Templating Mesoporous Zeolites[†]

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The application of templating methods to produce zeolite materials with hierarchical bi- or trimodal pore size distributions is reviewed with emphasis on mesoporous materials. Hierarchical zeolite materials are categorized into three distinctly different types of materials: hierarchical zeolite crystals, nanosized zeolite crystals, and supported zeolite crystals. For the pure zeolite materials in the first two categories, the additional meso- or macroporosity can be classified as being either intracrystalline or intercrystalline, whereas for supported zeolite materials, the additional porosity originates almost exclusively from the support material. The methods for introducing mesopores into zeolite materials are discussed and categorized. In general, mesopores can be templated in zeolite materials by use of solid templating, supramolecular templating, or indirect templating. In this categorization of templating methods, the nature of the interface between the zeolite crystal and the mesopore exactly when the mesopore starts to form is emphasized. In solid templating, the zeolite crystal is in intimate contact with a solid material that is being removed to produce the mesoporosity. Similarly, in supramolecular templating, the zeolite crystal is in direct contact with a supramolecular assembly of organized surfactants, which is removed to generate the mesopores. On the other hand, in the indirect templating method, the interface is between the zeolite crystal and solvent molecules, or possibly a gas phase. It is shown that the available templating approaches are quite versatile, and accordingly, it is possible to produce a very wide range of hierarchical zeolite materials. The resulting zeolite materials, featuring noncrystallographic mesopores in addition to the crystallographic micropores, exhibit significantly enhanced diffusional properties in comparison with purely microporous zeolite materials. These enhanced mass transport properties have been shown in several cases to result in significantly improved catalytic properties in a range of important reactions.

Introduction

Zeolites are crystalline aluminosilicates build from TO_4 tetrahedra ($T = Si, Al$) that are arranged in such a manner that intracrystalline pores and cavities of molecular dimensions are present. Typically, these zeolite pores have diameters in the range of 4–12 Å and they are therefore called micropores according to the IUPAC classification of porous materials.[1] The sizes and shapes of the micropores, and the cavities, are determined exclusively by the crystal structure of the zeolite. Thus, the micropores can be categorized as crystallographic micropores. Currently, more than 170 different zeolite structure types have been characterized and several new types still appear every year. Each zeolite structure type features a unique micropore system. In chemical industry, zeolites are among the most important families of materials with a multitude of technical applications.[2,3] Accordingly, there are numerous reviews that cover some of the currently most important industrial uses such as in ion-exchange,[2–5] sorption,[2–5] and heterogeneous catalysis[2,3,6–8] but also possible new, emerging applications[9–13] attract considerable attention. At the same time, there are significant ongoing efforts to continuously improve our fundamental understanding of zeolite materials and recent reviews describe, for example, state-of-the-art of hydrothermal zeolite synthesis,[14,15] the use of in situ characterization techniques to zeolite catalysts,[16] diffusion in zeolites,[17] zeolite membrane materials,[18] and the application of theoretical modeling in zeolite science.[19]

Much of the success of zeolites in chemistry and chemical engineering can be attributed to the presence of the well-defined micropores, which are responsible for the well-known molecular sieve effect. Thus, in heterogeneous catalysis, the availability of a wide range of zeolite structures with different micropore architectures makes it possible to conduct shape-selective catalysis, which represents one of the most significant achievements in the history of catalysis.[20] With shape-selective catalysts, it is possible to conduct highly selective catalytic transformations on the basis of the complete exclusion, or on the strongly hindered diffusion, of certain reactants, intermediates, or products in the zeolite micropores. Alternatively, shape-selectivity can occur because of the sterically confined reaction space present in the vicinity of the active sites that are preferably located in the zeolite micropores. This can favor one reaction path (transition state) over another.

Generally, zeolites are very versatile catalysts that can be tailored to achieve optimum performance in a wide range

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of catalytic reactions. Thus, the catalytically active sites in zeolite micropores can be acid sites that result from the charge compensation of the framework with protons, which is necessary when, for example, Al^{3+} substitutes Si^{4+} in the framework, or it can be redox-active sites resulting when the charge compensation is done by ion exchange with redox-active ions such as Fe(III), Cu(II), Co(II), or Ag(I) rather than with protons. Additionally, redox-active sites can be obtained by incorporating redox active metals ions, e.g., Ti, V, Mn, Fe, Co, Ga, Sn, etc., directly into the zeolite framework by isomorphous substitution of other T atoms. Therefore, zeolite catalysts attract significant attention in many areas of heterogeneous catalysis both for purely fundamental reasons because they can be tailored to allow careful and systematic studies of various structure–activity relationships and in numerous industrial applications where they can be active, selective, durable, and relatively inexpensive catalysts.

However, in numerous cases, the sole presence of micropores also imposes significant limitations on the range of reactions that are efficiently catalyzed by zeolite catalysts. This is clearly the case for reactions involving reactants or products that are so large that they are effectively excluded from the zeolite micropores. However, also for reactants and products that are smaller than the micropores, it is often not possible to explore the full potential of the zeolite catalysts. It is clear that if the zeolite catalyst could in principle transform the reactant(s) into the desirable product(s) at a rate higher than the rate of diffusion of reactants, intermediates, and products in the zeolite, then the overall reaction rate will be limited by the rate of diffusion. Thus, the reaction is in a diffusion-controlled regime and the effectiveness factor, which is the ratio of the actual rate of reaction to the rate that would have resulted for the reaction if no diffusion-limitation was present, can be significantly below 0.1. This would correspond to less than 10% of the zeolite actually being used for the catalytic reaction simply because mass transport to and from the active sites is hindered. Thus, several strategies have been pursued to increase the accessibility of the active sites in zeolite catalysts, and various aspects of these efforts have been reviewed and highlighted during the last years.[21–32]

Here, we review the possibilities for preparing mesoporous zeolites by templating approaches. Such mesoporous zeolites contain, in addition to the crystallographic micropore system characteristic of zeolites, also an independent mesopore system, i.e., a pore system with pore diameters in the range of 2−50 nm.[1] In all known cases today, the mesopore system in mesoporous zeolites can be considered a noncrystallographic pore system because the sizes and shapes of the mesopores are not related in any way to the crystal structure of the zeolite, and because the orientation of the individual pores is typically random. Certainly, this pore system is not ordered at the atomic level. Therefore, mesoporous zeolites can be considered hierarchical porous materials,[26] meaning they exhibit at least two types of pore systems that have sizes in distinctly different ranges, i.e., in the micropore range and the mesopore range. Such materials can be prepared by a range of different templated and nontemplated methods, as outlined below. Generally, the templating approaches makes it possible a priori to tailor the pore size of the mesopores by use of a mesopore template with a characteristic size, which after removal leaves behind mesopores with essentially the same size and shape as that of the mesopore template. Fundamentally, templating approaches to mesoporous zeolites are interesting as they turn out to define state-of-the-art in the design of hierarchical porous materials and thus they provide a benchmark for new materials and a constant source of inspiration for the development of new and improved methodologies. Obviously, it is possible that templating approaches to mesoporous zeolites could be important in supplying improved zeolite catalysts in a range of existing catalytic processes, but they could also facilitate an extension of the current scope of industrial zeolite catalysis to include completely new reactions. Moreover, mesoporous zeolites with their improved mass-transport properties could also find applications in separations, specifically when transient phenomena are of key importance, i.e., in non-steady-state systems such as hydrocarbon traps in automotive emission systems or in certain pressure-swing adsorption technologies.

Mesoporosity in Zeolites

During the past decade, significant efforts have been devoted to developing methods that introduce mesoporosity in zeolite materials by different approaches. In practice, the resulting mesoporous zeolite materials can be categorized into three distinctly different types of materials. Figure 1 shows schematic illustrations of these different types of materials that can be termed hierarchical zeolite crystals, nanosized zeolite crystals, and supported zeolite crystals, respectively, and it shows typical pore size distributions for the various materials. The first category of materials, the hierarchical zeolite crystals, includes ordinary zeolite crystals having additional porosity present in each individual zeolite crystal. Depending on their size, these additional pores are either mesopores (diameter below 50 nm) or macropores (diameter above 50 nm).[1] Accordingly, the hierarchical zeolite crystals could be further categorized as either mesoporous or macroporous zeolite crystals, but in the present context, this distinction is somewhat arbitrary and will not be used to strictly differentiate between materials except that our focus will be on the mesoporous zeolite crystals. Thus, the mesoporous zeolite crystals feature the typical crystallographic micropores characteristic of the given zeolite structure and an additional intracrystalline mesopore system. Finally, yet another pore system will exist as a consequence of the packing of the zeolite crystals in the material. This pore system is an intercrystalline pore system. The pore sizes and geometries of these pores are determined by the size, shape, and packing of the zeolite crystals in the material, which can obviously be packed more or less loosely. Typically, these intercrystalline pores are relatively large macropores because zeolite crystals normally have dimensions in the micrometer-range, and we will not discuss them in any detail. However, in some cases when the hierarchical zeolite crystals are very small (average crystal size below about 50 nm), it should be noted that they can contribute significantly to the observed mesoporosity.

