lamellar, hex = hexagonal, tub = randomly ordered tubular. [b] If porous (m^2/g). [c] In the products. [d] Crystalline. [e] Microporous. [f] Element(s) also incorporated in network. [g] Also $C_{22}H_{45}N(CH_3)_3^+Cl^-$. [h] Inverted hexagonal.

The initial publications on mesostructured aluminophosphates were dominated by reports on lamellar materials. Porous (i.e., nonlamellar) phases, which are the more promising ones with respect to their potential application in catalysis, have turned out to be more difficult to synthesize as compared to silica-based materials. However, many of the reports on lamellar aluminophosphates offer interesting aspects on the role of the surfactant and its influence on the mesostructure (as will be shown below). In the following, the literature will be reviewed in two sections: the first one focusing on lamellar materials and the other one on nonlamellar materials.

I-3. General Remarks. *Supramolecular Arrays of Amphiphiles as Structure Directors.* The structure-directed synthesis of aluminophosphate materials started in 1982 with the introduction of the above-mentioned crystalline microporous aluminophosphates and silicoaluminophosphates, the preparation of which involves single molecular units serving as structure-directing templates. The synthesis of the so-called mesostructured aluminophosphates, on the other hand, which are to be discussed here, uses supramolecular arrays of organic amphiphiles as structure-directing species. These are not adequately denoted as "templates", since a template, in the original sense, leads to one particular, structurally unique product; there is an unambiguous correlation between the choice of the template and the crystalline structure of the product. Contrary to that, supramolecular arrays of amphiphiles lead to mesostructures which can often be created by a variety of (amphiphilic) species; the resultant mesostructured products are periodically ordered but amorphous with respect to their short-range atomic structure.

Synthesis pH. The pH is a crucial factor in the synthesis, which is sometimes underestimated. The initial pH values in the reaction mixtures (which are sometimes not explicitly stated in the literature, but can usually be estimated from the compositions of the reaction mixtures) span a broad range from strongly acidic over neutral to slightly alkaline. In this context it must be stressed that phosphoric acid, which usually serves as the phosphorus source, brings high acidity to the synthesis system. On the other hand, a shift toward higher pH is often observed (or to be expected) during the synthesis, as phosphoric acid is used up in the course of the reaction. The choice of the surfactant as well as its relative quantity with respect to the inorganic reactants is another factor that may have strong influence on the pH conditions; for example, the alkaline potential of primary amine surfactants should not be underrated.

Short-Range Order in Mesostructured Aluminophosphates. The short-range order of the inorganic matrix is one of the most important aspects in the synthesis of noncrystalline mesostructured aluminophosphates. A regular $AlPO_4$ network consists of $[AlO_4]^-$ and $[PO_4]^+$ tetrahedra. The relative Al/P ratio in the final product is 1; characterization of the material (e.g., by $^{27}Al/^{31}P$ solid-state NMR) should reveal that both Al and P are entirely in a tetrahedral coordination. However, in reality the situation is usually different, as will be discussed below (cf. Table 1). The Al/P ratio may be greater or smaller than one, and Al is often found to

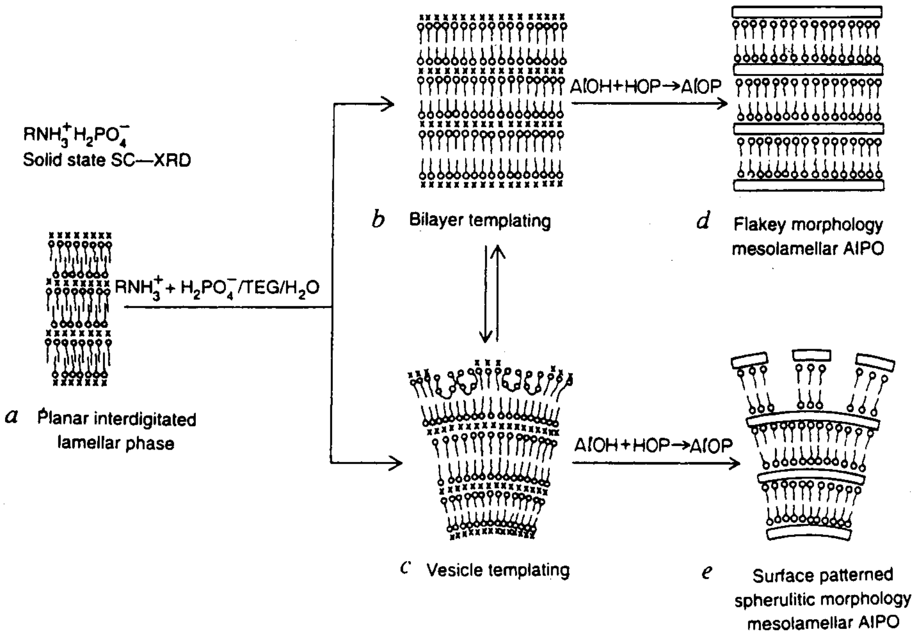

Figure 1. Schematic representation[14] of the structure-directing process in a synthesis of lamellar mesostructured aluminophosphates. (The circles with tail represent the surfactant cations, the crosses represent the dihydrogen phosphate anions, and the connected circles represent the TEG molecules.) The lower part depicts a bilayer-to-vesicle transformation, which is suggested to lead to spherical morphologies.

