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Repeated Templating[†]

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In recent years, a lot of research activity has focused on the synthesis of new ordered porous materials by utilization of porous matrices as templates. Since the matrices are themselves created by templating procedures, the entire process can be envisaged as "repeated templating". This review describes recent conceptual developments in the field of structure replication and summarizes the large number of publications on new functional materials prepared by this method.

Introduction

Inorganic materials with well-defined porosity are routinely synthesized by use of "templates". The creation of periodically ordered, uniform pore systems in the submicrometer size range requires the aid of one or more chemical species, the porogen, to direct the formation of the inorganic phase in a suitable way. The desired material is formed with the porogenic species being incorporated into the solid structure, resulting in a composite from which the porogen is finally removed to yield the pore system. By strict terms, the porogen is called a "template" only if the relationship between its own structure or chemical nature and the resulting solid structure in the porous material is univocal, that is, if the choice of a specific porogenic species will lead to a unique pore structure which cannot be realized by a different porogen. In all other cases, that is, if the relationship between the porogen and the resulting structure is less well-defined, the term "structure director" is more adequate. However, the borderline between these two cases is of a diffuse nature, which is why "template" is nowadays used quite frequently as a general expression for any species which is used to deliberately manipulate the structural or morphological features of the product. Microporous zeolites and zeolite-related materials are created by utilization of organic molecular units, which in most cases act as templates in the true sense; the large diversity of crystalline zeolite structures is to a large extent the result of the variety of applicable templates.[1–3] Contrary to that, the utilization of supramolecular aggregates of amphiphilic species for the synthesis of mesoporous materials (described in detail in some recent review articles[4–7]) follows less well-defined structural relationships, which is why the amphiphiles act as structure directors rather than as true templates. This review article particularly focuses on the utilization of rigid structure matrices for ordered mesoporous materials by replication.[7a,8–10] The underlying principle of this synthesis concept is the unambiguous, one-to-one transfer of the nanoscopic structure from the matrix to the final product. Hence, structure replication is a true templating procedure. If the structure matrix itself has been created by a templating mechanism (even if only by a more generous definition of the term), the entire process can be envisaged as "repeated templating".

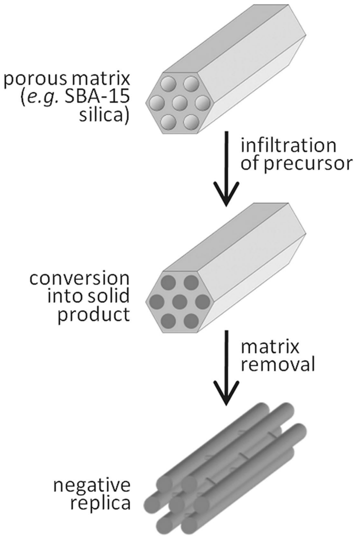

Figure 1. Schematic drawing of the structure replication concept (exotemplating, "hard" templating).

The general principle of structure replication is very straightforward. A porous solid material is used as a rigid matrix (template); that is, its pores are filled with one or more precursor species which react *in situ* to form the desired material. The matrix is finally removed to yield the product as its negative replica (Figure 1). In analogy to macroscopic procedures, this process is occasionally termed "casting" or "molding", with the matrix (template) acting as the "casting mold" and the product (replica) being the "cast". "Casting" on the nanometric length scale can consistently be termed as "nanocasting". Contrary to this quite simple approach, the mechanisms are much more complicated when molecular or supramolecular species are used as templates. In this case, the structure formation is very much a matter of mutual interaction between the single templating units and the inorganic precursor species forming the solid product. The formation mechanism is a highly cooperative process, as

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the periodic structure forms during, rather than prior to, the condensation of the inorganic species. This situation is observed for both microporous and ordered mesoporous materials (with exceptions, see below): Before the formation of the solid structure, the templating units (molecules in the former case, supramolecular aggregates in the latter case) are usually distributed isotropically in solution, that is, without translational periodicity. In fact, amphiphilic molecules may not even self-aggregate at this presynthesis stage; that is, their concentration may be below the critical micellization concentration. It is only by interaction with the inorganic units that the formation of periodic structures occurs. Schüth has suggested the term "endotemplating" for this mechanism and "exotemplating" for those cases where the long-range structure of the template (periodically ordered or not) is already present before the formation of the product and does not undergo any further structural changes during the formation.[11] Alternatively, the distinction between "soft" and "hard" templating may serve the same purpose of distinguishing between the two general mechanisms.[9] A special case is present when supramolecular templating involves very high concentrations of the amphiphilic species. In this case, the supramolecular aggregates as well as the translational periodic arrangement of the aggregates takes place before the addition of the inorganic precursors. In other words, a lyotropic liquid crystal is formed, and the condensation of the inorganic product occurs in the interstitial solvent domains between the micellar units. Accordingly, the structure of the final product is predefined by the lyotropic phase, and the mechanism is therefore reminiscent of exotemplating. This special case of structure formation by supramolecular templates is often called "true liquid-crystal templating",[12] and the terms "nanocasting" and "exotemplating" are also used in this context.[13] One might argue that the structural features of the liquid crystal may still be subject to subtle changes during the formation of the solid product; even though the symmetry may be fixed, the repeat distances may still change to a certain degree during the synthesis. Thus, from a puristic point of view and contrary to replication procedures involving solid-state matrices, true liquid-crystal templating is not exactly a case of "exotemplating" or "nanocasting".

This review provides a survey over syntheses of porous materials by structure replication using rigid matrices as exotemplates. According to the title, "Repeated Templating", we shall focus on exotemplates which themselves were created by templating mechanisms (either exo- or endotemplating, including cases of structure direction for which the term "templating" is inadequate by strict terms, as discussed above). In addition, many other examples of exotemplating syntheses of porous materials are found in the literature in which the matrices were not created by a preceding templating step. These include activated carbon,[14–16] porous membranes,[17–19] arrays of nano- or micrometer-sized particles,[20] aerogels and xerogels,[21–24] resins,[25,26] or structures of biological origin (e.g., wood and cellulose fibers);[27–31] such matrices will not be regarded in the following.

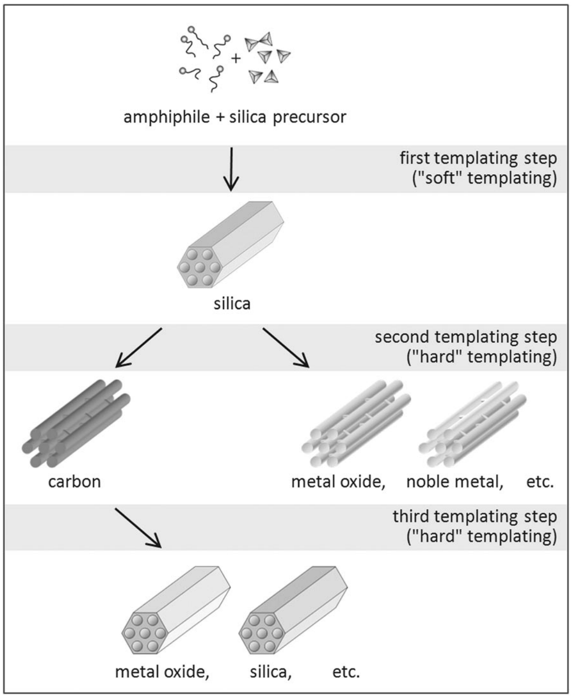

Figure 2. Schematic drawing of repeated templating for the synthesis of ordered mesoporous materials. The first step is "soft templating" (endotemplating), i.e., structure formation by utilization of amphiphilic structure directors; the following steps are "hard templating" (exotemplating).

The Concept of Repeated Templating

For the creation of periodically ordered porous materials by structure replication, two distinct types of structure matrices (exotemplates) are commonly used: (i) On the one hand, porous silica or aluminosilicate materials (e.g., mesoporous SiO_2 such as MCM-48,[32] SBA-15,[33] or KIT-6, as well as microporous zeolites) frequently serve as structure matrices; they are synthesized by "soft" templating procedures (endotemplating). (ii) On the other hand, mesoporous carbon materials (e.g., CMK-3)[34] are increasingly being utilized as structure matrices; their synthesis already involves the utilization of a "hard" structure matrix (exotemplate), usually silica. In both cases, the entire process can be envisaged as a repeated templating mechanism, namely, "soft/hard" templating in the former case and "soft/hard/hard" templating in the latter case (see Figure 2). The exotemplating approach has afforded a large variety of new, periodically ordered materials, such as carbon, noble metals, metal oxides, metal chalcegonides, or silicon carbide.

Since structure replication always requires that the structure matrix be first created by at least one preceding templating step, the question arises why this additional effort is worthwhile. First, many ordered porous materials cannot be synthesized by single templating. For example, only a limited range of mesoporous metal oxides has successfully been prepared by utilization of amphiphilic structure directors. Possible reasons may be the lack of suitable precursor species; a high tendency of the desired metal oxides to phase-separate from the amphiphilic species to form nonporous, crystalline phases; or pronounced redox activity of such systems during subsequent thermal combustion of the organic amphiphiles.[4] Second, a further advantage of rigid structure matrices over soft structure-directing units is that the formation of the product may occur at much higher temperatures. Soft templating is usually carried out under sol–gel conditions; high-temperature treatment, for example, in order to increase the stability or degree of crystallinity of the product, can only be accomplished at a later stage (before, during, or after template removal). Owing to the "soft" nature of the structuring units, such postsynthesis tempering often results in a substantial loss in porosity. Syntheses involving hard matrices, on the other hand, take place under solvent-free conditions, which allows for much higher temperatures. The solvent (if necessary), used to infiltrate the precursor species into the pores of the structure matrix, is usually removed prior to the conversion of the precursor into the respective product. Hence, much higher synthesis temperatures are possible during exotemplating reactions. The temperature limit is dictated only by technical issues (furnace temperature) or by potential chemical reactions between the matrix and the guest species, such as the formation of carbides at high temperatures in carbon matrices. The opportunity of high temperatures facilitates the synthesis of crystalline products without a loss of mesoscopic structure; the matrix serves as a rigid skeleton, preventing collapse of the product's pore system. In fact, this advantage has been exploited even for mesoporous materials prepared without hard matrices; postsynthetic filling of the pores with carbon or silica has been shown to increase the thermal stability of mesoporous transition metal oxides, thus facilitating high-temperature treatment for crystallization (Figure 3).[35,36] A similar stabilizing effect due to the presence of carbon has been shown for high-temperature treatment of mesoporous silica.[37] This illustrates the value of rigid matrices for increased stability during postsynthetic tempering.