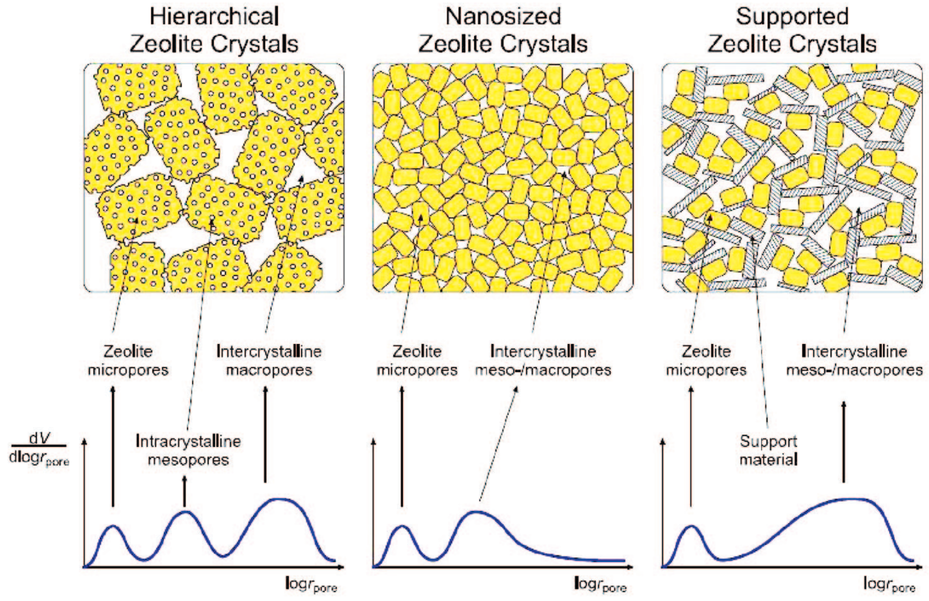

Figure 1. Categorization of hierarchical zeolite materials into hierarchical zeolite crystals, nanosized zeolite crystals, and supported zeolite crystals. The origin of the different types of pores in the materials is illustrated schematically.

The second category of materials, the nanosized zeolite crystals, includes ordinary zeolite crystals with typical crystal sizes below 100 nm, which is much smaller than what is usually seen for zeolites. Clearly, the nanosized zeolite crystals feature the conventional, intracrystalline, and crystallographically well-defined micropore system characteristic of zeolites. Moreover, it has an intercrystalline mesopore system, which results from the packing of the nanosized zeolite crystals in the material. This intercrystalline mesopore system is obviously analogous to the intercrystalline macropore system described above for the mesoporous zeolite crystals. However, because of the typically smaller sizes of the nanosized zeolite crystals compared to the hierarchical zeolite crystals, the resulting pores are also typically smaller. Thus, for the nanosized zeolite crystals, controlling the mesopore size and mesopore shape translates into controlling the size, shape, and packing of the nanosized zeolite crystals.

The third category of materials, the supported zeolite crystals, is characterized by the zeolite crystals being dispersed or supported in the pore system of another material. Thus, contrary to the mesoporous zeolite crystals and the nanosized zeolite crystals, the supported zeolite crystals are not a purely zeolitic material but instead a composite material, and the mesopores results mainly from the presence of the nonzeolitic material. Accordingly, supported zeolite crystals will feature an intracrystalline micropore system that is solely attributed to the zeolite crystals in the material. The pore sizes of the mesopores are largely determined by the support material, which can be a very disordered material such as a typical catalyst–support like amorphous silica, but it can also be a highly ordered material like a mesoporous molecular sieve. Thus, in principle, the mesopores could be categorized as either intercrystalline or intracrystalline mesopores depending on the nature of the support material. Moreover, it would be possible for the pore system to have micropores or macropores; for the present categorization, this is not important. Clearly, the presence of the zeolite crystals on the support material will alter the pore size of the material relative to that of the pure support. Here, the relative sizes of the zeolite crystals and the primary particles comprising the support material are of key importance for the pore size distribution; the packing of the material will clearly also be a key parameter in defining the porosity.

The vast majority of mesoporous (hierarchical) zeolite materials reported so far can be easily categorized as one of the three types of materials outlined above. However, it is clear that mesoporous zeolite materials that are simple combinations of materials from the different categories can also be envisaged, such as hierarchical nanosized zeolite crystals or supported hierarchical zeolites, and some of these materials are in fact already known. Nevertheless, the three categories seem to represent a useful way to distinguish between various mesoporous zeolite materials, and most importantly, the origin of the mesoporosity in the three different categories is fundamentally different, which makes the categorization easy to apply in practice. However, even though the origin of mesoporosity in the materials is fundamentally different, it is interesting to note that some of the preparative methods available to synthesize these mesoporous zeolite materials can in fact be tuned to produce different types of materials in the categorization. Figure 2 illustrates the templating methods available to produce hierarchical zeolites and emphasizes that some of these methods can in fact be used to produce different types of hierarchical zeolite materials. Thus, Figure 2 categorizes the templating methods available for producing hierarchical zeolites and provides a link between the methods and the materials.

Here, the preparative methods available for synthesizing hierarchical zeolites are termed: solid templating, supramolecular templating, and indirect templating. In addition, a number of nontemplated methods are available that yield mesoporous zeolite materials. In the solid templating method, the zeolite is grown in the presence of a solid material, which

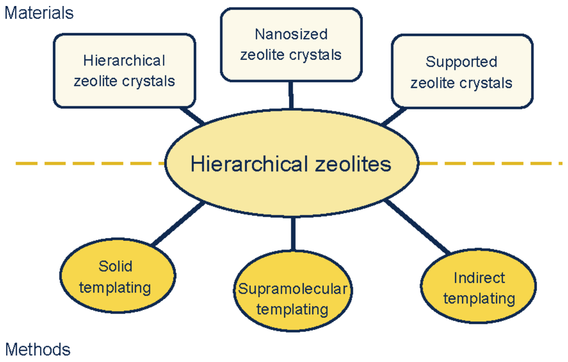

Figure 2. Categorization of templating methods available to synthesize hierarchical zeolite materials.

is eventually removed to generate porosity, and therefore,the solid acts as a pore template. Typically, the solid template is removed by combustion but in principle it might also be removed by dissolution or sublimation. In the supramolecular templating method, a supramolecular assembly of surfactants is used as the mesopore template. After crystallization, the template can typically be removed by combustion or extraction whereby porosity is generated. In the indirect templating method, a templated mesoporous nonzeolitic material is first formed,and in a separate step, the mesoporous nonzeolitic material is more or less completely transformed into the mesoporous zeolite, or the zeolite is deposited onto the templated mesoporous material. Thus, the templating effect is considered to be indirect, becausemplate is not present when the zeolite crystallizes. However, the resulting mesoporous zeolite material can still maintain some of the order or structure of the original template if only a limited reorganization of solid material occurs during zeolite crystallization or processing, for example, as in a pseudomorphic transformation. Thus, the approach can still be termed templating, albeit the templating is indirect. Thus, the present categorization emphasizes the nature of the interface between the zeolite crystal and the mesopore exactly when the mesopore forms. In solid templating, the zeolite crystal is in intimate contact with the solid material that is being removed to produce the mesoporosity. Similarly, in supramolecular templating, the zeolite crystal is in direct contact with the supramolecular assembly of organized surfactants that is removed to generate the pores. On the other hand, in the indirect templating method, the interface is between the zeolite crystal and solvent molecules, or possibly a gas phase.

Finally, there are a range of nontemplated methods that yield hierarchical zeolite materials. Here, the most prominent methods, such as dealumination,[21,22] desilication,[23] and detitanation[25] (jointly termed demetalation), are briefly introduced to enable a comparison of the templated and the most important nontemplated methods, but it is outside the scope of the present review to include all nontemplated methods available to prepare mesoporous zeolites.

Previously, the templating of solid, high-surface-area inorganic materials has been categorized as either endotemplating or exotemplating.[29] In that categorization, the solid templating method is clearly an example of exotemplating because the materials forms inside a rigid porous solid.