have 4-, 5-, and 6-fold coordination within the same sample; both Al and P may turn out be partially coordinated by units other than O−P or O−Al, respectively. A variety of reasons must be considered for any deviation from the “ideal” $AlPO_4$ network in each individual case. The condensation of the inorganic reactants may be incomplete, resulting in a partial coordination of Al or P with terminal (i.e., nonbridging) groups like O, OH, or OH_2; in addition to O−P, Al may be coordinated by a number of OH or OH_2 groups, leading to a coordination number of up to six. The mesostructured aluminophosphate sample may contain more or less significant amounts of aluminum oxide and/or oxyhydroxide species; these may either be part of the mesostructured product or be in a second (possibly X-ray amorphous) phase. Furthermore, the coordination environment of Al and P is different at the boundary between the inorganic domains and the surfactant (or at the pore walls) than “inside” the inorganic walls. Studies of the short-range order in noncrystalline materials will usually lack completeness; modern NMR methods, which correlate different nuclei (e.g., Al, P, H, C, N) with each other, are probably the most promising approach to obtain as much information as possible.

II. Review

II-1. Lamellar Mesostructured Aluminophosphates. The first periodically ordered mesostructured aluminophosphate materials that were synthesized using supramolecular arrays of single-headgroup surfactants as structure-directing species were reported in 1995 by Oliver and Ozin et al.,[14−17] who employed primary long-chain amine surfactants ($C_nH_{2n+1}NH_2$, $n = 10, 11$) in a medium of tetraethylene glycol (TEG) and low quantities of water; phosphoric acid (H_3PO_4 85%) and pseudo-boehmite (poorly crystallized boehmite, γ-AlO(OH), with significant amounts of water) served as the inorganic reactants. According to powder X-ray diffraction (PXRD), the products have lamellar mesostructures with Al/P ratios around 0.5, which suggests that considerable amounts of the phosphate units are not interconnected with Al units. Particular attention was paid to the morphological properties of these materials, which exhibit, among featureless flake-like particles, hollow spherical units and shell-like structures with diameters between 1 and 500 μm and regular surface patterns or macropores, as shown by scanning electron microscopy (SEM). These hierarchical structures resemble certain morphologies of siliceous *diatom* or *radiolaria* biominerals. The authors consider TEG to play an important role in the generation of the spherical particles, as they suggest that it serves as both solvent and cosurfactant during the synthesis: In the absence of the Al source a mesolamellar alkylammonium phosphate ($R{-}NH_3^+H_2PO_4^-$) is formed, which exhibits lyotropic behavior with water[18] and can be recrystallized.[19] TEG is believed to induce a curvature in the bilayers of this phase, which leads to the formation of vesicles and, thus, to spherical aluminophosphate structures (Figure 1).

About simultaneously, two other groups (Sayari et al. and Gao et al.) independently reported the synthesis of lamellar mesostructured aluminophosphates, again utilizing neutral long-chain amines; these works were the first to focus on the mesostructural properties and the short-range order of the products rather than merely morphological aspects: Sayari et al.[20,21] carried out their syntheses under aqueous conditions using primary as well as tertiary amine surfactants ($C_nH_{2n+1}NH_2$, $n = 8$, 10, 12, and $C_{12}H_{25}N(CH_3)_2$), H_3PO_4, and aluminum oxide; the initial pH in the reactions was 2.5−3.5. The relative amounts of Al and P as well as of the surfactant used in the syntheses were systematically changed; the resultant Al/P ratios in the products varied over a broad range (ca. 0.5−2). The authors also observed coaxial cylindrical layers by TEM with indications that the