Finally, the question arises why ordered mesoporous carbon matrices are often used for structure replication instead of silica matrices, since the carbon materials are themselves created by utilization of silica matrices. The reason for this seemingly unnecessary additional templating step lies in the procedure of removing the structure matrix after the formation of the product. To remove a silica matrix, chemical treatment with either hydrofluoric acid (HF) or concentrated sodium hydroxide solution (NaOH) is necessary. These rather harsh conditions may be harmful to the desired product, preventing the selective etching of the matrix. For example, the amphoteric character of ZnO prohibits its synthesis by direct replication from a silica matrix. A carbon matrix, on the other hand, can be removed by controlled thermal combustion, which extends its usability to a larger variety of products. However, it should not be concealed that the removal of carbon still presents a major problem in some cases, since its thermal combustion releases large amounts of thermal energy, which may be harmful to the pore structure of the product.

The Procedure of Structure Replication

In the first step of a structure replication procedure, the pores of the matrix are filled with the precursor for the desired product, for example, sucrose or other polymerizable organic compounds for carbon, or metal salts (especially nitrates) for metal oxides. In most cases, this is accomplished by impregnation with a precursor solution, either by so-called "wet impregnation" or by the "incipient wetness" technique (Figure 4). In the former case, the matrix is dispersed as a powder in a dilute solution; the dissolved precursor species diffuse into the pores where they are adsorbed to the pore walls; this will often result in limited loading of the pores with the precursor, requiring several impregnation cycles. In the latter method, a saturated precursor solution is used, and the volume of the solution is restricted to the total pore volume of the matrix to be filled. The purpose of this practice is that the solution is entirely drawn into the pores by capillary forces, and no precursor material is deposited on the outer surface of the matrix; the incipient wetness technique usually leads to higher loading than wet impregnation.

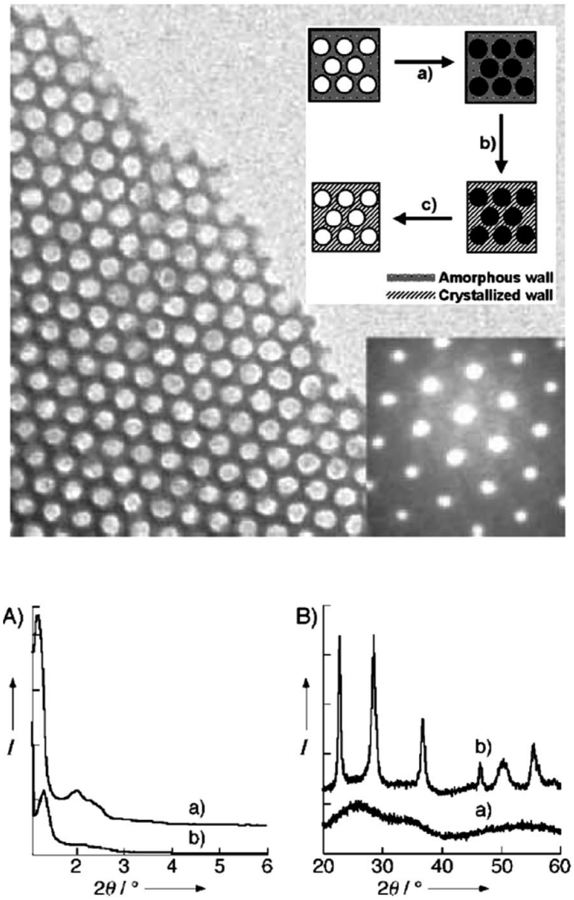

Figure 3. TEM image and ED pattern of crystallized mesoporous Nb-Ta oxide and XRD patterns (a) before and (b) after crystallization. The conceptual scheme (inset) describes how the postsynthetic creation of a carbon skeleton inside the pores strengthens the mesopore structure sufficiently for the crystallization of the oxide walls at high temperatures.[35]

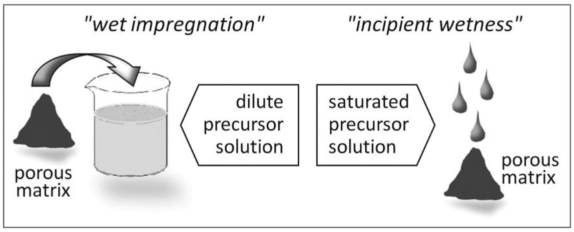

Figure 4. Schematic drawing of the "wet impregnation" and "incipient wetness" techniques for the infiltration of precursor species into porous structure matrices.

Another means to avoid deposition of substantial amounts of the precursor species on the exterior surface of the matrix (instead of inside the pores) is to use porous matrices consisting of large particles, that is, to minimize the outer surface area in the first place. Replication from such materials, for example, silica monoliths[38–40] or spherical particles with sizes in the micrometer range,[41–44] will be discussed below. They are particularly attractive as structure matrices anyway, since the replicas will show the same well-defined morphology, which makes them interesting for a variety of applications, such as gas sensing, chromatography, or catalysis.

Interaction of the precursor species with the pore walls may involve hydrogen bonding, coordination of metal ions (e.g., by silanol groups), Coulomb interaction (e.g., with oxygen in the pore walls), and van der Waals forces, which facilitate the migration of metal ions.[8] A versatile tool to improve the interaction between the matrix and the guest species is to modify the pore walls, for example, by increasing the amount of free silanol groups in silica[45,46] or by attaching suitable functional groups, such as vinyl[47] or amino[48] groups for increased complexation of metal ions; these approaches will be discussed below. In a similar way, the surface of a carbon matrix can be modified to increase the number of polar functionalities and, thus, to facilitate impregnation with polar or charged precursor species.[49] Another strategy to facilitate the infiltration aims at the choice of solvents with suitable polarity to improve the wettability of the pore walls; a porous carbon matrix, for example, may require less-polar solvents than porous silica, due to a more hydrophobic character of the pore walls. However, the choice of a less-polar solvent may reduce the solubility of the precursor; thus, a balance between the two aspects should be found. Other approaches to efficiently infiltrate the precursor species into the structure matrices include the choice of two immiscible solvents,[50,51] vapor-phase infiltration,[52–54] or infiltration with precursors in the liquid/molten state without a solvent,[55] as will be discussed below.

After successful infiltration of the precursor into the pores of the matrix and subsequent removal of the solvent, the formation of the desired product is usually accomplished at elevated temperatures. In most cases, the reaction inside the pores goes along with substantial contraction (especially as gaseous byproducts may also form), which is why the pores of the matrix will not be entirely filled with the product species. Therefore, one or two repeated infiltration/reaction cycles are usually necessary before the matrix can be removed by the above-mentioned methods. The remaining product is the negative replica of the structure matrix. If mesoporous carbon is used as the matrix, then the final product is the positive replica of the original starting silica matrix, from which the carbon structure was replicated in the first step (Figure 2).

Mesoporous Carbon

Historically, mesoporous carbon materials were the first examples of structure replication by utilization of ordered mesoporous matrices. This is why they are best suited to illustrate the conceptual ideas and opportunities of this method. (Prior to this, microporous zeolites had been used for the synthesis of carbon structures by replication, but the structural fidelity was not as high as for mesoporous carbon, as will be discussed below.) However, the number of publications on mesoporous carbon has meanwhile increased to a degree which cannot be completely covered in a short review article like this. Thus, the following survey only takes into account the conceptually most significant papers but does not attempt to be exhaustive; some recent reviews[8,9,56,57] are recommended for further reading.