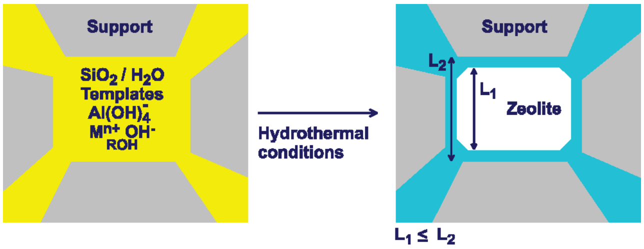

Figure 3. Confined space synthesis of nanosized zeolite crystals inside a porous support resulting in supported zeolite crystals. The underlying idea is that the zeolite crystals will not grow larger than the pores, and the support will disperse the zeolite crystals. Some supports may be removed by proper chemical treatments, making it possible to isolate the nanosized zeolite crystals.

Contrary to this, the supramolecular templating is a perfect example of endotemplating, where the templating species are occluded in the forming solid.

In the following sections, we will present the preparative methods available for templating mesoporous zeolites and the resulting mesoporous zeolite materials in more detail. We will use the categorization of the preparative methods outlined in Figure 2 to organize the discussion. This should clearly illustrate the significant efforts that have already been devoted to this field and should indicate where new discoveries could be possible or desirable.

Solid Templating

Solid templating is a very versatile method for synthesizing mesoporous materials featuring all three types of porosities shown in Figure 1. As examples, solid templating has been applied to produce macroporous MFI zeolite crystals by applying polystyrene beads[33] or ion-exchange resins[34] as the macropore template and nanosized ZSM-5 crystals by carrying out the crystallization in the confined space of amorphous carbon black and then removing the carbon black by combustion.[35] Also, the third class of hierarchical porous materials, the supported zeolite crystals, are simply available by crystallizing zeolites on, for example, a porous carbon and not removing the carbon afterward, resulting in carbon-supported zeolite crystals.[35]

Templating with Carbon Nanoparticles, Nanofibers, and Nanotubes. Solid templating employing porous carbons as the mesopore template can be tuned to produce mesoporous zeolite crystals, nanosized zeolite crystals, or carbon-supported zeolite crystals. Nanosized crystals are produced when zeolite crystallization takes place in the confined space of a porous carbon with little or no encapsulation of the carbon particles during synthesis. By this approach, it is possible to control the size of the zeolite crystals by proper choice of carbon template, as shown schematically in Figure 3.

Using the confined space synthesis approach in the voids of carbon blacks or carbon aerogels (see next section), a variety of different zeolites including ZSM-5, zeolite β, zeolite X, zeolite A, and zeolite Y with controllable crystal sizes have been reported.[35–38]

Contrary to the nanosized zeolite crystals prepared in the confined space of porous carbons, the so-called mesoporous zeolite single crystals contain a network of mesopores within

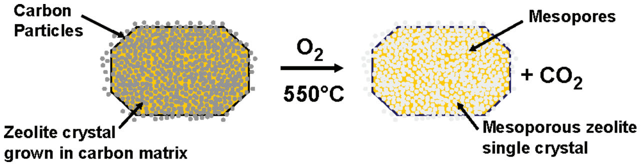

Figure 4. Growth of a zeolite crystal around carbon particles resulting in a zeolite crystal embedded with carbon particles. The carbon particles may subsequently be removed by combustion, yielding a porous spongelike zeolite single crystal.

each individual zeolite crystal.[39] These materials are produced when the porous carbon material is encapsulated by the growing zeolite crystals during synthesis, resulting in zeolite crystals embedded with carbon after zeolite crystallization. Removal of the embedded carbon matrix after synthesis results in porous zeolite single crystals, as shown schematically in Figure 4.

Whether nanosized crystals or mesoporous crystals are obtained by carbon-templating is determined by the experimental factors that influence nucleation rates relative to growth rates.[40] With relatively high nucleation rates, nanosized zeolites are favored, whereas relatively high growth rates favor mesoporous zeolite single crystals. In practice, it is even possible to obtain hybrid materials, nanosized hierarchical zeolite crystals.[40] So far, the carbon-templating methodology has been applied to produce mesoporous zeolite single crystals of MFI,[39,41,42] MEL,[43] MTW,[44] and BEA[41] framework structures as well as hierarchical aluminum phosphates of CHA[45] and AFI[45] framework structures. A thorough study on the application of different carbon templates as well as different synthesis conditions with the goal of finding a low-cost route to ZSM-5 was recently reported by Chou et al.[46] Also, carbon nanotubes have been applied as combustible carbon templates in the synthesis of mesoporous zeolites, resulting in mesoporous zeolite crystals containing relatively straight and uniformly sized mesopore channels that extend throughout the entire crystals.[47,48] The same can be obtained using carbon nanofibers that are much cheaper than nanotubes.[49]

Recent installments in the field of mesoporous single crystals prepared by carbon-templating are the application of microwave heating to facilitate crystal growth[50] and the successful adoption of the fluoride route for conventional zeolite synthesis to work for carbon-templating of mesoporous zeolite single crystals.[45] By the latter method, the synthesis of related aluminum phosphate materials in mesoporous modifications has proved possible.

Carbon Templates Formed Prior to Zeolite Synthesis. Preformed carbon templates made by carbonization of various materials have been applied in the synthesis of mesoporous zeolites. Pinnavaia et al. applied colloidal imprinted carbon (CIC), made by carbonizing at 900 °C pitch imprinted with colloidal silica and etching away the silica by hydrofluoric acid leaching, as a solid template for the synthesis of nanosized ZSM-5 in the confined space of the CIC.[51] By varying the size of the silica colloid used for imprinting the pitch, CICs of different pore size distributions can be obtained. Consequently, nanosized zeolite crystals of different size ranges can be obtained by tuning the CIC template. Colloidal silica has also very recently been used to template a porous carbon prepared by partial carbonization of sucrose with sulfuric acid and subsequently removing the silica template by hydrofluoric acid leaching.[52] Application of this carbon as a mesopore template resulted in mesoporous silicalite-1 single crystals.

The preparation of carbon–silica composite materials by carbonization of various molecules in the pores of ordered mesoporous materials such as MCM-41 and SBA-15 is a field of its own.[53] These so-called CMK materials have been applied as starting materials for crystallization of zeolites as the carbon template is already intimately admixed with the silica source. Remarkably, this was reported almost simultaneously by three independent research groups.[54–56] Cho et al. described procedures for the preparation of mesoporous zeolite powders, monoliths and films, which involved carbonization of a phenol-formaldehyde resin in the pores of MCM-41, MCM-48, and SBA-15 and the subsequent application of these carbon–silicate mixtures as starting materials for zeolite crystallization.[54] The XRD patterns of the afforded materials revealed the presence of ZSM-5 crystals as well as disordered mesoporous phases, suggesting that the amorphous pore walls of the mesoporous templates are partly transformed into ZSM-5 crystals and encapsulate carbon during the course of the crystallization. After zeolite crystallization, the carbon embedded in the zeolite crystals is removed by combustion, resulting in mesoporous zeolite crystals. The powdered mesoporous zeolite sample as well as the monolith and the film all exhibited high mesopore surface areas and volumes. Yang et al. reported a similar procedure, applying a carbon replica of SBA-15, so-called CMK-3, as the mesopore template.[55] The prepared materials were highly crystalline mesoporous ZSM-5 samples having mesopore surface areas and mesopore volumes up to 382 m^2/g and 0.37 mL/g, respectively. The report by Sakthivel et al. describes the use of CMK-1 and CMK-3 mesoporous carbon molecular sieve replicas of MCM-48 and SBA-15, respectively, as the mesopore templates.[56] CMK-1 or CMK-3 were impregnated with ZSM-5 gel components and subjected to hydrothermal treatment for 1–5 days. This resulted, after calcination, in aluminosilicate replicas of the mesoporous carbon templates, denoted RMM-1 and RMM-3, featuring the characteristic cubic and hexagonal low-index reflections in the XRD patterns. No ZSM-5 reflections were observed in the XRD patterns of the materials subjected to hydrothermal treatment for 3 days or less; however, FTIR revealed the presence of zeolite secondary structural building units by featuring a broad absorption at ca. 540 cm^{-1}. Thus, RMM-1 and RMM-3 appears in fact to be composite materials consisting of mesoporous MCM-48-type and SBA-15-type with nanosized zeolite structural units embedded in the pore walls. Reports on the transformation of CMK-3 into ZSM-5 by vapor-phase transport of the structure-directing agent can also be found.[57,58] Recently, Fang and Hu reported the use of CMK-5, another carbon replica of SBA-15, to produce an ordered mesoporous aluminosilicate material with zeolite crystals embedded in the pore walls, as revealed by the XRD pattern.[56] The material, denoted as OMZ-1 by the authors, had a mesopore surface area and mesopore volume of 389 m^2/g and 0.50 mL/g, respectively.