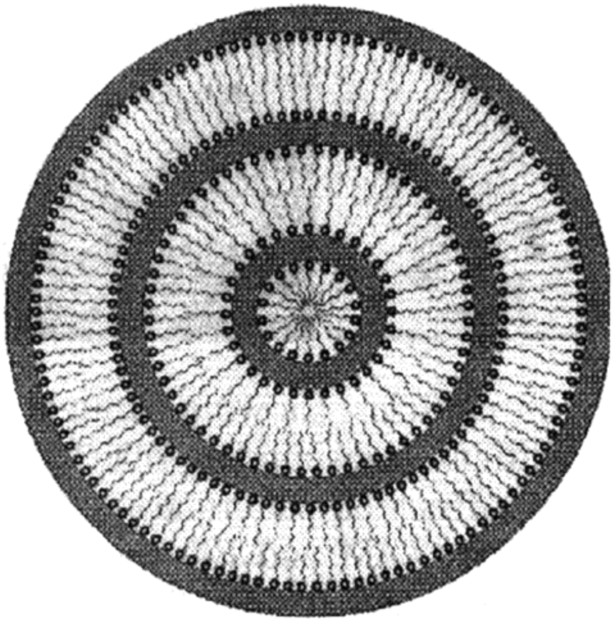

Figure 2. Schematic representation[22] of the coaxial cylindrical arrangement of aluminophosphate/surfactant bilayers (cross section). The proposed mechanism for the formation is a layer-by-layer growth originating in the center.

growth of these curved layers originates from the center of the cylinders (Chenite et al.[22]). This structural feature, which was previously not observed among mesostructured inorganic/surfactant composite materials, suggests that, despite the apparent existence of rodlike surfactant arrangements (as found in the centers of the cylinders), a layered structure growth is favored in the inorganic/surfactant composite (Figure 2). Gao et al.[23,24] carried out a similar synthesis employing primary amine surfactants ($C_nH_{2n+1}NH_2$, $n = 6$, 8, 10, 12), aluminum isopropoxide ($Al[O^iPr]_3$), and H_3PO_4; however, they conducted their syntheses under predominantly nonaqueous conditions using a 1:1 mixture of ethylene glycol (EG) and a primary alcohol ($C_nH_{2n+1}OH$, $n = 4-8$). The materials have Al/P ratios around 2.

Fröba and Tiemann[25] used an anionic surfactant with a phosphate headgroup ($C_{12}H_{25}OPO[OH]_2$) to synthesize lamellar mesostructured aluminophosphates from $Al(O^iPr)_3$ and H_3PO_4 in a strongly acidic aqueous synthesis. They demonstrated that under appropriate conditions (i.e., in the absence of H_3PO_4 as a source of P) the surfactant phosphate headgroup can be incorporated in the inorganic network; thus, the surfactant may serve as both the structure-directing species and a reactant (Figure 3). The Al/P ratio as well as the relative amount of the surfactant was systematically varied within a wide range; the products were examined by Al K-edge XANES spectroscopy. The short-range structure of these products was comprehensively investigated by extensive 1- and 2-dimensional solid-state NMR studies (Schulz et al.[26]). A very similar synthesis was later reported by Tanaka and Chikazawa.[27,28]

Several more reports were made on syntheses of lamellar mesostructured aluminophosphates. Khimyak and Klinowski[29−31] used a cationic ammonium surfactant (CTACl, $C_{16}H_{33}N[CH_3]_3{}^+Cl^-$) under aqueous conditions. The pH was varied by addition of changing amounts of tetramethylammonium hydroxide (TMAOH); the Al/P ratio in the products is less than 1. Kimura et al.,[32,33] Pophal et al.,[34] and Perez O. et al.[35] also used cationic hexadecyltrimethylammonium surfactants under aqueous conditions; a short-chain amine surfactant was used by Eswaramoorthy et al.[36] (see below).

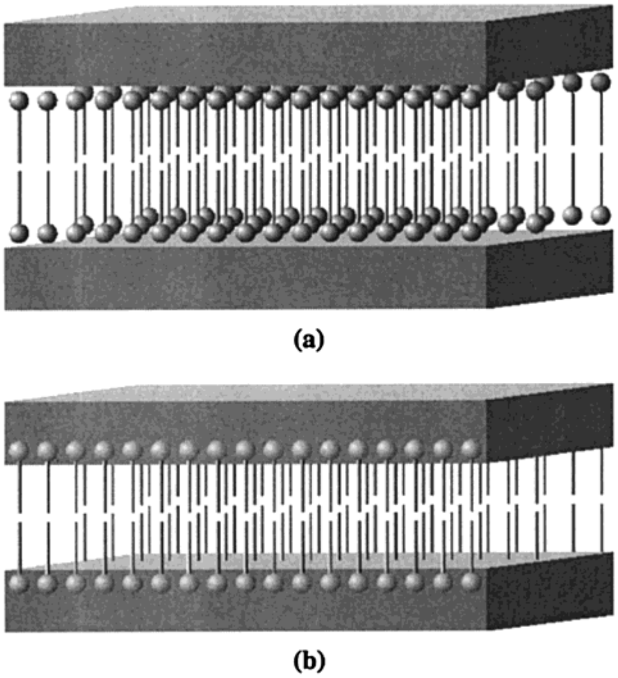

Figure 3. Schematic representation[25] of lamellar mesostructured aluminophosphates synthesized with the utilization of a surfactant carrying a phosphate headgroup. In the "normal" case (a) the surfactant bilayers reside between adjacent $AlPO_4$ layers. When no free phosphate groups are available during the synthesis, the surfactant headgroups are part of the inorganic layers; i.e., the surfactant serves as both the structure-directing agent and a reactant (b).