In 1999, Ryoo et al. reported the first synthesis of mesoporous carbon, CMK-1.[58] They infiltrated a solution of sucrose and H_2SO_4 into the pores of MCM-48[32] silica with cubic $Ia\bar{3}d$ symmetry, subsequently polymerized and carbonized the sugar, and finally removed the silica matrix by leaching with NaOH. A similar synthesis was published almost simultaneously by Hyeon et al., who used MCM-48-analogous aluminosilicate as the matrix and a phenol/formaldehyde resin as the carbon source.[59] CMK-1 thus obtained is not exactly a replica of MCM-48, since its symmetry is somewhat lower than $Ia\bar{3}d$. This is because the pore architecture of MCM-48 silica consists of two distinct channel systems which are not connected with each other. When these are filled with carbon, the removal of the silica must necessarily induce a displacement of the two resulting carbon subframeworks relative to each other; this has been elucidated in detail by Solovyov et al., who carried out modeling studies on X-ray diffraction and TEM data.[53b,60]

The same situation, that is, the absence of interconnections between adjacent mesopores, is found in another prominent mesoporous silica phase, MCM-41;[32] in this case, the material is generally not suitable as a matrix for structure replication, since its pore system comprises linear mesopores which are arranged parallel to each other with a two-dimensional hexagonal *p*6*mm* symmetry. Using this structure as a "replication" matrix results in bundles of linear rods of the respective product, which, upon removal of the silica, lose their hexagonal arrangement due to the absence of links between them. This situation was observed for carbon[61] and for Pt[62] (see below) nanowires prepared inside the pores of MCM-41 silica. However, SBA-15 silica,[33] which has the same two-dimensional hexagonal *p*6*mm* pore system symmetry as MCM-41 silica, presents a different situation: As a result of a different synthesis method, especially the utilization of a long-chain block copolymer instead of a cationic ammonium surfactant as the structure-directing agent, the parallel mesopores are not only larger but, in particular, connected with each other by randomly distributed micropores. Hence, in the respective replica, the hexagonal structure is preserved, since the resulting linear rods are linked with each other. Accordingly, the synthesis of a mesoporous carbon with *p*6*mm* symmetry, CMK-3,[34] was achieved soon after the first reports on cubic CMK-1. The finding that SBA-15 silica produces replicas without a loss of symmetry actually terminated an ongoing controversy over whether or not micropores truly exist in SBA-15. On the basis of physisorption data, the existence of micropores had been assumed by several authors, but it was also evident that they were absent in some specific samples. When structure replication (for CMK-3 carbon[63] as well as Pt,[64] see below) was used as a tool for elaborate structural investigation, it was clarified that the degree of microporosity depends in fact on the exact synthesis conditions (such as pH or temperature) during the synthesis of SBA-15.

Meanwhile a large-pore cubic $Ia\bar{3}d$ silica phase prepared by the utilization of long-chain block copolymers was reported by several groups.[65–67] This material, often denoted as KIT-6,[67] has the same mesopore symmetry as MCM-48 silica but, like hexagonal SBA-15, exhibits micropores connecting the two channel systems.[68] (In other words, the difference between the two cubic silica phases KIT-6 and MCM-48 is analogous to that between the two 2-dimensional hexagonal silica phases SBA-15 and MCM-41.) Accordingly, the carbon replica of KIT-6 silica, denoted as CMK-8,[67] maintains the $Ia\bar{3}d$ symmetry after removal of the silica matrix, owing to the fact that the two carbon subframeworks are rigidly connected with each other.

When silica phases with larger mesopores are used as the matrices for structure replication, an interesting variant in the synthesis of mesoporous carbon is possible. As long as only a limited amount of the respective carbon precursor is infiltrated into the matrix, the silica pore walls are only coated with a layer of carbon instead of being filled entirely. The carbon replica then exhibits two modes of pores, one (as always) resulting from the removal of the silica matrix, the other one originating from the fact that a fraction of the original pore volume in the silica matrix was never filled with carbon. For example, utilization of hexagonal SBA-15 or cubic KIT-6 silica results in bimodal porous carbon materials designated as CMK-5[56,69–71] and CMK-9,[67] respectively. These products can be envisaged as ordered networks of hollow carbon tubes (Figure 5).

Lindén et al. presented a particularly interesting silica material and demonstrated its applicability as a matrix for the preparation of mesoporous carbon by structure replication. By combining the concept of PEG-induced controlled phase separation (for the generation of macroporosity)[72] with the utilization of a surfactant as a structure director for ordered mesopores, they created monolithic silicas with hierarchical multimodal porosity.[38] Consequently, the replication procedure resulted in multimodal porous carbon monoliths[73] as well as some metal oxide monoliths (see below).

Recently, Parmentier et al. reported the synthesis of microporous carbon by using zeolite EMC-2 as a structure matrix. The product exhibits an X-ray diffraction signature which proves a very high degree of structural fidelity in the replication process (Figure 6).[74] Kyotani et al. have used zeolite Y for a similar synthesis and showed a high degree of structural order by HRTEM.[75] Several other groups have used different kinds of zeolites as matrices for the preparation of microporous carbon materials with large surface areas. In most cases, the role of the zeolite matrix is not exactly defined; a true replication can often not be proven due to a lack of well-resolved X-ray diffraction data, but a pronounced impact of the zeolite matrix on the regular microporosity and high specific surface of the products is obvious.[76–81]

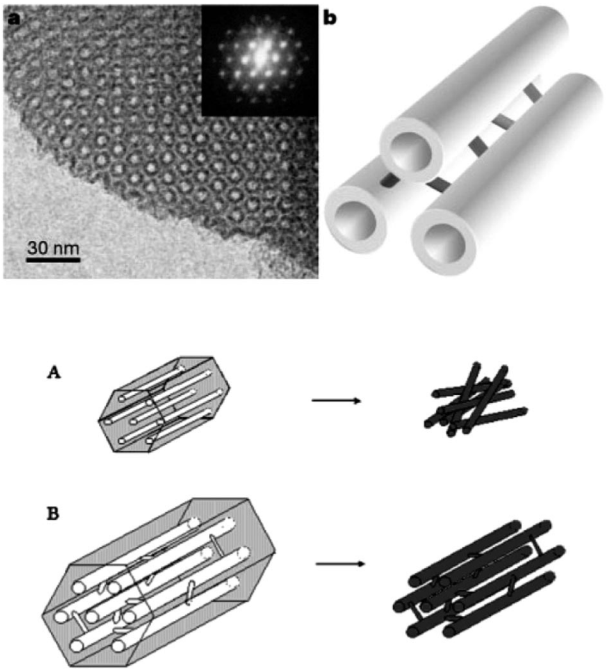

Figure 5. (Top) TEM image and schematic representation of mesoporous CMK-5 carbon created by coating of the pore walls of SBA-15 silica (rather than by complete filling of the pores).[69] The carbon replica consists of hexagonally arranged hollow tubes linked with each other by spacers which originate from the micropores in SBA-15. The latter are responsible for the conservation of the hexagonal symmetry (B, bottom); their absence makes replication impossible in the case of MCM-41 silica (A).[56b]

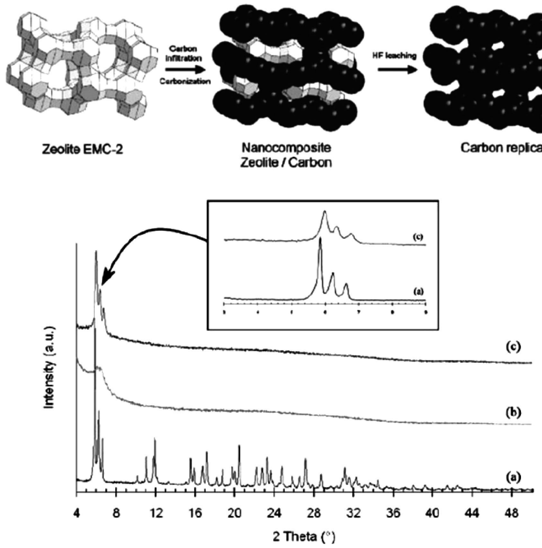

Figure 6. Top: Schematic drawing of the synthesis of ordered microporous carbon by utilization of EMC-2 zeolite as a structure matrix. Bottom: The powder XRD patterns (a, EMC-2 zeolite; b, carbon replica; c, carbon replica after heat treatment) show that the hexagonal structure of the matrix is conserved.[74]

As mentioned above, many other syntheses of ordered mesoporous carbon materials are found in the literature which are not subject to meticulous discussion here; Table 1 summarizes the examples presented in this article.

Mesoporous Noble Metals

Immediately after mesoporous silica phases had been shown to be suitable as structure matrices for mesoporous

Table 1. Some Examples of Ordered Porous Carbon Materials Synthesized by Structure Replication Using Porous Silica or Aluminosilicate Matrices[a]

structure matrix[b]	replica
2D hexagonal ($p6mm$) silica (MCM-41)[32]	bundles of linear carbon rods[61]
2D hexagonal ($p6mm$) silica (SBA-15)[33]	2D hexagonal ($p6mm$) carbon (CMK-3),[34,63]
($Ia\bar{3}d$) silica	bimodal 2D hex. ($p6mm$) carbon (CMK-5)[56,69–71]
cubic ($Ia\bar{3}d$) silica (MCM-48)[32]	cubic[c] carbon (CMK-1)[58–60]
cubic ($Ia\bar{3}d$) silica (KIT-6)[65–68]	cubic ($Ia\bar{3}d$) carbon (CMK-8)[67] bimodal cubic ($Ia\bar{3}d$) carbon (CMK-9)[67]
cubic ($Fm\bar{3}m$) silica (FDU-12)[82,83]	cubic ($Fm\bar{3}m$) carbon[82]
multimodal porous silica monoliths[38]	multimodal porous carbon monoliths[73]
zeolite EMT	microporous carbon[74]
zeolite Y	microporous carbon[75]

[a] This list is not meant to be exhaustive but summarizes the most important syntheses discussed in the text. [b] Names in parentheses are examples; other designations may apply (e.g., depending on the synthesis protocol). [c] Symmetry lower than $Ia\bar{3}d$.