Very recently, two different approaches involving the preparation and application of porous carbons prepared by carbonizing sucrose were reported.[60,61] The first report applied hydrothermal treatment of a sucrose−ammonia mixture followed by carbonization of the mixture at 850 °C.[60] The afforded porous carbon was the impregnated with silicalite-1 synthesis gel mixture and subjected to hydrothermal treatment to allow for the zeolite phase to crystallize. The zeolite material resulting after combustion of the carbon consisted of homogeneously sized mesoporous silicalite-1 single crystals. The second report concerned the preparation of a carbon−silica composite material made simply by impregnating a solution of sucrose onto silica gel and carbonizing the material at elevated temperature.[61] The carbon−silica composite was then applied as silica source for the crystallization of mesoporous ZSM-5 single crystals. Also, silica−carbon composites made by carbonization of rice husks have been applied as starting materials for synthesis of mesoporous zeolites.[62]

Use of Aerogel, Polymer, and Resin Templates. The first report on the utilization of carbon aerogels for templating mesoporous zeolites appeared in 2003.[63] Tao et al. prepared a mesoporous ZSM-5 monolith with bimodal pore size distribution comprising very uniformly sized mesopores (average diameter of 11 nm) using a carbonized resorcinol−formaldehyde aerogel, i.e., a carbon aerogel, as the mesopore template. The carbon aerogel was impregnated with ZSM-5 synthesis gel components and subjected to hydrothermal treatment to allow for the crystallization of the zeolite phase. During the course of the crystallization, the zeolite crystals grew in the confined space of the carbon aerogel producing a phase-pure mesoporous ZSM-5 powder consisting of nanosized crystals. The same methodology was also applied for the synthesis of mesoporous NaY, resulting in a highly mesoporous NaY material (mesopore volume 1.37 cm^3/g) consisting of nanosized crystals.[38] Because the porosity of carbon aerogels are quite easy to tune by, for example, varying the molar ratios of the starting materials, resorcinol, and formaldehyde, the porosity of the resultant zeolite materials are also easily tuned. This was demonstrated for mesoporous ZSM-5 samples produced from two different carbon aerogels prepared by carbonization of resorcinol−formaldehyde aerogels.[64] The ZSM-5 sample produced from a carbonized 2:1 RFA had a mesopore volume of 0.98 cm^3/g, whereas a ZSM-5 sample produced from a 1:1 RFA had a mesopore volume of 0.34 cm^3/g.

Also, noncarbonized resorcinol−formaldehyde aerogels have been used to synthesize mesoporous zeolites, exemplified with the synthesis of nanosized zeolite A by crystallization in a resorcinol−formalde aerogel.[65] Thus, although resorcinol-formaldehyde aerogels are not as porous as their carbonized analogues, and therefore result in less mesoporous zeolites, as shown in a comparative study of mesoporous ZSM-5 samples,[66] they offer interesting possibilities for synthesizing other zeolite framework structures in mesoporous form. Another advantage of resorcinol−formaldehyde aerogels is that they are easily produced in monolithic form, paving the way for monolithic self-supported mesoporous zeolite catalysts. The preparation of macroporous monolithic silicalite-1 foams was reported 2001 by Yoon et al. by growing zeolite crystals on polyurethane foam,[67] and recently, mesoporous monolithic silicalite-1 was prepared from resorcinol−formaldehyde aerogel templates were shown to exhibit high catalytic activity as well as excellent selectivity in the Beckmann rearrangement of cyclohexanone oxime.[68]

Very recently, Xiao et al. reported the use of a cationic polymer as mesopore template for the synthesis of mesoporous zeolite β.[69] The synthesis involved adding the polymer to a zeolite β synthesis gel and crystallization of the mixture under hydrothermal conditions. Subsequent calcination of the product afforded mesoporous zeolite β with a mesopore size distribution of 5–40 nm, which exhibited higher conversion and better selectivity than a conventional zeolite β sample in catalytic alkylation of benzene with 2-propanol. Also, mesoporous ZSM-5 could be prepared using this methodology. Another very recent strategy concerning the use of polymers for templating mesoporosity in zeolites was reported by the group of Pinnavaia.[70] A silane-functionalized polymer was impregnated with ZSM-5 gel components and subjected to hydrothermal treatment. During crystallization of the zeolite phase, the silyl groups were hydrolyzed and attached to the surface of the nucleating zeolite crystals, thereby incorporating the polymer in the zeolite crystal. After calcination of the polymer, mesoporous zeolite crystals are obtained. The main advantage of this templating method is that the intracrystalline mesopores of the resulting crystals are small and homogeneously sized (average pore size 2.0–3.0 nm).

Macrotemplating using polystyrene beads was one of the first types of solid templating of hierarchical zeolites to be reported.[33] Stein et al. impregnated zeolite synthesis gel components onto a close-packed array of polystyrene beads. After crystallization and removal of the latex spheres, a macroporous beehive structure with walls of silicalite-1 was obtained. Similarly, core−shell building blocks consisting of latex-beads coated with zeolites were used to prepare macroporous zeolite monoliths.[71] Using ion-exchange resin beads as the template, researchers obtained mesoporous silicalite-1 microspheres by crystallization of a silicalite-1 synthesis gel adsorbed onto anionic ion-exchange resin beads.[34] The calcined silicalite-1 microspheres exhibited a typical type IV N_2 physisorption isotherm and contained mesopores centered at 40 nm. Also hierarchical palladium-containing zeolite β[72] and vanadium-containing AlPO-5[73] have been reported by resin-macrotemplating.

Use of Solid Biological Templates. Another interesting approach for the preparation of hierarchical zeolites is by use of biological templates, which offer a wide range of different material shapes. So far, a few examples of using solid biological templates have appeared to illustrate the possibilities for controlling the morphology of zeolite materials. They represent an attractive alternative compared to the standard templates such as polymers, carbons, or other synthetic templates, because many biological templates are abundant and often relatively inexpensive. Mann et al.[74] demonstrated how organized bacterial superstructures can be used as 3D templates for the fabrication of ordered inorganic–organic fibrous composites.[74,75] They prepared MCM-41 silica-based fibers containing hierarchically organized pore structures at the meso- and microscopic length scales.[74] Bacterial templates were also applied to create hierarchically structured zeolite fibers containing ordered pores at the meso- and microscopic length scales.[76] The stable aqueous dispersion of preformed zeolite nanoparticles as building blocks for the infiltration of a bacterial supercellular thread was used by reversible swelling. Macroscopic bacterial threads were produced from cell cultures of mutant FJ7 strain of *Bacillus subtilis*. The final zeolite fibers showed a high surface area and a unidirectional patterned architecture. Along the same lines, hierarchical MFI zeolites were prepared through templating with wood cells giving materials with controlled micro-, meso-, and macropores that are clearly replicas of the original biological template.[77] Moreover, the leaves and stems of *Equisetum arvense*, a plant rich in amorphous silica, has been used to produce hierarchical MFI and BEA structures with order at all three levels.[78–80]

Finally, starch gels have also been used a solid template to fabricate zeolite materials with a hierarchical micro-, meso-, macropore organization.[81] The macroporous monoliths consisting of a continuous mesoporous framework of microporous silicalite were prepared by incorporating 50 nm sized zeolite nanoparticles into freshly prepared viscous starch gels, followed by air-drying and calcination. Macropores with sizes between 0.5 and 50 μm were created by varying the amount of starch and the starch/silicalite weight ratio. Mesoporous thin films of microporous silicalite, 2–15 μm in thickness, were also prepared by using gels containing low concentrations of starch (about 2 wt %).

Supramolecular Templating

In the supramolecular templating method, an organized assembly of surfactant molecules is used as the template for creating intercrystalline or intracrystalline meso-/macropores in a zeolite material. Thus, in all supramolecular templating approaches to mesoporous zeolites, the zeolite crystal is in direct contact with the supramolecular template when it is starts being removed from the zeolite material to generate the porosity.

Direct Crystallization of Zeolites in the Presence of Supramolecular Templates. Soon after the discovery of the mesoporous molecular sieves,[82,83] Beck et al. more systematically explored the use of alkyltrimethylammonium surfactants to serve as structure-directing agents, or templates, for the formation of microporous or mesoporous molecular sieve frameworks[84] to elucidate which factors favor molecular and supramolecular templating. An early attempt to prepare a mesoporous aluminosilicate material that possessed microporosity and acidity analogous to zeolites via dual templating, i.e., using both molecular and supramolecular templates, in a one-step synthesis was reported by Karlsson et al.[85] This approach is based on the idea that the molecular templates could direct zeolite crystallization in the mesopore walls while the mesoporous structure was simultaneously formed according to the supramolecular templating mechanism of the surfactant micelles. The group investigated whether simultaneously supramolecular aggregation and molecular templating by using mixtures of alkyltrimethylammonium surfactants with different chain lengths could be was achieved. However, it turned out that the two templating systems worked in a competitive, rather than cooperative, manner, resulting in the formation of bulk zeolite without any mesoporosity, amorphous mesoporous material, or their physical mixtures.