Another synthesis of lamellar aluminophosphates that deserves to be discussed was published as early as 1993 by Kraushaar-Czarnetzki et al.,[37] who employed long-chain alkylene diamine "bolaform" surfactants ($H_2N-[CH_2]_n-NH_2$, $n = 8$, 10, 12), H_3PO_4, and $Al(O^iPr)_3$ under aqueous conditions; they also incorporated Co and Si into the network. The inorganic parts of these materials are crystalline, with the empirical formula $Al_3H_3(PO_4)_4$; i.e., they exhibit a three-dimensional periodicity on the atomic scale, although no crystal data are available in the paper. A very similar synthesis utilizing the same kinds of diamine surfactants, but under nonaqueous conditions (ethylene glycol, EG), was more recently reported by Feng et al.,[38] who also provided crystal data (the inorganic layers have the formula $Al_{13}(PO_4)_{18}H$). The diamines are arranged in monolayers between the crystalline inorganic sheets, as can be deducted from the correlation between chain length and interlayer distance. However, the precise atomic positions could not be determined for all of the C atoms. Materials prepared with different chain lengths turn out to have the same inorganic composition and architecture but varying interlayer distances. The surfactant arrangement can be adequately termed as "supramolecular". This structure-directing process is a special situation at the boundary between "classic" template-directed synthesis and structure-direction via supramolecular amphiphile arrays: The inorganic layers exhibit a crystal structure which is formed only by the utilization of this specific surfactant headgroup; nevertheless, the relationship between the surfactant and the inorganic crystal structure is not unambiguous, since the latter is not affected by a variation in the surfactant chain length. The fact that the organic layers consist of diamine monolayers rather than of less well-defined bilayers of single-headgroup surfactants apparently leads to a better "structural communication" between two adjacent inorganic layers and, thus, to a higher degree of periodic order on the atomic scale.

Cheng et al.[39] used primary amine surfactants with short hydrocarbon chains ($C_nH_{2n+1}NH_2$, $n = 4, 6, 8$) to synthesize layered materials from H_3PO_4 and pseudoboehmite under aqueous conditions. The inorganic sheets of the products may be assumed to be crystalline (empirical formula $AlPO_3(OH)_2$); on the basis of NMR and IR data, which reveal that both Al and P are entirely in tetrahedral coordination, the authors suggest a monolayer structure similar to the silicate layers of the naturally occurring mineral *kanemite*. However, no crystal data are available. The exact arrangement of the alkylamine molecules in the interlayer region is not clear, but they can be exchanged against Na or K cations as well as hexadecyltrimethylammonium surfactant cations. In the latter case, a restructuring of the inorganic domains is observed, resulting in a mesostructure with presumably disordered tubular surfactant arrangement, which is thermally unstable and collapses upon removal of the surfactant.

II-2. Nonlamellar Mesostructured Aluminophosphates. One of the principal goals in the synthesis of mesostructured aluminophosphates is to remove the organic amphiphile after the synthesis of the initial inorganic/organic composite in order to create a porous material with molecular sieve properties that may serve as, for example, size-selective catalysts or catalyst supports. For this purpose it is necessary that the inorganic network extends in all three dimensions and is stable enough to maintain its mesostructure after the removal of the organic part. Several papers on the first nonlamellar mesostructured aluminophosphates (some of which contain additional elements in the network) were published independently in 1997 (refs 40−52):

Feng et al.[40] employed a cationic ammonium surfactant (CTABr, $C_{16}H_{33}N[CH_3]_3{}^+Br^-$) with $Al(O^iPr)_3$, H_3PO_4, and HF as reactants under aqueous conditions (pH adjusted to 8.3 by addition of TMAOH). Their product has an Al/P ratio slightly above 1 and consists of a three-dimensional inorganic network in which the surfactant is arranged in hexagonally packed rodlike (columnar) arrays, comparable to MCM-41 silica. However, the product turned out to be not stable enough to maintain its mesostructure upon removal of the surfactant; the structure transforms to a lamellar phase at elevated temperatures and collapses when the amphiphile is removed by calcination.