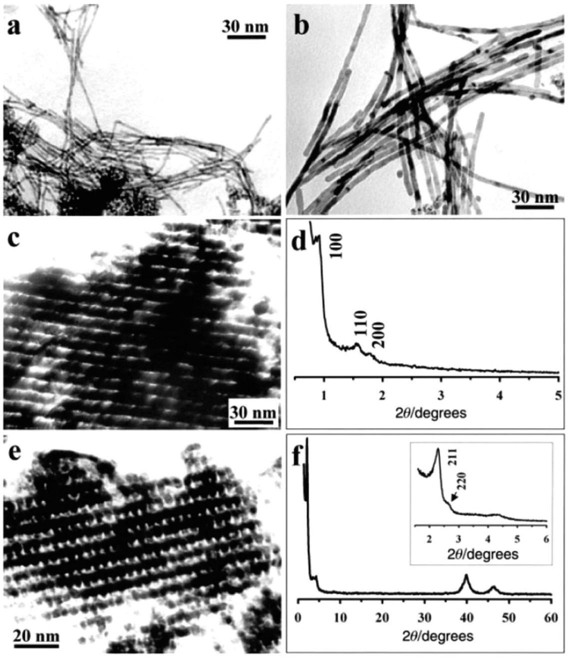

Figure 7. TEM images of Pt structures prepared with (a,b) 2D-hexagonal MCM-41 silicas, (c) 2D-hexagonal SB-15 silica, and (e) cubic MCM-48 silica. Contrary to SBA-15, MCM-41 produces loosely arranged Pt wires instead of hexagonal replicas, due to the absence of links between the parallel pores. Also shown are the XRD patterns of the (d) hexagonal and (f) cubic Pt replicas.[62b]

Table 2. Summary of Ordered Mesoporous Noble Metals Synthesized by Structure Replication Using Porous Silica or Aluminosilicate Matrices

structure matrix[a]	replica
2D hexagonal ($p6mm$) silica (MCM-41)[32]	bundles of linear Pt rods[62,84]
2D hexagonal ($p6mm$) silica (SBA-15)[33]	2D hexagonal ($p6mm$) Pd,[52] Pt,[62,64,86] Au,[86] and Ag[86]
cubic ($Ia\bar{3}d$) silica (MCM-48)[32]	cubic[b] Pd,[52] Pt,[84] and Os[87]
cubic ($Ia\bar{3}d$) silica (KIT-6)[65–68]	cubic ($Ia\bar{3}d$) Pt[67]

[a] Names in parenthesis are examples; other designations may apply (e.g., depending on synthesis protocol). [b] Symmetry lower than $Ia\bar{3}d$.

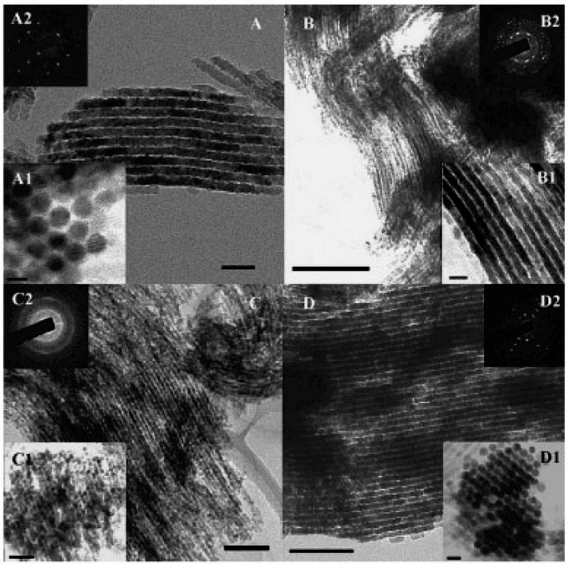

Figure 8. TEM images and ED patterns of (A) Cr_2O_3, (B) Mn_xO_y, (C) Fe_2O_3, and (D) Co_3O_4 replicas of mesoporous SBA-15 silica.[88b]

carbon, the same concept was applied to the synthesis of mesoporous noble metals. Terasaki and Ryoo et al. filled the mesopores of MCM-41 silica (two-dimensional hexagonal $p6mm$) with platinum by infiltration of a soluble Pt(II) salt, $Pt(NH_3)_4(NO_3)_2$, and subsequent reduction to Pt(0) with H_2 gas at elevated temperatures.[62] Removal of the silica host matrix with a 10% HF solution resulted in loosely bundled Pt nanowires, as mentioned above. The same authors also used cubic MCM-48 silica to obtain Pt replicas (analogous to CMK-1 carbon replicas, Figure 7).[84] The presence of Pt inside the silica pores turned out to provide a facile tool for elaborate TEM investigation of the pore systems, as the presence of a metal with high density in the pores strongly increases the optical contrast under the electron microscope; in this context, Ko and Ryoo had earlier created Pt wires in the pores of various silica hosts without removal of the silica.[85] Subsequently, large-pore silicas were used as the structure matrices for several noble metals: Ryoo and Jaroniec et al. prepared Pt replicas of hexagonal SBA-15 silica, thereby proving the existence of interchannel micropores in SBA-15, as discussed above,[62,64] Stucky et al. reported the synthesis of Pt, Au, and Ag wires in the pores of SBA-15,[86] and Kleitz and Ryoo et al. used cubic KIT-6 silica for Pt replicas.[67] In addition, Cheon et al. prepared Pd nanostructures by using MCM-48 and SBA-15 silicas as the structure matrices for chemical vapor infiltration of a metal-organic precursor;[52] Park et al. prepared Os replicas from MCM-48 silica.[87] All mentioned syntheses are summarized in Table 2.

Mesoporous Metal Oxides

The first report on the synthesis of ordered mesoporous metal oxides by utilization of mesoporous silica phases as structure matrices was made in 2003 by Zhao et al.,[88] who used various large-pore silicas with cubic ($Ia\bar{3}d$, $Im\bar{3}m$) or 2-dimensional hexagonal (SBA-15, $p6mm$) symmetries to prepare several metal oxide replicas, including In_2O_3, Co_3O_4, Cr_2O_3, and Fe_2O_3 (Figure 8). Solutions of the respective metal nitrates (e.g., in ethanol) were infiltrated into the silica pores; after solvent evaporation, the nitrates were converted to the metal oxides at 550 °C. Removal of the silica matrices was accomplished by dissolution in either NaOH (2 mol L^{-1}) or HF (10%). Most of the resulting metal oxides exhibited a high degree of crystallinity, with the single-crystalline domains extending over several repeat distances of the mesoscopic pore structures. The authors elucidated the significance of efficient pore filling during the impregnation step. Apart from repeated impregnation/drying/heating cycles to maximize the pore filling, it was found that using microwave-digested silica was beneficial to the impregnation process.[88a] The microwave treatment, involving H_2O_2 and HNO_3, was used instead of conventional calcination to remove the structure-directing block copolymers after the synthesis of the silica materials,[45] yielding a larger number of silanol groups at the pore walls, which, in turn, facilitated the impregnation with polar solvents. Failure to reach a high degree of loading of the silica pores resulted in some loss of symmetry in those replicas which were prepared with cubic silica matrices, owing to insufficient filling of the micropores connecting the mesopore channels.[88c] The authors also used monolithic silicas[39] for some replications in order to minimize the undesired deposition of metal oxides at the external surface.[88a]

Another strategy to improve the impregnation efficiency was introduced by Schüth et al., who used cubic KIT-6 ($Ia\bar{3}d$) and 2-dimensional hexagonal SBA-15 (*p*6*mm*) silica with vinyl-functionalized pore walls[47] for replication of Co_3O_4. The Co_3O_4 replicas exhibited interesting magnetic properties related to the limited domain sizes and large surface/volume ratios.[89] The vinyl groups presumably trap the cobalt cations inside the pores by chelating them, resulting in high degrees of pore filling. A similar approach was chosen by He and Zhou et al., who impregnated amino-functionalized SBA-15 silica with acidic precursor solutions ($K_2Cr_2O_7$ and $H_3PW_{12}O_{40}$) for Cr_2O_3a−c and WO_3.[48a–c] The same authors also used cubic KIT-6 silica for Cr_2O_3[48b] and for Co_3O_4,b as well as the cubic silica phases FDU-12 ($Fm\bar{3}m$) and SBA-16 ($Im\bar{3}m$) for Co_3O_4;[55] in the latter case, the precursor, $Co(NO_3)_2 \cdot 6H_2O$, was melted and infiltrated into the pores without solvent. Another interesting impregnation technique was used by Davidson et al., who prepared mesoporous Mn_xO_y[50] and Co_3O_4[51] by dispersing SBA-15 silica in hexane and adding dropwise a saturated aqueous solution of $Mn(NO_3)_2$ or $Co(NO_3)_2$, respectively, to the dispersion. Owing to the surface polarity of the silica matrix, the aqueous phase was preferentially drawn into the pores. The volume of the aqueous solution corresponded to the total pore volume of the silica matrix, analogous to the incipient wetness technique; thus, deposition of the precursor species outside the pores was minimized in a similar way.

Lindén et al. used hierarchically porous silica monoliths as matrices for the synthesis of likewise multimodal porous Co_3O_4, SnO_2, and Mn_xO_y monoliths (Figure 9);[90] both the monolithic nature and the hierarchical pore architecture of such materials make them particularly interesting for various applications in which control over the diffusion of gases or liquids on the pores plays an important role, such as heterogeneous catalysis, gas sensing, or chromatography. Several other mesoporous metal oxides were prepared by the utilization of silica matrices, including CeO_2,[91,92,93a] Fe_2O_3,[94a] MnO_2,[94b,95] WO_3,[93] RuO_2,[96] and Co_3O_4.[97,98] All syntheses are listed in Table 3.