Lamellar surfactant-directed silicate mesophases with molecularly ordered inorganic frameworks were prepared by Chmelka et al. Prior to hydrothermal treatment at 135 °C, these materials possessed lamellar mesostructural order with amorphous silica frameworks. However, hydrothermal treatment/calcination of these thin fragile materials at temperatures $>$140 °C, resulted in decomposition of the surfactant, leading to subsequent degradation of the framework order and therefore loss of mesoporosity.[86,87] Thus, it is not straightforward to obtain crystalline zeolites containing both micro- and mesoporous structures in a single phase if the aluminosilicate gel is directly crystallized in the presence of both ordinary organic mesopore-directing surfactants and molecular templates for the zeolite. However, Ryoo et al. elegantly circumvented this difficulty by developing a direct synthesis route to mesoporous zeolites with easily tuned, uniform mesopores using amphiphilic organosilanes, $[(CH_3O)SiC_3H_6N(CH_3)_2C_nH_{2n+1}]Cl$, as supramolecular templates.[88] Designed in this manner, the surfactants are not expelled from the aluminosilicate sphere during the zeolite crystallization process, making it possible for the surfactants to transform the zeolite crystal growth into a mesoporous structure. In a typical synthesis, the amphiphilic organosilane is added to the initial synthesis composition of MFI zeolite containing the tetrapropylammonium ion as a structure-directing agent for the MFI zeolite. An equivalent synthesis principle was applied to the synthesis of mesoporous LTA zeolite crystals.[88] The mesopore diameters of the mesoporous MFI zeolite crystals could be systematically varied by changing the chain length of the organosilane and/or the hydrothermal synthesis temperature. For $n = 12$, 16, and 18, pore diameters of 2.1, 3.1, and 3.9 nm, respectively were obtained, but a mesopore diameter up to 20 nm could be obtained under proper synthesis conditions. The mesoporous MFI zeolite crystals exhibited superior catalytic activity and selectivity in the jasminaldehyde and vesidryl synthesis reactions compared to a purely microporous MFI zeolite and Al-MCM-41. In addition, these hierarchical zeolite crystals have also shown a remarkably high resistance to deactivation in some catalytic applications.[89] Ryoo et al. later extended the synthesis strategy, using organosilane surfactants as a supramolecular template, to also comprise aluminophosphate compositions.[90] The resulting aluminophosphates exhibited mesoporous structures and in the proposed synthesis mechanism, the organic tail of the surfactant directs the mesoporous structure while the silica moiety is incorporated in the resultant aluminophosphate frameworks (see Figure 5).

Surfactant-Mediated Assembly of Zeolite Seeds into Mesoporous Structures. After the discovery of mesoporous MCM-41 molecular sieves,[91] it was found that the incorporation of aluminum into the framework introduced mild acidic

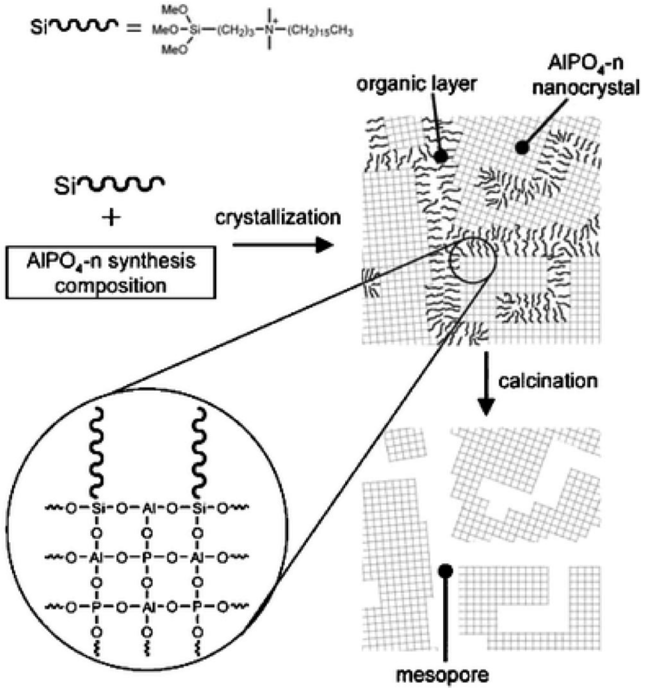

Figure 5. Proposed synthesis mechanism for hierarchical aluminophosphate crystals (HP-ALPO-*n*) prepared by supramolecular templating. Reprinted with permission from ref 90. Copyright 2006 Royal Society of Chemistry.

functionality. However, it can also lead to a loss of structural integrity in the mesoporous aluminosilicate materials because of the amorphous nature of their frameworks and relatively thin walls.[92–94] Metal-supported MCM-41 catalysts have yielded promising results in reactions such as hydrocracking, hydrodesulfurization, and hydrodenitrogenation because of their high surface areas and regular pore dimensions.[95–98] But the lower thermal, hydrothermal, and mechanical stability and the low acidity of M41S materials seems to limit their practical catalytic applications.[8] Because these parameters are critically important for the potential applications of mesoporous molecular sieves in catalysis, significant efforts have been made to solve this problem. Thus, many different synthesis procedures were designed to improve the acidity and hydrothermal stability of ordered mesoporous materials.[21] Recently, important advances have been made in improving the structural integrity of Al-MCM-41 through direct assembly[99] and postsynthesis modification methods.[100–103] However, one of the most promising strategies for improving the structural order, hydrothermal stability, and acidity of mesoporous aluminosilicates was suggested by Pinnavaia et al. The approach is based on the surfactant-directed assembly of the nanosized aluminosilicate precursors that normally nucleate the formation of conventional microporous zeolites. These protozeolitic nanoclusters, also known as zeolite seeds, are supposed to promote zeolite nucleation by admitting AlO_4 and SiO_4 connectivities that resemble the secondary structural units in crystalline zeolites.[104] Usually, they are particles 10−50 nm in size that can be synthesized simply by reducing the synthesis time normally required for the preparation of micrometer-sized zeolite crystals.[105] The nanosized zeolite seeds were used as building blocks, which were directly assembled into hexagonal, cubic, wormhole, and foamlike framework structures using supramolecular templating.[106] This method has been applied for the controlled assembly of steam-stable aluminosilicate mesostructures from zeolite FAU, MFI, and BEA seeds.[105,107–110] For the preparation of these templated mesostructures, a variety of different assembly conditions were applied.[111] Particularly, it was shown that the obtained MSU (Michigan State University) mesoporous materials with FAU zeolite seeds have a unique hydrothermal stability[105] that is attributed to the assembly of the Na^+-nucleated zeolite seeds under hydrothermal conditions in the presence of cetyltrimethylammonium ions. This afforded hexagonal MSU-S mesostructures with Si:Al ratios in the range of 1.6:1 to 10:1. The replacement of Na^+ by NH_4^+ ions in the as-made materials followed by calcination yielded exceptionally acidic and steam-stable mesostructures. However, the resulting materials were found to contain some occluded carbon, which is formed during the calcination process. This occluded carbon also contributes to the structural stability, which was illustrated by the observation that calcined samples with lower carbon contents exhibited a larger loss in surface area and pore volume upon steaming. Therefore, the steam-stability at 800 °C was in part a consequence of the exceptional acidity of a framework that resulted in the formation of structure-stabilizing carbon by partial template decomposition, and not entirely the result of a stable aluminosilicate framework.[107]

The same method was also applied for the preparation of mesostructures with MFI and BEA zeolitic seeds, which were formed using the typical molecular organic structure directing agents, such as tetrapropylammonium (TPA^+) and tetraethylammonium (TEA^+) ions, respectively.[106,112] The resulting mesoporous, Al-MSU-S with MFI zeolite seeds (Al-MSU-S_{MFI}) and Al-MSU-S with BEA zeolite seeds (Al-MSU-S_{BEA}) are remarkably steam-stable even in the absence of occluded carbon.[106] Additionally, it was shown that increasing the steaming temperature up to 800 °C does not lead to destruction of the long-range hexagonal order of the MSU-S aluminosilicate mesostructures and that substantial mesoporosity was maintained whereas the mesoporosity of MCM-41 was completely lost by the same treatment.[100] MSU materials containing LTZ seeds have also been prepared,[113] and the idea of using zeolite seeds as precursors to assemble hydrothermally stable and strongly acidic large pore mesoporous materials has been extended more recently to include SBA-15 under acidic assembly conditions.[114] Similarly, it has been shown that by using essentially the same synthesis strategy, a one-step synthesis of a highly stable mesoporous molecular sieve, MMS-H, with a structure analogous to MCM-48 but also containing zeolite secondary building units, could be obtained.[115–118] The MMS-H material was synthesized by first preparing a micellar solution of the surfactants cetyltrimethylammonium bromide and 1,3-diacetoxy-1,1,3,3-tetrabutyltin oxide polyethylene glucol dodecyl ether (Brij 30). Then the zeolite secondary building units and mesoporous phase were formed in situ by adding tetrapropylammonium hydroxide followed by crystallization. Adsorption/desorption curves of calcined MMS-H samples exhibited typical type IV isotherms with a broad hysteresis loop characteristic of capillary condensation in mesoporous channels. These new materials possess uniform mesopores with a bimodal pore size distribution and pore sizes of 2.3–2.6 and 3.6–3.7 nm, respectively. Typical BET surface areas of about 1000 m^2/g and wall thicknesses of about 1.6 nm are observed, which is somewhat larger than that of conventional MCM-48 materials having a wall thickness of typically 0.8–1.2 nm. The hydrothermal stability of the MMS-H material was also examined, and it showed a superior stability compared to a physical mixture of mesoporous Al-MCM-48 molecular sieve and microporous ZSM-5 zeolite.