Zhao and Luan et al.[41,42] used CTACl, H_3PO_4, and aluminum hydroxide under aqueous conditions with a pH of 8.5 (or above). They obtained products with Al/P ratios higher than 1, exhibiting mesostructures in which the surfactant arrangement consists of randomly ordered (nonlinear) tubelike arrays. Their products are calcinable in flowing oxygen at a temperature of 500 °C; i.e., the surfactant can be thermally removed with only partial network collapse (leading to a small decrease of the specific surface areas), yielding mesoporous materials with high specific surface areas around 700 m^2/g. They also incorporated Si into the inorganic network, which lead to an increase in stability and surface area in the products (ca. 900 m^2/g). Particular attention should be paid to their subsequent reports on mesoporous aluminophosphates containing transition metals embedded in the network.[43−45] The incorporation of Mn (Mn/Al up to 0.2) lead to a better thermal stability, whereas V (V/Al up to 0.1) caused a decrease in structural order and stability. The preparation of metal-substituted materials is one of the most important goals in the synthesis of mesoporous aluminophosphates; the generation of acidic sites and/or reactive metal ion valence states in the network is necessary for many catalytic applications, such as oxidation reactions.

Very similar synthesis conditions were employed by Kimura et al.,[46] who synthesized mesostructures with hexagonal symmetry under aqueous conditions, utilizing CTACl, H_3PO_4, and $Al(O^iPr)_3$. By calcination at 600 °C in air they obtained porous materials with surface areas around 450 m^2/g and comparably low pore diameters with physisorption data indicating micropores rather than mesopores. However, the utilization of a longer hydrocarbon chain in the surfactant ($C_{22}H_{45}N[CH_3]_3{}^+Cl^-$) as well as the addition of triisopropylbenzene to the synthesis mixture, which presumably causes a "swelling" of the rodlike surfactant arrays, subsequently resulted in a significant increase in pore size from micro- to mesoporous (surface area > 700 m^2/g).[47,48] This group demonstrated how the symmetry of the mesostructured products (i.e., lamellar or hexagonal) depends on the synthesis conditions.[33] The starting pH was adjusted to 8−10; the Al/P ratio is greater than 1 in most of the products. In lamellar materials the condensation of the aluminophosphate network is relatively complete, as indicated by NMR data; the hexagonal phases, on the other hand, consist of a less condensed network. This is consistent with the observation that higher synthesis temperatures lead to lamellar phases, whereas hexagonal materials are formed only at low temperatures (<130 °C). Their formation seems to proceed by transition of a layered phase which is composed of aluminophosphate oligomers and surfactant cations into a hexagonal phase with further condensation of the oligomers (Figure 4).

Chakraborty et al.[49,50] reported the aqueous synthesis of hexagonal silicoaluminophosphate materials with surface areas of ca. 900 m^2/g after calcination at 600 °C in nitrogen and air. They used CTACl, H_3PO_4, and $Al(O^iPr)_3$ under aqueous conditions with a rather low pH of 2.5. Powder XRD data indicate that the degree of structural order in these materials is remarkably high. However, the overall content of Si in the samples is quite low (about 2−3% with respect to either Al or P); the Al/P ratio is about 1.

An interesting synthesis route for the preparation of mesoporous aluminophosphate-based materials was introduced by Holland et al.,[51,52] who utilized polyoxometalate clusters ($AlO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}$, $GaO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}$) as Al or Al/Ga sources, respectively. These positively charged clusters are pre-

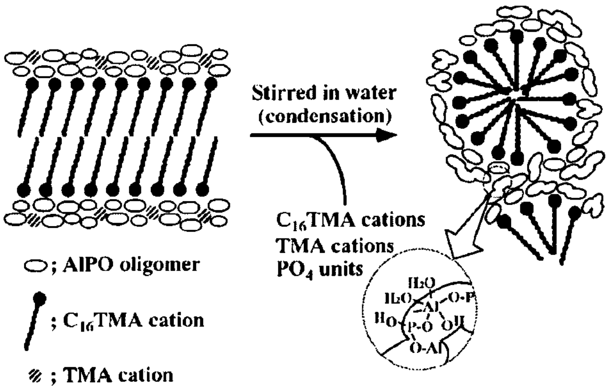

Figure 4. Schematic representation[33] of the proposed formation mechanism of a hexagonal aluminophosphate under aqueous alkaline conditions. In a first step a lamellar arrangement of surfactant bilayers and inorganic sheets containing discrete aluminophosphate oligomers is formed. The curvature in the surfactant arrangement, which leads to the formation of a hexagonal mesostructure, is then generated during the proceeding condensation of the inorganic units. $C_{16}TMA = C_{16}H_{33}(CH_3)_3N^+$; $TMA = (CH_3)_4N^+$.

cipitated as layered salts of an anionic surfactant (SDS, $C_{12}H_{25}OSO_3^-Na^+$) under pH conditions which prevent covalent linking of adjacent cationic units. A mesostructured network is then formed in aqueous solution by addition of phosphate ions as linking species; the pH is adjusted to ca. 3. This process is accompanied by a phase transition from a layered to a nearly hexagonal structure. NMR data indicate that during the phosphate linking step the clusters break up, leading to a uniform (gallo)aluminophosphate network with an Al/P ratio of 1.3. The surfactant can be removed by anion exchange extraction, yielding specific surface areas up to 630 m^2/g; the products are thermally stable up to 350 °C. The anion exchange properties were further investigated (Kron et al.[53]).