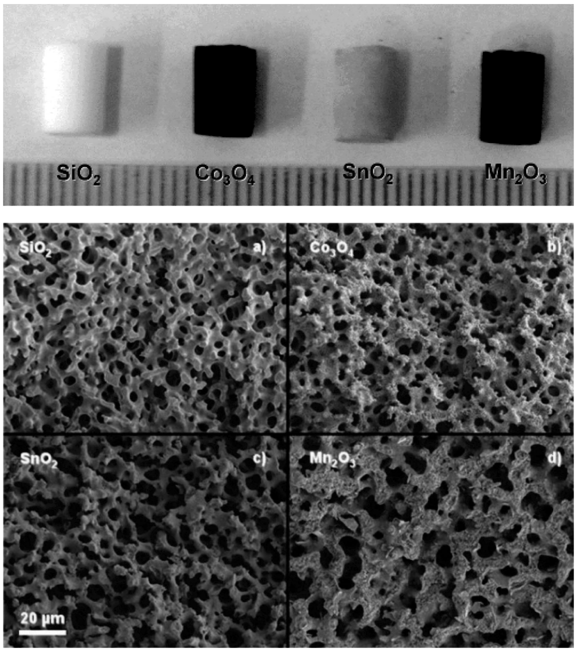

Figure 9. Photograph (top) and SEM images (bottom) of a hierarchically porous SiO_2 monolith and of Co_3O_4, SnO_2, and Mn_2O_3 monolith replicas.[90b]

Table 3. Summary of Ordered Mesoporous Metal Oxides (including SiO_2) Synthesized by Structure Replication Using Porous Silica, Aluminosilicate, or Carbon Matrices

structure matrix[a]	replica
2D hexagonal (*p*6*mm*) silica (SBA-15)[33]	CeO_2,[88b,91,93] Co_3O_4,[48b,51,88b,89b–c,97,134,137] Cr_2O_3,[48a–c,88b] Fe_2O_3,[88b] In_2O_3,[88b] MnO_2,[50,95] Mn_xO_y,[88b] NiO,[88b] WO_3[48c–f,93]
2D hexagonal (*p*6*mm*) silica monoliths[39]	In_2O_3[88a]
cubic ($Ia\bar{3}d$) silica (KIT-6)[65–68]	CeO_2,[91,92,93a] Co_3O_4,[48b,88c,89a,c,97] Cr_2O_3,[48b,f] Fe_2O_3,[94a] In_2O_3,[88c] MnO_2,[94b] RuO_2,[96] WO_3[93]
cubic ($Ia\bar{3}d$) silica monoliths[39]	In_2O_3[88a]
cubic ($Fm\bar{3}m$) silica (FDU-12)[112,113]	Co_3O_4[55]
cubic (Im3;¯*m*) silica (SBA-16)[33b], (FDU-1)[114,115]	Co_3O_4,[55,88b] In_2O_3[88b]
multimodal porous silica monoliths[38]	Co_3O_4,[90] MnO_2,[90b] Mn_2O_3,[90b] SnO_2[90b]
2D hexagonal (*p*6*mm*) carbon (CMK-3)[34,63]	Al_2O_3,[99b,107] CeO_2,[104] $CoAl_2O4$,[109] CuO,[108] MgO,[103] SiO_2,[54,99–101] ZnO[105,106]
cubic carbon (CMK-1)[58–60]	SiO_2[102]
mesoporous carbon spheres [42]	Al_2O_3,[42] ZrO_2,[42] TiO_2[42]
mesoporous hollow carbon spheres[110]	TiO_2[110]

[a] Names in parentheses are examples; other designations may apply (e.g., depending on synthesis protocol).

Mesoporous metal oxides have also been prepared by the utilization of mesoporous carbon; as discussed above, this extends the structure replication concept to a larger variety of products, including those which are not stable against the harsh conditions necessary for the removal of silica matrices. The first material created by using mesoporous carbon as a structure matrix was silica, as reported about simultaneously

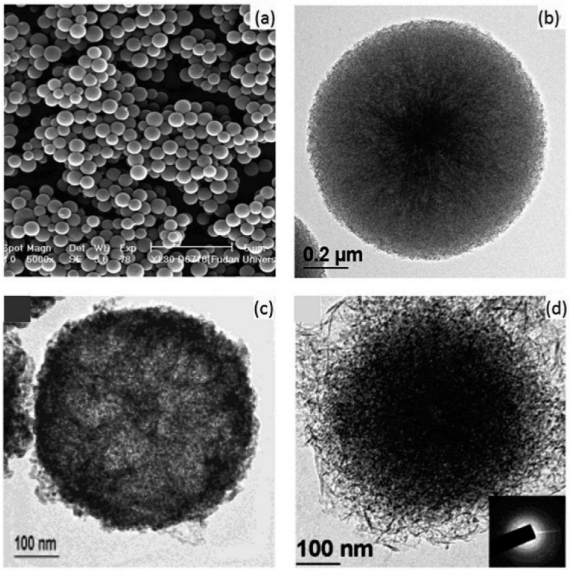

Figure 10. (a) SEM and (b) TEM images of mesoporous carbon spheres and TEM images of (c) ZrO_2 and (d) Al_2O_3 replicas.[42]

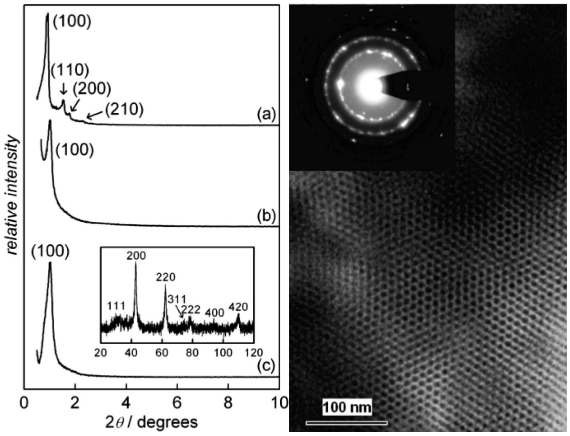

Figure 11. (Left) Powder X-ray diffraction diagrams of (a) SBA-15 silica, (b) CMK-3 carbon, and (c) mesoporous MgO, created by consecutive templating. The low-angle signatures confirm that the hexagonal (*p*6*mm*) pore arrangement is conserved in both replication steps. (Right) TEM/SAED diagram of mesoporous MgO.[103b]

by Schüth et al.[99] and by Kim et al.[100] Both groups used CMK-3 carbon as the matrix; since CMK-3 is the negative replica of mesoporous SBA-15 silica, this second replication back to silica yields nothing else than a positive (i.e., structurally identical) replica of the original material. However, with these first two reports, it was demonstrated that mesoporous carbon is generally suitable as a structure matrix. Similar syntheses were then reported by Xiao et al.[101] and by Parmentier et al.;[54] the latter group used a vapor-phase infiltration technique. Yu et al. used CMK-1 carbon as a structure matrix for silica.[102] As described above, CMK-1 is not exactly a negative replica of MCM-48 silica from which it is replicated, since the symmetry of its pore system is lower; hence, the second replication yields a new mesoporous silica material with the same lower symmetry.

After these first publications on the successful utilization of mesoporous carbon as matrices, a variety of new mesoporous metal oxides was synthesized by using CMK-type carbon exotemplates. Tang et al. used mesoporous carbon with uniform spherical morphology for the generation of mesoporous TiO_2, Al_2O_3, and ZrO_2 with likewise spherical shape (Figure 10);[42] incomplete impregnation of the matrices with the metal oxide precursors resulted in preferential filling of the pores in the outer region of the carbon spheres, which led to hollow mesoporous metal oxide spheres. Tiemann et al. used CMK-3 carbon to synthesize mesoporous MgO[103] (Figure 11), CeO_2,[104] and ZnO,[105] the latter being an example for a metal oxide which cannot be replicated from silica, since it is soluble in both HF and NaOH solutions, necessary for the removal of a silica matrix. Mesoporous ZnO was shown to exhibit size-related optical properties[105a] as well as promising activity in gas sensing.[105b] Replication of ZnO from CMK-3 carbon was also reported by Polarz and Schüth et al.[106] Further syntheses include Al_2O_3,[99b,107] CuO,[108] and bimodal macro-/mesoporous $CoAl_2O_4$ spinel.[109] Mokaya and Xia used hollow spheres of CMK-type mesoporous carbon for the synthesis of various metal oxides, such as TiO_2, Al_2O_3, ZrO_2, or MgO; the spherical, hollow morphology was conserved, while the porosity seems to be less well-defined in the metal oxide products than in the carbon matrix.[110] The latter seems also to be the case for a series of metal oxides prepared by Kim et al., including SiO_2, TiO_2, ZrO_2, and Al_2O_3.[111]

Other Mesoporous Materials

Another interesting system in the field of structure replication is silicon carbide. Zhao et al. infiltrated a polycarbosilane precursor into SBA-15 and KIT-6 silicas to obtain the respective mesoporous SiC replicas;[116] in a similar way, they also used CMK-3 as a matrix.[116b] About simultaneously, Kaskel et al. reported a comparable procedure using SBA-15 as the matrix and infiltrating the precursor both as a liquid and from the vapor phase.[117] Smarsly et al. infiltrated a precursor for carbon into bimodal macro-/mesoporous silica monoliths (synthesized by PEG-induced controlled-phase separation without a template[72]); the resultant carbon reacted with the silica matrix to form porous SiC after removal of residual (nonreacted) SiO_2;[40] this synthesis is an elegant variation of the structure replication idea, since the matrix (silica) also acts as a reactant. Prior to these publications, a series of reports on the utilization of mesoporous matrices for the generation of SiC had been made; these syntheses succeeded in creating highly dispersed SiC inside the matrices but did not yield ordered mesoporous replicas.[118–121] Another nonoxide ceramic material, mesoporous boron nitride, was synthesized by Bois et al., who found that CMK-3 was more suitable as the structure matrix than SBA-15 silica.[122] Vinu et al. prepared mesoporous materials containing carbon, boron, and nitrogen with variable stoichiometry.[123] Mesoporous CdS was synthesized by Zhao et al. from a single-source precursor, cadmium thioglycolate, by utilization of SBA-15 silica.[124,125] Caruso et al. used porous silica spheres[43] for a layer-by-layer deposition of oppositely charged polyelectrolytes and subsequent cross-linking to obtain the respective polymer replica.[126]