Related families of materials are the cocalled MAS/MTS materials[119–125] and mesoporous TUD-1 containing zeolite nanocrystals.[126] MAS and MTS materials are mesoporous aluminosilicates or titanosilicates formed by assembly of zeolite nanoclusters. To date, several types of MAS and MTS materials have been prepared using this methodology. Seeds of zeolite β have been utilized for the assembly of MAS-5[119] and MAS-7[120] using CTAB and Pluronic P123 to guide the assembly processes, respectively. Pluronic P123 have also been used to assemble MAS-9[121] and MTS-9[120,122] from MFI-structured ZSM-5-type and TS-1-type seeds. MAS-3 and MAS-8 have been assembled from zeolite L-type seeds and Pluronic P123 in alkaline and acidic solution, respectively.[123] Using CTAB, researchers have assembled MTS-5 and MTS-8 from TS-1-type seeds in alkaline and acidic solution, respectively.[124] Similarly, it is also possible to prepare ordered micro/mesoporous composite materials containing zeolite nanocrystals as thin films by spin-coating solutions containing zeolite seeds and solutions containing silica/surfactants, simultaneously.[127,128]

Surfactant-Mediated Coating of Zeolite Crystals with Mesoporous Materials. In 1996, it was reported by van Bekkum et al. that zeolite Y crystals can be coated with a thin layer of a mesoporous MCM-41-type material.[129] The coating procedure involved impregnating FAU crystals with CTA-Cl and subjecting the material to MCM-41 synthesis conditions. This resulted in FAU crystals overgrown with 5–20 nm thick layers of MCM-41 structured materials. The prepared material exhibited higher conversion of heavy molecules in vacuum gas oil cracking than USY. Recently, a MOR/MCM-41 was reported by a similar procedure.[130] However, in a comparative study of the catalytic performance in palm oil cracking of MCM-41/β materials prepared using this methodology with an MCM-41/β material prepared by the seed-assembly methodology described above, it was shown that the material prepared by seed-assembly exhibited higher conversion as well as higher selectivity toward liquid gasoline.[131]

Delamination of Layered Zeolite Structures. For some zeolite materials, it is possible to rationally design nanosized zeolite crystals by an approach called delamination.[132–134] It has been found by Corma et al. that zeolites with layered precursors, such as MCM-22 or ferrierite, can be synthesized as lamellar precursors with a surfactant intercalated between two neighboring zeolite layers.[135–138] Thus, by completely swelling the layered zeolite precursor, the individual zeolite layers are separated or exfoliated while the structure of the layers is preserved. Upon removal of the surfactant swelling agent, the intercalated structure collapses to form a material composed of zeolite sheets that are packed together in such a way that that essentially all active sites are directly accessible from the external surface as illustrated in Figure 6.[136]

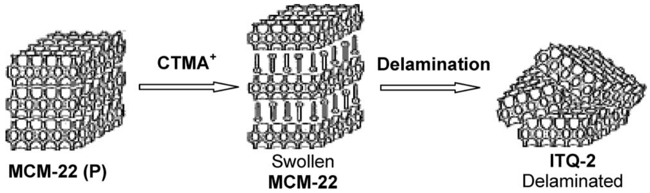

Figure 6. Scheme for the preparation of delaminated material ITQ-2 from a lamellar zeolite precursor (MCM-22 (P)). Adapted from ref 134.

Thus, the delaminated or exfoliated zeolites are sheetlike structures that are nanosized in one direction and significantly larger in the other two directions. Accordingly, they often show significant mesoporosity. By adding suitable inorganic guest molecules functioning as pillars, control of the interlayer distance can also be achieved. These materials possess a high thermal/hydrothermal stability and acidity, which is characteristic for zeolite materials and the accessibility of the acid sites was found to be significantly improved even for larger organic molecules.[135] Accordingly, delaminated zeolites exhibited improved properties in a wide range of catalytic applications.[139–143] The main role of the surfactant is to separate the individual zeolite layers by swelling the layered precursor, and in the swollen material, the interlayer distance is clearly determined by the surfactant. During removal of the surfactant, the layered zeolite structure must necessarily collapse unless pillars are present; therefore, there is only limited control over the resulting pore size. However, it is clear that the porosity of the sheetlike structure somehow reflects the use of the delaminating agent.

Use of Microemulsions and Reverse Micelles to Prepare Nanosized Zeolite Crystals. Another example of supramolecular templating of mesoporous zeolites is the use of zeolite crystallization in microemulsions or reverse micelles. Microemulsions or reverse micelles can successfully function as nanoreactors for the zeolite growth[144] in a completely analogous way to the voids in porous carbon materials in the confined space synthesis method (Figure 3). Thus, in the presence of microemulsions or reverse micelles, zeolite crystals can form only with a size smaller than that of the individual microemulsion droplets and that provides a convenient approach to controlling the crystal size and thereby to some extent the pore size. Reverse micelles prepared from a surfactant in an oil–water mixture were originally used to attempt to control the crystallization of a microporous zinc phosphate.[145] Later, Lin and Yates[146] used microemulsions to control the size of silicalite-1. In their work, the microemulsions were prepared by mixing the synthesis gel, an aqueous phase, an oil phase, toluene cetyltrimethylammonium bromide, and *n*-butanol. Zeolite crystals obtained from the microemulsions were found to exhibit relatively narrow size distributions. Similarly, Lee and Shantz also used microemulsions for zeolite synthesis and used the method to form platelet aggregates and spheres of silicalite-1,[147] but apparently with limited control of the

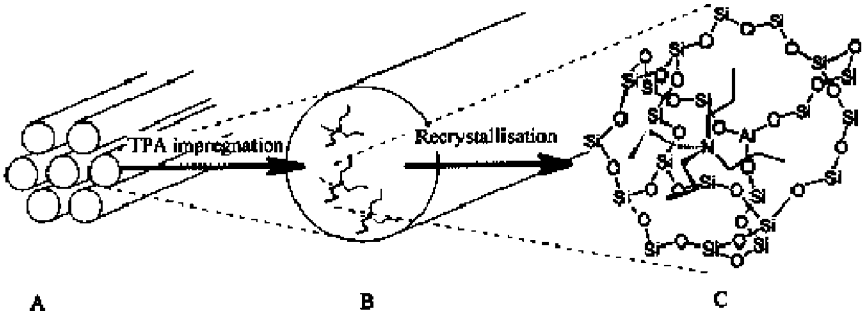

Figure 7. Schematic representation of the pore wall crystallization approach. An ordered mesoporous material is impregnated with a zeolite structure-directing agent and subjected to hydrothermal crystallization conditions resulting in partial crystallization of the mesoporous silica to zeolite structural units. Reprinted with permission from ref 148. Copyright 2001 American Chemical Society.

porosity. They used a microemulsion of heptane, surfactant, butanol, and the synthesis gel. Just as is the case for the delamination method, it is not completely clear to what extent the surfactant used in the microemulsion and reverse micelle techniques controls or influences the pore size in the resulting hierarchical zeolite material.

Indirect Templating

In the categorization of methods and materials in Figure 2, hierarchical zeolite materials formed by an ordered transformation of another templated mesoporous material into a hierarchical zeolite or by a controlled deposition of a zeolite onto a templated material are also considered to be templated, albeit indirectly. There are only a few different preparative approaches belonging to the category, the majority of which related to partial (secondary) zeolite crystallization of ordered mesoporous materials.