Following these initial publications, several more mesoporous aluminophosphates with randomly ordered tubular pore arrangement were reported. Cabrera et al.[54] used CTABr, H_3PO_4, and $Al(O^sBu)_3$ under slightly alkaline aqueous conditions (pH adjusted to 8−9 by addition of triethylamine) and obtained products with Al/P ratios between 1.3 and 6.7, the relative amount of Al being correlated with the pore size, which ranged from microporous (low amounts of Al; 480 m^2/g) to mesoporous (high amounts of Al; 650 m^2/g). Calcination was achieved at 500 °C under flowing air atmosphere. Similar synthetic conditions were used by Khimyak and Klinowski,[31] who used CTABr under aqueous conditions to prepare tubular porous materials from H_3PO_4 and $Al(O^iPr)_3$; the Al/P ratio in the products is between 0.6 and 1, and pore sizes range from micro- to mesoporous with specific surface areas up to 990 m^2/g (calcination at 500 °C in air). Kapoor and Raj[55] used CTABr, H_3PO_4, and $Al(O^iPr)_3$ under aqueous conditions to synthesize materials with Al/P ratios of 1.25 and surface areas up to 800 m^2/g (calcination at 400 °C in air); they also incorporated Ti in the network, which lead to an increase in thermal stability. These materials were successfully tested with respect to their catalytic activity for the epoxidation of olefins. Primary amine surfactants ($C_nH_{2n+1}NH_2$, $n = 12, 14, 16$) were employed by Tiemann et al.,[56] who used H_3PO_4 and $Al(O^iPr)_3$ in alcohol and obtained materials, which are thermally stable up to 500 °C, with Al/P ratios slightly above 1 and specific surface areas up to 690 m^2/g. Eswaramoorthy et al.[36] prepared microporous rather than mesoporous materials utilizing a short-chain alkylamine ($C_6H_{13}NH_2$), H_3PO_4, aluminum hydroxide, and HF under predominantly aqueous conditions at neutral pH; depending on the synthesis conditions, the products exhibited Al/P ratios from 0.5 to 1 and limited thermal stability, and calcination at 300 °C led to a removal of only 60% of the amine. Cheng et al.[39] obtained tubular mesostructures by surfactant ion exchange in layered materials as mentioned above.

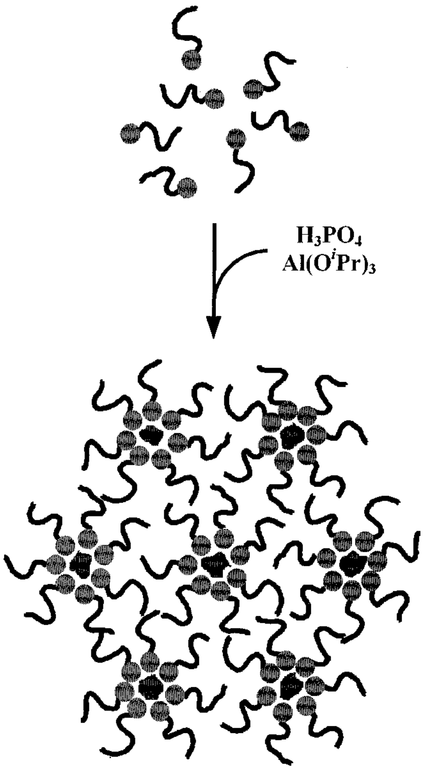

Figure 5. Schematic representation[57] of the synthesis of a well-ordered hexagonal mesostructured aluminophosphate under nonaqueous conditions. The structure formation is a cooperative process, since no lyotropic phase exists in the alcoholic surfactant solution before the addition of the inorganic reactants. The proposed structure of the product is inverted hexagonal; i.e., in the rodlike arrangements (cross section shown) the surfactant headgroups are turned inward, encapsulating the inorganic domains.