Rigid mesoporous structure matrices have also been used for the synthesis of replicas which are composed of zeolitic secondary building units. The matrix is infiltrated with a mixture containing the same species as for a regular zeolite synthesis; that is, a "soft" template, such as tetrapropylammonium, is present to create micropores in addition to the mesopores originating from the utilization of the "hard" structure matrix. Hence, a bimodal micro-/mesoporous zeolitic product is obtained. Such syntheses were reported by Liu et al.[127] and by Mokaya et al.,[128] who both used CMK-3 carbons as exotemplates for the synthesis of ZSM-5-analogous aluminosilicates. Prior to that, Pinnavaia et al. had used mesoporous carbon with spherical pores, synthesized by colloidal imprinting, to prepare ZSM-5 with uniform spherical morphology;[129] Stein et al. had used polystyrene spheres as a template to generate a bimodal micro-/macroporous silicalite-analogous material.[130]

Fields of Application

The concept of repeated templating provides a versatile means to prepare a large variety of new mesoporous materials with well-ordered pore systems. This will lead to new applications in various fields where functional materials with high stability, large surface-to-volume ratio, tunable porosity, and well-defined morphology are desired. For example, many mesoporous materials, especially semiconducting metal oxides, are interesting for application as gas sensors. Such "chemiresistors" are of high technological relevance; they are being used as battery-powered devices in such fields as the detection of toxic and explosive gases (e.g., carbon monoxide, methane), for oxygen control in combustion exhaust car emission, or for control of air quality in automobile cabins or living spaces.[131–133] Apart from large specific surface areas, uniform pore sizes and pore architectures are of particular concern, since these parameters determine the diffusion of gas molecules through the sensing material; the role of mesoporosity and other structural aspects in gas sensors has been subject to some recent review articles.[134–136] The concept of repeated templating has facilitated the synthesis of new mesoporous gas sensors, such as WO_3,[93] Co_3O_4,[137] or ZnO.[105b] The materials showed promising sensing performances, for example, with respect to response time, operation temperature, or overall sensitivity.

Mesoporous materials with large specific surface areas and high stability are also interesting for electrochemical applications.[138] Hyeon et al. demonstrated that mesoporous carbon (replicated from MCM-48 silica) shows very good performance as an electrochemical double-layer capacitor,[139] which might find application in fast-dischargeable power sources (supercapacitors), for example, in electrically operated vehicles. Similar findings were reported by Zhao et al. for mesoporous carbon monoliths.[39a] Ryoo et al. loaded mesoporous carbon with platinum for usage as an electrode catalyst in fuel cells; they observed improved cell efficiencies at comparably low Pt loadings, which they attributed to the high dispersion and stability of the Pt clusters.[69] Smarsly and Maier et al. used carbon monoliths with multimodal porosity (replicated from porous silica monoliths) for storage of lithium. These materials showed promising behavior as electrode materials in rechargeable lithium batteries.[140] Bruce et al. investigated the electrochemical properties of mesoporous $LiCoO_4$,[97a] Co_3O_4,[97b] and MnO_2[94b] materials (replicated from SBA-15 and KIT-6 silicas) for potential application in lithium batteries. They observed interesting effects such as improved charge/discharge behavior attributable to the high surface-to-volume ratios.

Table 4. Some Further Examples of Ordered Porous Materials Synthesized by Structure Replication Using Porous Silica or Carbon Matrices

structure matrix[a]	replica
2D hexagonal (*p*6*mm*) silica (SBA-15)[33]	CdS,[124,125] SiC,[116a,117] carbon nitride,[123a]
cubic ($Ia\bar{3}d$) silica (KIT-6)[65–68]	SiC,[116a]
2D hexagonal (*p*6*mm*) carbon (CMK-3)[34,63]	SiC,[116b] BN,[122,123b] boron/carbon nitride,[123a] "mesoporous zeolite"[127,128]
cubic carbon (CMK-1)[58–60]	"mesoporous zeolite"[127]
mesoporous silica spheres[43]	mesoporous polyelectrolyte[126]

[a] Names in parentheses are examples; other designations may apply (e.g., depending on synthesis protocol).

Heterogeneous catalysis is another general field of application for ordered, mesoporous materials prepared by templating concepts.[141,142] In particular, porous metal oxides are potentially interesting as catalysts or catalyst supports. In this context, control over morphology in combination with large specific surface areas is probably the most significant advantage of the repeated templating method, while periodicity in the pore arrangement may be less important.[143] Some examples of mesoporous materials prepared by repeated templating which were tested for catalytic performance include CeO_2 as a support for CuO[91] or iron oxide;[104] porous polymers with spherical particle morphology (replicated from porous silica matrices) show a high loading capacity for the immobilization of enzymes.[126]

As mentioned above, Lindén et al. have prepared several porous metal oxides as large monolithic bodies or uniform spherical particles. Control over particle morphology is particularly promising for application of mesoporous materials in separation and chromatography. Other potential applications of mesoporous materials prepared by repeated templating may arise from the above-mentioned size-related properties with respect to magnetic[89,94a] or optical[105a,106] behavior.

Concluding Remarks

In summary, the concept of utilizing ordered porous solids as matrices for structure replication has created a large variety of new functional materials. Former restrictions, frequently encountered in sol–gel-based syntheses which involved molecular or supramolecular structure directors, have been overcome. Porous materials which are themselves prepared by templating are used as matrices for repeated templating. This allows not only replication of the porosity of the respective material but also conservation of its morphology during the nanocasting procedure.

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References

(1) Baerlocher, C.; Meier, W. M.; Olsen, D. H. *Atlas of Zeolite Framework Types*, 5th ed.; Elsevier: Amsterdam, 2001.