Partial Crystallization of Preformed Mesoporous Materials. Zeolite materials with hierarchical porosity can be produced by crystallization of mesoporous molecular sieves such as MCM-41 in the presence of appropriate molecular zeolite structure-directing agents. In our categorization of materials, they can be considered supported zeolite crystals when a partial crystallization leads to nanosized zeolite crystals supported on (or incorporated into) an amorphous mesoporous matrix. The generalized process is shown schematically in Figure 7, and it comprises the following two steps:

(i) assembly of an (amorphous) mesoporous phase by templating;

(ii) partial (secondary) crystallization of the amorphous material to a zeolite phase.

The “reverse” process, i.e., surfactant-mediated assembly of preformed zeolite seeds into mesoporous zeolite materials, was dealt with in the previous section. In its prototypical form, i.e., in the absence of templates to support the mesoporous material during zeolite crystallization, the indirect templating approach requires delicate optimization of synthesis conditions because zeolite crystallization conditions are generally quite severe (strong base and high temperatures). As will be shown, several measures are usually taken to ensure mesoporosity in the resulting zeolite composite material. Typically, they include

(i) applying less severe zeolite crystallization conditions and/or more stable, i.e., thicker-walled, starting materials;

(ii) retarding the disintegration of the mesoporous phase by adding supporting surfactants during the (secondary) zeolite crystallization step;

(iii) filling the mesoporous phase with carbon affording, a so-called CMK material, and applying this for the zeolite synthesis (in such a case the templating method is considered to be solid templating as discussed above).

The synthetic approach of partially crystallizing ordered mesoporous silicates was conceptually introduced in 1997 by Jansen et al., who showed that hexagonally ordered mesoporous silica ion-exchanged with tetrapropyl ammonium (TPA) cations can be partially crystallized in glycerol to afford mesoporous materials containing very small protozeolitic, or embryonic ZSM-5, tectosilicate structures within the pore walls, as evidenced by an absorption at ca. 550 cm^{-1} in the FTIR spectrum.[149]

The approach was further developed with the successful crystallization of true zeolite structural units (visible by XRD) in the pore walls of mesoporous silicates. This was achieved by Huang et al. who reported a procedure for the preparation of MCM-41 containing small ZSM-5 crystals in the pore walls.[150] First, a zeolite synthesis gel containing the surfactant cetyltrimethylammonium bromide in addition to the zeolite synthesis gel components (water glass, sodium aluminate, and TPA-Br) was allowed to self-assemble into a hexagonally ordered mesoporous silica by heating the gel to 100 °C at pH 11 for 2 days. Subsequently, the afforded MCM-41 material containing TPA cations was heated to 125 °C at pH 9.5 for a period of 1–12 days. The latter treatment resulted in the partial transformation of the MCM-41 material into small ZSM-5 crystals. With a crystallization time of 2 days, a disordered hexagonal mesoporous silicate containing small ZSM-5 crystals was obtained; however, even more prolonged crystallization times caused the hexagonal mesoporous structure to become increasingly disordered and eventually transform into a lamellar structure that was not stable under calcination. At about the same time as Huang et al. reported synthesis of ZSM-5/MCM-41 composites, van Bekkum et al. reported that crystallization of ZSM-5 from MCM-41 impregnated with TPA at 170 °C for only 1 h caused the mesoporous framework to collapse along with the appearance of small ZSM-5 peaks in the XRD pattern.[148] However, if the crystallization step is carried out in the presence of the surfactant hexadecylamine, the collapse of the mesoporous silicate can be retarded, resulting in a material containing

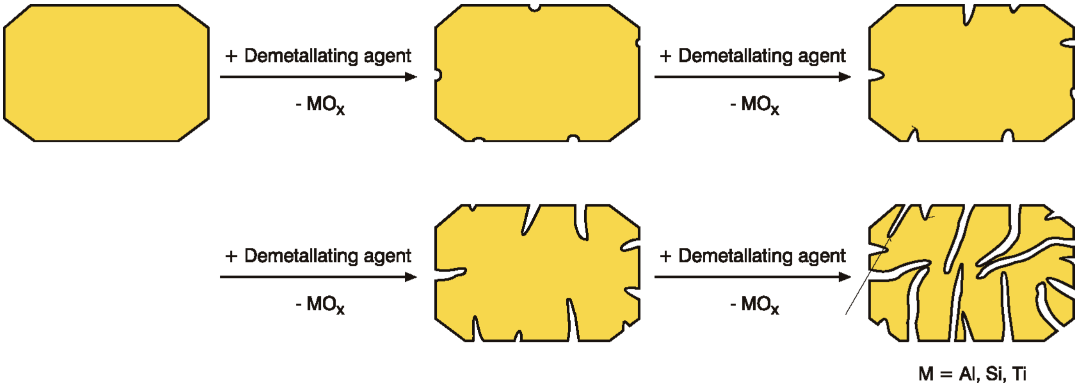

Figure 8. Nontemplated demetalation of zeolites to generate mesoporous zeolite crystals.

small zeolite crystals while retaining some degree of mesoporosity. Nonetheless, hydrothermal treatment for 2 h caused the mesoporous silicate to collapse even in the presence of the supporting surfactant.

A related class of materials was reported by Trong On and Kaliaguine in 2001.[151,152] These SBA-15/MFI composite materials, the so-called UL-ZSM-5[151] and UL-TS-1,[152] were synthesized using larger-pore SBA-15 as the starting material instead of smaller-pore MCM-41. By applying thick-walled mesoporous materials and carrying out the zeolite crystallization step at comparatively low temperatures (120 or 130 °C), they were able to produce materials exhibiting large mesopore volumes (1.25–1.83 cm^3/g) and high degrees of zeolite crystallinity (up to 42% after 5 days of hydrothermal treatment) at the same time.[151] The materials were synthesized by impregnation of TPA-OH onto calcined SBA-15 with the desired elemental composition and subsequent hydrothermal treatment. For the synthesis of UL-ZSM-5, hydrothermal treatment was carried out at 130 °C for a period of 1–5 days, resulting in an increasingly crystalline product with ZSM-5 structure retaining some of the mesoporosity of the starting material. The synthesis of UL-TS-1 from a titanium-containing SBA-15 starting material was also reported by the same authors.[152]

A mesoporous composite material containing ZSM-5 very similar to those described above was reported by Hidrobo et al.[153] A mesoporous aluminosilicate prepared by hydrothermal treatment of an aluminosilicate gel also containing the biopolymer chitosan as mesopore template was impregnated with TPA-OH and crystallized at 160 °C for 3 days. After calcination, a mesoporous material containing ZSM-5 crystals was obtained.

Deposition of Zeolite Seeds onto Templated Mesoporous Materials. Composite materials comprising zeolites dispersed onto mesoporous materials have been produced by impregnating preformed large-pore mesoporous materials such as SBA-15[154] or mesostructured cellular foams (MCFs)[155] with zeolite seeds and subsequently subjecting the seeded materials to hydrothermal treatment conditions. Starting from SBA-15, the procedure resulted in a highly mesoporous SBA-15/ZSM-5 composite material with very uniform mesopore size distribution centered at 5.4 nm.[154] A similar procedure starting from siliceous MCF allowed for the preparation of mesoporous ZSM-5 and NaY materials, however, with much larger mesopores (15.5–17.5 nm diameter).[155] Also, very small beta seeds supported on MCM-41 were prepared by impregnation using a colloidal beta seed solution.[156]

Zeolitization of Diatomaceous Earth. Also silica-rich diatomaceous earth has been applied for the synthesis of mesoporous zeolites. The synthesis involves attaching zeolite seeds to the surface of diatoms and crystallizing the diatom-supported seeds into zeolite crystals retaining the basic morphology of the diatom.[157–160] Because diatoms are very rich in silica, they are used as a source of silicon at the same time. Thus, the majority of the silicon in the zeolite comes from the diatoms rather than from the zeolite synthesis gel mixture. As a multitude of diatom species are known, the application of these can be envisaged to provide excellent possibilities for tailoring hierarchical porosity in zeolites.

Nontemplated Approaches to Mesoporous Zeolites

In addition to the templating methods used to prepare mesoporous zeolites that are discussed extensively above, it should be noted that several nontemplated approaches also exist. It is outside the scope of the present review to discuss these in detail but it is interesting to note that nontemplated routes to all the three categories of hierarchical zeolite materials defined in Figure 1 have been reported. For the preparation of hierarchical zeolite crystals, the demetalation approach seems to be the only viable nontemplated route to produce additional intracrystalline porosity in zeolite crystals. Generally, the demetalation method involves the synthesis of a conventional, purely microporous zeolite, which is then treated chemically to preferentially extract one of the constituent metallic elements of the zeolite. The most well-studied demetalation methods are dealumination and desilication and recent reviews gives excellent accounts of state-of-the art for these methods.[21–23] Recently, detitanation was also reported as a means to introduce intracrystalline mesoporosity in titanosilicate materials,[161–163] which could indicate that the full scope of the demetalation approaches has not yet been fully explored. Figure 8 illustrates the basic principle of the demetalation approach.