Tiemann and Fröba et al.[57,58] also reported the nonaqueous synthesis of a mesostructured aluminophosphate with a hexagonal symmetry, utilizing an anionic surfactant ($C_{12}H_{25}OPO(OH)_2$), H_3PO_4, and $Al(O^iPr)_3$. Apart from a relatively well-ordered mesostructure, this material exhibits several unusual properties, including a relatively short periodic distance as well as the tendency to transform into a lamellar phase at elevated temperatures, as was investigated by temperature- and time-resolved in-situ X-ray diffraction studies. To explain these uncommon properties, an inverted arrangement of the surfactant molecules was suggested for this material. In this structure the surfactant molecules are ordered in hexagonally arranged rodlike assemblies with their headgroups turned inward instead of outward. Accordingly, the surfactant cannot be removed without collapse of the mesostructure (Figure 5). The mechanism of this synthesis was found to be highly cooperative: The alcoholic solution of the surfactant (even in high concentrations up to 50% w/w) is optically isotropic and exhibits no X-ray diffractions; it is only upon the addition of the inorganic reactants that a mesostructure is being formed.

II-3. Summary. Syntheses of mesostructured aluminophosphates have been reported by several scientific groups over the past few years. The literature spans a wide range of different synthesis systems, including the utilization of various types of surfactants (cationic, neutral, anionic) as structure-directing agents, aqueous as well as nonaqueous media, and pH conditions from strongly acidic to slightly alkaline. A summary of the literature is given in Table 1. There is no unambiguous correlation between the synthesis conditions and the respective mesostructural properties of the products; however, a tendency is apparent that cationic ammonium surfactants more often lead to tubular arrangements (and, thus, to porous materials after surfactant removal) than neutral or anionic surfactants. The diversity in the syntheses reported in the literature gives promising perspectives for future work.