(2) Cheetham, A. K.; Férey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268–3292.
(3) Cundy, C. S.; Cox, P. A. *Chem. Rev.* **2003**, *103*, 663–701.
(4) Schüth, F. *Chem. Mater.* **2001**, *13*, 3184–3195.
(5) Soler-Illia, G. J. A. A.; Sanchéz, C.; Lebeau, B.; Patarin, J. *Chem. Rev.* **2002**, *102*, 4093–4138.
(6) Hoffmann, F.; Cornelius, M.; Morell, J.; Fröba, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3216–3251.
(7) (a) Wan, Y.; Yang, H.; Zhao, D. *Acc. Chem. Res.* **2006**, *39*, 423–432. (b) Wan, Y.; Shi, Y. F.; Zhao, D. Y. *Chem. Commun.* **2007**, 897–926. (c) Wan, Y.; Zhao, D. *Chem. Rev.* **2007**, *107*, 2821–2860.
(8) Yang, H.; Zhao, D. *J. Mater. Chem.* **2005**, *15*, 1217–1231.
(9) Lu, A.-H.; Schüth, F. *Adv. Mater.* **2006**, *18*, 1793–1805.
(10) Valdés-Solís, T.; Fuertes, A. B. *Mater. Res. Bull.* **2006**, *41*, 2187–2197.
(11) Schüth, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 3604–3622.
(12) (a) Attard, G. S.; Glyde, J. C.; Göltner, C. G. *Nature* **1995**, *378*, 366–368. (b) Göltner, C. G.; Antonietti, M. *Adv. Mater.* **1997**, *9*, 431–436. (c) Göltner, C. G.; Henke, S.; Weissenberger, M. C.; Antonietti, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 613–616. (d) Göltner-Spickermann, C. *Top. Curr. Chem.* **2003**, *226*, 29–54.
(13) Förster, S. *Top. Curr. Chem.* **2003**, *226*, 1–28.
(14) Wakayama, H.; Itaharam, H.; Tatsuda, N.; Inagaki, S.; Fukushima, Y. *Chem. Mater.* **2001**, *13*, 2392–2396.
(15) Schwickardi, M.; Johann, T.; Schmidt, W.; Schüth, F. *Chem. Mater.* **2002**, *14*, 3913–3919.
(16) Blanco, J.; Petre, A. L.; Yates, M.; Martin, M. P.; Suarez, S.; Martin, J. A. *Adv. Mater.* **2006**, *18*, 1162–1165.
(17) Martin, C. R. *Chem. Mater.* **1996**, *8*, 1739–1746.
(18) Chae, W. S.; Lee, S. W.; Kim, Y. R. *Chem. Mater.* **2005**, *17*, 3072–3074.
(19) Wu, Y.; Livneh, T.; Zhang, Y. X.; Cheng, G.; Wang, J.; Tang, J.; Moskovit, M.; Stucky, G. D. *Nano Lett.* **2004**, *4*, 2337–2342.
(20) (a) Stein, A. *Microporous Mesoporous Mater.* **2001**, *44–45*, 227–239. (b) Stein, A.; Schroden, R. C. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 553–564.
(21) Tao, Y. S.; Kanoh, H.; Kaneko, K. *J. Am. Chem. Soc.* **2003**, *125*, 6044–6045.
(22) (a) Li, W.-C.; Lu, A.-H.; Weidenthaler, C. M.; Schüth, F. *Chem. Mater.* **2004**, *16*, 5676–5681. (b) Li, W.-C.; Lu, A.-H.; Schmidt, W.; Schüth, F. *Chem.—Eur. J.* **2005**, *11*, 1658–1664. (c) Li, W.-C.; Lu, A.-H.; Schüth, F. *Chem. Mater.* **2005**, *17*, 3620–3626. (d) Li, W. C.; Comotti, M.; Lu, A.-H.; Schüth, F. *Chem. Commun.* **2006**, 1772–1774.
(23) Lee, D. W.; Park, S. J.; Ihm, S. K.; Lee, K. H. *Chem. Mater.* **2007**, *19*, 937–941.
(24) Valdés-Solís, T.; Marbán, G.; Fuertes, A. B. *Chem. Mater.* **2005**, *17*, 1919–1922.
(25) Shi, Z.-G.; Xu, L.-Y.; Feng, Y.-Q. *J. Non-Cryst. Solids* **2006**, *352*, 4003–4007.
(26) Wang, M. L.; Wang, C. H.; Wang, W. *J. Mater. Chem.* **2007**, *17*, 2133–2138.
(27) (a) Sieber, H.; Hoffmann, C.; Kaindl, A.; Greil, P. *Adv. Eng. Mater.* **2000**, *2*, 105–109. (b) Sieber, H. *Mater. Sci. Eng., A* **2005**, *412*, 43–47.
(28) Shigapov, A. N.; Graham, G. W.; Mccabe, R. W.; Plummer, H. K. *Appl. Catal., A* **2001**, *210*, 287–300.
(29) Persson, P. V.; Hafren, J.; Fogden, A.; Daniel, G.; Iversen, T. *Biomacromolecules* **2004**, *5*, 1097–1101.
(30) Deshpande, A. S.; Burgert, I.; Paris, O. *Small* **2006**, *2*, 994–998.
(31) Liu, Z. T.; Fan, T. X.; Zhang, D. *J. Am. Ceram. Soc.* **2006**, *89*, 662–665.
(32) (a) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710–712. (b) 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. (c) Vartuli, J. C.; Schmitt, K. D.; Kresge, C. T.; Roth, W. J.; Leonowicz, M. E.; McCullen, S. B.; Hellring, S. D.; Beck, J. S.; Schlenker, J. L.; Olson, D. H.; Sheppardt, E. W. *Chem. Mater.* **1994**, *6*, 2317–2326.
(33) (a) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548–552. (b) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024–6036.
(34) (a) Jun, S.; Joo, S. H.; Ryoo, R.; Kruk, M.; Jaroniec, M.; Liu, Z.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **2000**, *122*, 10712–10713. (b) Ryoo, R.; Joo, S. H.; Jun, S.; Tsubakiyama, T.; Terasaki, O. *Stud. Surf. Sci. Catal.* **2001**, *135*, 7–O-01. (c) Solovyov, L. A.; Shmakov, A. N.; Zaikovskii, V. I.; Joo, S. H.; Ryoo, R. *Carbon* **2002**, *40*, 2477–2481.
(35) Katou, T.; Lee, B.; Lu, D.; Kondo, J. N.; Hara, M.; Domen, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2382–2385.
(36) Shirokura, N.; Nakajima, K.; Nakabayashi, A.; Lu, D.; Hara, M.; Domen, K.; Tatsumi, T.; Kondo, J. N. *Chem. Commun.* **2006**, 2188–2190.
(37) Parmentier, J.; Vix-Guterl, C.; Gibot, P.; Reda, M.; Ilescu, M.; Werckmann, J.; Patarin, J. *Microporous Mesoporous Mater.* **2003**, *62*, 87–96.
(38) (a) Smått, J.-H.; Schunk, S.; Lindén, M. *Chem. Mater.* **2003**, *15*, 2354–2361. (b) Yang, C. M.; Smått, J. H.; Zibrowius, B.; Lindén, M. *New J. Chem.* **2004**, *28*, 1520–1525.
(39) (a) Yang, H.; Shi, Q.; Liu, X.; Xie, S.; Jiang, D.; Zhang, F.; Yu, C.; Tu, B.; Zhao, D. *Chem. Commun.* **2002**, 2842–2843. (b) Yang, H.; Shi, Q.; Tian, B.; Xie, S.; Zhang, F.; Yan, Y.; Tu, B.; Zhao, D. *Chem. Mater.* **2003**, *15*, 536–541.
(40) Sonnenburg, K.; Adelhelm, P.; Antonietti, M.; Smarsly, B.; Nöske, R.; Strauch, P. *PCCP* **2006**, *8*, 3561–3566.
(41) (a) Schumacher, K.; Grün, M.; Unger, K. K. *Microporous Mesoporous Mater.* **1999**, *27*, 201–206. (b) Unger, K. K.; Kumar, D.; Grün, M.; Büchel, G.; Lüdtke, S.; Adam, T.; Schumacher, K.; Renker, S. *J. Chromatogr., A* **2000**, *892*, 47–55.
(42) Dong, A.; Ren, N.; Tang, Y.; Wang, Y.; Zhang, Y.; Hua, W.; Gao, Z. *J. Am. Chem. Soc.* **2003**, *125*, 4976–4978.
(43) Schulz-Ekloff, G.; Rathousky, J.; Zukal, A. *J. Inorg. Mater.* **1999**, *1*, 97–102.
(44) Smått, J.-H.; Schüwer, N.; Järn, M.; Lindner, W.; Lindén, M. *Microporous Mesoporous Mater.* **2007**, doi:10.1016/j.micromeso.2007.10.003.
(45) Tian, B.; Liu, X.; Yu, C.; Gao, F.; Luo, Q.; Xie, S.; Tu, B.; Zhao, D. *Chem. Commun.* **2002**, 1186–1187.
(46) Yang, C.-M.; Zibrowius, B.; Schmidt, W.; Schüth, F. *Chem. Mater.* **2004**, *16*, 2918–2925.
(47) Wang, Y. Q.; Yang, C. M.; Zibrowius, B.; Spliethoff, B.; Lindén, M.; Schüth, F. *Chem. Mater.* **2003**, *15*, 5029–5035.
(48) (a) Zhu, K.; Yue, B.; Zhou, W.; He, H. *Chem. Commun.* **2003**, 98–99. (b) Dickinson, C.; Zhou, W.; Hodgkins, R. P.; Shi, Y.; Zhao, D.; He, H. *Chem. Mater.* **2006**, *18*, 3088–3095. (c) Zhou, W.; Zhu, K.; Yue, B.; He, H.; Dickinson, C. *Stud. Surf. Sci. Catal.* **2004**, *154*, 924–930. (d) Zhu, K.; He, H.; Xie, S.; Zhang, X.; Zhou, W.; Jin, S.; Yue, B. *Chem. Phys. Lett.* **2003**, *377*, 317–321. (e) Yue, B.; Tang, H.; Kong, Z.; Zhu, K.; Dickinson, C.; Zhou, W.; He, H. *Chem. Phys. Lett.* **2005**, *407*, 83–86. (f) Jiao, K.; Zhang, B.; Yue, B.; Ren, Y.; Liu, S.; Yan, S.; Dickinson, C.; Zhou, W.; He, H. *Chem. Commun.* **2005**, 5618–5620.
(49) Jun, S.; Choi, M.; Ryu, S.; Lee, H. Y.; Ryoo, R. *Stud. Surf. Sci. Catal.* **2003**, *146*, 37–40.
(50) Impéror-Clerc, M.; Bazin, D.; Appay, M.-D.; Beaunier, P.; Davidson, A. *Chem. Mater.* **2004**, *16*, 1813–1821.
(51) Lopes, I.; El Hassan, N.; Guerba, H.; Wallez, G.; Davidson, A. *Chem. Mater.* **2006**, *18*, 5826–5828.
(52) Kang, H.; Jun, Y. W.; Park, J. I.; Lee, K. B.; Cheon, J. *Chem. Mater.* **2000**, *12*, 3530–3532.
(53) (a) Parmentier, J.; Saadhallah, S.; Reda, M.; Gibot, P.; Roux, M.; Vidal, L.; Vix-Guterl, C.; Patarin, J. *J. Phys. Chem. Solids* **2004**, *65*, 139–146. (b) Parmentier, J.; Solovyov, L. A.; Ehrburger-Dolle, F.; Werckmann, J.; Ersen, O.; Bley, F.; Patarin, J. *Chem. Mater.* **2006**, *18*, 6316–6323.
(54) Parmentier, J.; Vix-Guterl, C.; Saadallah, S.; Reda, M.; Illescu, M.; Werckmann, J.; Patarin, J. *Chem. Lett.* **2003**, *32*, 262–263.
(55) Yue, W.; Hill, A. H.; Harrison, A.; Zhou, W. *Chem. Commun.* **2007**, 2518–2520.
(56) (a) Ryoo, R.; Joo, S. H.; Jun, S.; Tsubakiyama, T.; Terasaki, O. *Stud. Surf. Sci. Catal.* **2001**, *135*, 07–O-01. (b) Ryoo, R.; Joo, S. H.; Kruk, M.; Jaroniec, M. *Adv. Mater.* **2001**, *13*, 677–681.
(57) (a) Lee, J.; Han, S.; Hyeon, T. *J. Mater. Chem.* **2004**, *14*, 478–486. (b) Lee, J.; Kim, J.; Hyeon, T. *Adv. Mater.* **2006**, *18*, 2073–2094.
(58) Ryoo, R.; Joo, S. H.; Jun, S. *J. Phys. Chem. B* **1999**, *103*, 7743–7746.
(59) Lee, J.; Yoon, S.; Hyeon, T.; Oh, S. M.; Kim, K. B. *Chem. Commun.* **1999**, 2177–2178.
(60) Solovyov, L. A.; Zaikovskii, V. I.; Shmakov, A. N.; Belousov, O. V.; Ryoo, R. *J. Phys. Chem. B* **2002**, *106*, 12198–12202.
(61) Tian, B. Z.; Che, S. N.; Liu, Z.; Liu, X. Y.; Fan, W. B.; Tatsumi, T.; Terasaki, O.; Zhao, D. Y. *Chem. Commun.* **2003**, 2726–2727.
(62) (a) Liu, Z.; Sakamoto, Y.; Ohsuna, T.; Hiraga, K.; Terasaki, O.; Ko, C. H.; Shin, H. J.; Ryoo, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 3107–3110. (b) Shin, H. J.; Ko, C. H.; Ryoo, R. *J. Mater. Chem.* **2001**, *11*, 260–261.
(63) (a) Shin, H. J.; Ryoo, R.; Kruk, M.; Jaroniec, M. *Chem. Commun.* **2001**, 349–350. (b) Joo, S. H.; Ryoo, R.; Kruk, M.; Jaroniec, M. *J. Phys. Chem. B* **2002**, *106*, 4640–4646.
(64) Ryoo, R.; Ko, C. H.; Kruk, M.; Antochshuk, V.; Jaroniec, M. *J. Phys. Chem. B* **2000**, *104*, 11465–11471.
(65) Liu, X.; Tian, B.; Yu, C.; Gao, F.; Xie, S.; Tu, B.; Che, R.; Peng, L.-M.; Zhao, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 3876–3878.
(66) Flodström, K.; Alfredsson, V.; Källrot, N. *J. Am. Chem. Soc.* **2003**, *125*, 4402–4403.
(67) Kleitz, F.; Choi, S. H.; Ryoo, R. *Chem. Commun.* **2003**, 2136–2137.
(68) Sakamoto, Y.; Kim, T. W.; Ryoo, R.; Terasaki, O. *Angew. Chem., Int. Ed.* **2004**, *43*, 5231–5234.
(69) Joo, S. H.; Choi, S. J.; Oh, I.; Kwak, J.; Liu, Z.; Terasaki, O.; Ryoo, R. *Nature* **2001**, *412*, 169–172.
(70) Che, S.; Lund, K.; Tatsumi, T.; Iijima, S.; Joo, S. H.; Ryoo, R.; Terasaki, O. *Angew. Chem., Int. Ed.* **2003**, *42*, 2182–2185.
(71) Kruk, M.; Jaroniec, M.; Kim, T.-W.; Ryoo, R. *Chem. Mater.* **2003**, *15*, 2815–2823.
(72) Ishizuka, N.; Minakuchi, H.; Nakanishi, K.; Soga, N.; Tanaka, N. *J. Chromatogr., A* **1998**, *797*, 133–137.
(73) (a) Taguchi, A.; Smått, J.-H.; Lindén, M. *Adv. Mater.* **2003**, *15*, 1209–1211. (b) Lu, A.-H.; Smått, J.-H.; Backlund, S.; Lindén, M. *Microporous Mesoporous Mater.* **2004**, *72*, 59–65. (c) Lu, A.-H.; Smått, J.-H.; Lindén, M. *Adv. Funct. Mater.* **2005**, *15*, 865–871.
(74) Gaslain, F. O. M.; Parmentier, J.; Valtchev, V. P.; Patarin, J. *Chem. Commun.* **2006**, 991–993.
(75) Ma, Z.; Kyotani, T.; Liu, Z.; Terasaki, O.; Tomita, A. *Chem. Mater.* **2001**, *13*, 4413–4415.
(76) (a) Kyotani, T.; Nagai, T.; Inoue, S.; Tomita, A. *Chem. Mater.* **1997**, *9*, 609–615. (b) Kyotani, T.; Ma, Z.; Tomita, A. *Carbon* **2003**, *41*, 1451–1459. (c) Matsuoka, K.; Yamagishi, Y.; Yamazaki, T.; Setoyama, N.; Tomita, A.; Kyotani, T. *Carbon* **2005**, *43*, 876–879.
(77) Enzel, P.; Bein, T. *Chem. Mater.* **1992**, *4*, 819.