It is clear that mesopores result from demetalation only if the dissolution process proceeds in a quite special way that clearly cannot involve complete dissolution of the zeolite crystals at the same rate from all faces of the parent crystal. Moreover, it is seen that the obtained mesoporosity depends directly on the amount of dissolved material, and that there is a priori no way to directly control the pore size. Typically, the conditions required to partly dissolve zeolite crystals are quite harsh because zeolites are typically quite stable materials. Thus, the dissolution process usually involves strong acids or bases, or strongly complexing agents.[21–23,161] The selective extraction process leads to removal of some of the metallic or semimetallic components of the zeolite, typically in the form of soluble oxoanions, but it can also be in the form of complexed species. Originally, the dealumination method has attracted most attention because the importance of this method in producing ultrastable zeolite Y crystals for industrial used in catalytic cracking.[22] However, the selective extraction of silicon from zeolite crystals has been known for a long time,[164–169] but recently a series of systematic studies of this approach by Groen, Mouljin, Perez-Ramirez, and co-workers[170–173] has provided detailed insight into the synthesis factors that control the porosity and into the properties of these materials, especially the improved diffusion[173] and the enhanced catalytic properties in some applications.[174]

For the preparation of nanosized zeolite crystals, several nontemplated methods have been reported and these methods were recently carefully reviewed.[175] Typically, these methods involve synthesis of the zeolite nanocrystals from clear solutions and gels under experimental conditions that are controlled to favor nucleation over crystal growth. Even though it is often possible to rationalize why a given synthesis scheme leads to nanosized zeolites, there appear to be few versatile methods that allow the use of a certain preparative protocol to yield a wide range of different mesoporous zeolites. Rather, it appears that special synthesis schemes have to be developed for each desired zeolite material.

Finally, it is also possible to produce supported zeolite crystals by many different nontemplated routes. Actually, most industrial zeolite catalysts are indeed supported zeolite crystals produced simply because pure zeolites cannot easily be shaped into tablets or extrudates of sufficient mechanical strength for industrial applications or because the zeolite itself is too active to be useful in the pure form for the desired catalytic application. The industrial supported zeolite crystal catalysts are normally produced by extrusion of a zeolite-support composite paste obtained by careful mixing of the constituents, possibly with inclusion of various additives or by spray-drying an appropriately prepared slurry of the zeolite and the support(s) and any required binders. Thus, there are numerous examples in the catalytic literature of supported zeolite crystals acting as heterogeneous catalysts in a very wide range of reactions.[2,3]

Concluding Remarks

During the past decade, hierarchical zeolites materials and methods for their preparation have attracted continually increasing attention. Much of this attention can be attributed to the fundamental interest in developing preparative methods that allow careful tailoring of the properties of solid materials but also to the technical interest in developing heterogeneous zeolite catalysts with improved accessibility of the active sites located inside the micropores. Today, numerous preparative approaches have been reported to yield different hierarchical zeolite materials featuring intracrystalline micropores and intracrystalline or intercrystalline meso-/macropores. Here, we have tried to categorize both the hierarchical zeolite materials and the methods available for their synthesis and give a detailed overview of the available literature described templating approaches to hierarchical zeolites, and to mesoporous zeolites in particular. In our categorization, we distinguish between three distinctly different types of hierarchical zeolite materials, the hierarchical zeolite crystals, the nanosized crystals, and the supported zeolite crystals. For the templating approaches available to synthesize hierarchical zeolites, we categorize these methods as solid templating, supramolecular templating, and indirect templating. Hopefully, this terminology can be useful in the future development of the field. From the detailed discussion of the materials and the methods given above, it should be clear that it is simple to use the present scheme to categorize the vast majority of the currently published materials and templating approaches. However, it is also clear that in some cases, it is not straightforward to directly establish to which category a given hierarchical zeolite material belongs. However, this typically arises when there is only limited characterization of the material, so that it is not possible to determine whether the material is adequately described as hierarchical zeolite crystals or nanosized zeolite crystals or supported zeolite crystals. Often efficient discrimination between the three categories of hierarchical zeolite materials cannot be done solely on the basis of measured pore size distributions and X-ray diffraction studies of the materials but typically also requires careful electron microscopy studies. Thus, in future characterization studies of new hierarchical zeolite materials, the present categorization can be used as a tool to help select the techniques that will provide the information required to give a detailed description of the structure of the material, and the reasons for its hierarchical porosity. It is noted that hierarchical zeolite materials that are actually hybrids between, or physical mixtures of, the prototypical materials in the categorization can easily be envisaged. This could be hierarchical nanosized zeolite crystals or supported nanosized zeolite crystals, both of which are in fact already known, but also hierarchical supported zeolites could be easily prepared.

Whereas the categorization of the materials is usually straightforward provided that sufficiently detailed characterization is available, it is often more difficult to correctly categorize the templating method into one of the three types. For solid templating and supramolecular templating, the challenge is clearly not to establish whether, for example, a solid or a supramolecular assembly of surfactants is present during zeolite synthesis. Rather, it can be quite difficult to firmly establish to what extent the solid or the supramolecular assembly of surfactants actually acts as template and thereby directly controls the size and shape of the meso-/macropores in the resulting hierarchical zeolite material. This challenge is even more pronounced for the indirect templating method, because here the original template is no longer present when the hierarchical zeolite material is formed. However, if the hierarchical zeolite is formed in, for example, a pseudomorphic transformation of another templated mesoporous material, the resulting material can still be considered to be templated, albeit indirectly. Similarly, zeolite nanocrystals or seeds deposited carefully onto the pore walls of a templated mesoporous material can be considered a templated hierarchical zeolite material even though the template is not present during the deposition. However, in practice, it turns out that by the indirect templating method, some disorder is typically introduced when, for example, the pore walls of mesoporous molecular sieves or diatoms are crystallized into zeolites, and this clearly makes it difficult to establish in which cases the term templating is properly used. However, the problem of introducing some disorder during synthesis is not unique for the indirect templating method because often some disorder is also introduced when a solid or a supramolecular template is removed. This disorder can be either a structural collapse as in the case of the delamination or it can be a partial amorphization of the zeolite crystal. Again, this is not a problem for the present categorization of templating methods but it pinpoints the necessity to carefully characterize the synthesized hierarchical zeolite materials to clearly identify the role of the template and fully understand to what extent it controls the resulting pore size distribution. It is noted that it is not only for fundamental reasons that it is desirable to clearly understand and control the factors that determine the pore structure of hierarchical zeolites. When these materials are used as heterogeneous catalysts, it is typically desirable to maximize the accessibility of the active sites to fully utilize the catalytic potential of the material and at the same time to minimize the volume of void space in the material since this leads to a lower catalytic activity on a volume basis, which is often the industrially important parameter. Thus, the optimal porosity is often a compromise between accessibility and the volumetric density of active site, and this compromise can be quite different from reaction to reaction, and even for the same reaction it can vary significantly from one set of reaction conditions to another. Recently, it has been convincingly demonstrated using different probe molecules that both templated and nontemplated hierarchical zeolites do, as expected, exhibit significantly faster diffusion than conventional zeolites featuring only micropores.[50,173,176] Thus, it seems reasonable to attribute the improved performance of hierarchical zeolite catalysts observed in numerous cases to the improved mass-transport properties. Some examples of this are given in the discussion above. However, so far, mesoporous zeolite crystals prepared by solid templating with carbon nanoparticles have been the most extensive studied examples of templated zeolite catalysts, and significantly improved performance has been observed in a number of acid-catalyzed hydrocarbon reactions,[176–180] but also in important environmental technologies[181,182] and in some selective oxidations.[43,183] Similarly, there are also several examples that nanosized zeolite crystals prepared by supramolecular templating of zeolite seeds yields, for example, improved hydrocarbon conversion catalysts[123,184–186] and recently, remarkable catalytic activities were reported for mesoporous zeolite crystals synthesized by supramolecular templating.[88,89] The fact that improved catalytic performances are also observed in several examples using hierarchical zeolite catalysts prepared by nontemplated methods[179] supports the notion that the enhanced activity and/or selectivity can be attributed to the presence of a hierarchical structure with increased accessibility of the active sites. Thus, it appears likely that in the coming years, hierarchical zeolite materials will continue to attract increasing attention. This will undoubtedly lead to an even more detailed insight into the materials and templating methods described here, but hopefully also to completely new discoveries. Furthermore, the use of mesoporous zeolites as catalysts is also expected to gain importance in the coming years and it will be interesting to see if the possibilities for templating mesoporous zeolites will lead to significantly improved or maybe even completely new heterogeneous catalysts.

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