References

(1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710−712.
(2) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834−10843.
(3) Bagshaw, S. A.; Prouzet, E.; Pinnavaia, T. J. *Science* **1995**, *269*, 1242−1244.
(4) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147−1160.
(5) Ryoo, R.; Kim, J. M.; Ko, C. H.; Shin, C. H. *J. Phys. Chem.* **1996**, *100*, 17718−17721.
(6) Hou, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky, G. *Nature* **1994**, *368*, 317−321.
(7) Behrens, P. *Angew. Chem. Int. Ed.* **1996**, *35*, 515−518.
(8) Sayari, A.; Liu, P. *Microporous Mater.* **1997**, *12*, 149−177.
(9) Ying, J. Y.; Mehnert, C. P.; Wong, M. S. *Angew. Chem. Int. Ed.* **1999**, *38*, 56−77.
(10) Ciesla, U.; Schüth, F. *Microporous Mesoporous Mater.* **1999**, *27*, 131−149.
(11) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146−1147.
(12) Lok, B. M.; Messina, C. A.; Patton, R. L.; Gajek, R. T.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1984**, *106*, 6092−6093.
(13) Hartmann, M.; Kevan, L. *Chem. Rev.* **1999**, *99*, 635−663.
(14) Oliver, S.; Kuperman, A.; Coombs, N.; Lough, A.; Ozin, G. A. *Nature* **1995**, *378*, 47−50.
(15) Oliver, S.; Coombs, N.; Ozin, G. A. *Adv. Mater.* **1995**, *7*, 931−935.
(16) Ozin, G. A.; Oliver, S. *Adv. Mater.* **1995**, *7*, 943−947.
(17) Ozin, G. A. *Acc. Chem. Res.* **1997**, *30*, 17−27.
(18) Oliver, S. R. J.; Ozin, G. A. *J. Mater. Chem.* **1998**, *8*, 1081−1085.
(19) Oliver, S. R. J.; Lough, A. J.; Ozin, G. A. *Inorg. Chem.* **1998**, *37*, 5021−5028.
(20) Sayari, A.; Karra, V. R.; Reddy, J. S.; Moudrakovski, I. L. *Chem. Commun.* **1996**, 411−412.
(21) Sayari, A.; Moudrakovski, I.; Reddy, J. S.; Ratcliffe, C. I.; Ripmeester, J. A.; Preston, K. F. *Chem. Mater.* **1996**, *8*, 2080−2088.
(22) Chenite, A.; Le Page, Y.; Karra, V. R.; Sayari, A. *Chem. Commun.* **1996**, 413−414.
(23) Gao, Q.; Xu, R.; Chen, J.; Li, R.; Li, S.; Qui, S.; Yue, Y. *J. Chem. Soc., Dalton Trans.* **1996**, 3303−3307.
(24) Gao, Q.; Chen, J.; Xu, R.; Yue, Y. *Chem. Mater.* **1997**, *9*, 457−462.
(25) Fröba, M.; Tiemann, M. *Chem. Mater.* **1998**, *10*, 3475−3483.
(26) Schulz, M.; Tiemann, M.; Fröba, M.; Jäger, C. *J. Phys. Chem. B* **2000**, *104*, 10473−10481.
(27) Tanaka, H.; Chikazawa, M. *J. Mater. Chem.* **1999**, *9*, 2923−2927.
(28) Tanaka, H.; Chikazawa, M. *Mater. Res. Bull.* **2000**, *35*, 75−84.
(29) Khimyak, Y. Z.; Klinowski, J. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2241−2247.
(30) Khimyak, Y. Z.; Klinowski, J. *Chem. Mater.* **1998**, *19*, 2258−2265.
(31) Khimyak, Y. Z.; Klinowski, J. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5275−5285.
(32) Kimura, T.; Sugahara, Y.; Kuroda, K. *Phosphorus Res. Bull.* **1996**, *6*, 205−208.
(33) Kimura, T.; Sugahara, Y.; Kuroda, K. *Chem. Mater.* **1999**, *11*, 508−518.
(34) Pophal, C.; Schnell, R.; Fuess, H. *Stud. Surf. Sci. Catal.* **1997**, *105*, 101−108.
(35) Perez, O. J. O.; Borade, B. B.; Clearfield, A. *J. Mol. Struct.* **1998**, *470*, 221−228.
(36) Eswaramoorthy, M.; Neeraj, S.; Rao, C. N. R. *Microporous Mesoporous Mater.* **1999**, *28*, 205−210.
(37) Kraushaar-Czarnetzki, B.; Stork, W. H. J.; Dogterom, R. J. *Inorg. Chem.* **1993**, *32*, 5029−5033.
(38) Feng, P.; Bu, X.; Stucky, G. D. *Inorg. Chem.* **2000**, *39*, 2−3.
(39) Cheng, S.; Tzeng, J.-N.; Hsu, B.-Y. *Chem. Mater.* **1997**, *9*, 1788−1796.
(40) Feng, P.; Xia, Y.; Feng, J.; Bu, X.; Stucky, G. D. *Chem. Commun.* **1997**, 949−950.
(41) Zhao, D.; Luan, Z.; Kevan, L. *Chem. Commun.* **1997**, 1009−1010.
(42) Luan, Z.; Zhao, D.; He, H.; Klinowski, J.; Kevan, L. *J. Phys. Chem. B* **1998**, *102*, 1250−1259.
(43) Zhao, D.; Luan, Z.; Kevan, L. *J. Phys. Chem. B* **1997**, *101*, 6943−6948.
(44) Luan, Z.; Zhao, D.; Kevan, L. *Microporous Mesoporous Mater.* **1998**, *20*, 93−99.
(45) Luan, Z.; Zhao, D.; He, H.; Klinowski, J.; Kevan, L. *Stud. Surf. Sci. Catal.* **1998**, *117*, 103−110.
(46) Kimura, T.; Sugahara, Y.; Kuroda, K. *Chem. Lett.* **1997**, 983−984.
(47) Kimura, T.; Sugahara, Y.; Kuroda, K. *Chem. Commun.* **1998**, 559−560.
(48) Kimura, T.; Sugahara, Y.; Kuroda, K. *Microporous Mesoporous Mater.* **1998**, *22*, 115−126.
(49) Chakraborty, B.; Pulikottil, A. C.; Das, S.; Viswanathan, B. *Chem. Commun.* **1997**, 911−912.
(50) Chakraborty, B.; Pulikottil, A. C.; Viswanathan, B. *Appl. Catal. A* **1998**, *167*, 173−181.
(51) Holland, B. T.; Isbester, P. K.; Blanford, C. F.; Munson, E. J.; Stein, A. *J. Am. Chem. Soc.* **1997**, *119*, 6796−6803.
(52) Holland, B. T.; Isbester, P. K.; Munson, E. J.; Stein, A. *Mater. Res. Bull.* **1999**, *34*, 471−482.
(53) Kron, D. A.; Holland, B. T.; Wipson, R.; Maleke, C.; Stein, A. *Langmuir* **1999**, *15*, 8300−8308.
(54) Cabrera, S.; Haskouri, J. E.; Guillem, C.; Beltrán-Porter, A.; Beltrán-Porter, D.; Mendioroz, S.; Marcos, M. D.; Amorós, P. *Chem. Commun.* **1999**, 333−334.
(55) Kapoor, M. P.; Raj, A. *Appl. Catal. A* **2000**, *203*, 311−319.
(56) Tiemann, M.; Schulz, M.; Jäger, C.; Fröba, M. *Chem. Mater.*, in press.
(57) Tiemann, M.; Fröba, M.; Rapp, G.; Funari, S. S. *Chem. Mater.* **2000**, *12*, 1342−1348.
(58) Tiemann, M.; Fröba, M.; Rapp, G.; Funari, S. S. *Stud. Surf. Sci. Catal.* **2000**, *129*, 559−566.

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