(78) Rodriguez-Mirasol, J.; Cordero, T.; Radovic, L. R.; Rodriguez, J. J. *Chem. Mater.* **1998**, *10*, 550–558.
(79) Johnson, S. A.; Brigham, E. S.; Ollivier, P. J.; Mallouk, T. E. *Chem. Mater.* **1997**, *9*, 2448–2458.
(80) Meyers, C. J.; Shah, S. D.; Patel, S. C.; Sneeringer, R. M.; Bessel, C. A.; Dollahon, N. R.; Leising, R. A.; Takeuchi, E. S. *J. Phys. Chem. B* **2001**, *105*, 2143–2152.
(81) (a) Yang, Z. X.; Xia, Y. D.; Mokaya, R. *Microporous Mesoporous Mater.* **2005**, *86*, 69–80. (b) Yang, Z. X.; Xia, Y. D.; Mokaya, R. *Stud. Surf. Sci. Catal.* **2005**, *156*, 573–580. (c) Yang, Z. X.; Xia, Y. D.; Sun, X. Z.; Mokaya, R. *J. Phys. Chem. B* **2006**, *110*, 18424–18431.
(82) Fan, J.; Yu, C. Z.; Gao, T.; Lei, J.; Tian, B. Z.; Wang, L. M.; Luo, Q.; Tu, B.; Zhou, W. Z.; Zhao, D. Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 3146–3150.
(83) Fan, J.; Yu, C.; Lei, J.; Zhang, Q.; Li, T.; Tu, B.; Zhou, W.; Zhao, D. *J. Am. Chem. Soc.* **2005**, *127*, 10794–10795.
(84) Shin, H. J.; Ryoo, R.; Liu, Z.; Terasaki, O. *J. Am. Chem. Soc.* **2001**, *123*, 1246–1247.
(85) Ko, C. H.; Ryoo, R. *Chem. Commun.* **1996**, 2467–2468.
(86) Han, Y. J.; Kim, J. M.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 2068–2069.
(87) Lee, K.; Kim, Y. H.; Han, S. B.; Kang, H.; Park, S.; Seo, W. S.; Park, J. T.; Kim, B.; Chang, S. *J. Am. Chem. Soc.* **2003**, *125*, 6844–6845.
(88) (a) Yang, H.; Shi, Q.; Tian, B.; Lu, Q.; Gao, F.; Xie, S.; Fan, J.; Yu, C.; Tu, B.; Zhao, D. *J. Am. Chem. Soc.* **2003**, *125*, 4724–4725. (b) Tian, B.; Liu, X.; Yang, H.; Xie, S.; Yu, C.; Tu, B.; Zhao, D. *Adv. Mater.* **2003**, *15*, 1370–1374. (c) Tian, B.; Liu, X.; Solovyov, L. A.; Liu, Z.; Yang, H.; Zhang, Z.; Xie, S.; Zhang, F.; Tu, B.; Yu, C.; Terasaki, O.; Zhao, D. *J. Am. Chem. Soc.* **2004**, *126*, 865–875.
(89) (a) Wang, Y.; Yang, C.-M.; Schmidt, W.; Spliethoff, B.; Bill, E.; Schüth, F. *Adv. Mater.* **2005**, *17*, 53–56. (b) Salabas, E. L.; Rumplecker, A.; Kleitz, F.; Radu, F.; Schüth, F. *Nano Lett.* **2006**, *6*, 2977–2981. (c) Rumplecker, A.; Kleitz, F.; Salabas, E. L.; Schüth, F. *Chem. Mater.* **2007**, *19*, 485–496.
(90) (a) Smått, J.-H.; Spliethoff, B.; Rosenholm, J. B.; Lindén, M. *Chem. Commun.* **2004**, 2188–2189. (b) Smått, J.-H.; Weidenthaler, C.; Rosenholm, J. B.; Lindén, M. *Chem. Mater.* **2006**, *18*, 1443–1450.
(91) Shen, W.; Dong, X.; Zhu, Y.; Chen, H.; Shi, J. *Microporous Mesoporous Mater.* **2006**, *85*, 157–162.
(92) Laha, S. C.; Ryoo, R. *Chem. Commun.* **2003**, 2138–2139.
(93) (a) Rossinyol, E.; Arbiol, J.; Peiro, F.; Cornet, A.; Morante, J. R.; Tian, B.; Zhao, D. *Sens. Actuators, B* **2005**, *109*, 57–63. (b) Rossinyol, E.; Prim, A.; Pellicer, E.; Arbiol, J.; Ramirez, F.; Peiro, F.; Cornet, A.; Morante, J. R.; Solovyov, L. A.; Tian, B. Z.; Bo, T.; Zhao, D. Y. *Adv. Funct. Mater.* **2007**, *17*, 1801–1806.
(94) (a) Jiao, F.; Harrison, A.; Jumas, J.-C.; Chadwick, A. V.; Kockelmann, W.; Bruce, P. G. *J. Am. Chem. Soc.* **2006**, *128*, 5468–5474. (b) Jiao, F.; Bruce, P. G. *Adv. Mater.* **2007**, *19*, 657–660.
(95) Zhu, S.; Zhou, Z.; Zhang, D.; Wang, H. *Microporous Mesoporous Mater.* **2006**, *95*, 257–264.
(96) Shen, W. H.; Shi, J. L.; Chen, H. R.; Gu, J. L.; Zhu, Y. F.; Dong, X. P. *Chem. Lett.* **2005**, *34*, 390–391.
(97) (a) Jiao, F.; Shaju, K. M.; Bruce, P. G. *Angew. Chem., Int. Ed.* **2005**, *44*, 6550–6553. (b) Shaju, K. M.; Jiao, F.; Débart, A.; Bruce, P. G. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1837–1842.
(98) Wang, Y. M.; Wu, Z. Y.; Wang, H. J.; Zhu, J. H. *Adv. Funct. Mater.* **2006**, *16*, 2374–2386.
(99) (a) Lu, A.-H.; Schmidt, W.; Taguchi, A.; Spliethoff, B.; Tesche, B.; Schüth, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 3489–3492. (b) Schüth, F.; Czuryskiewicz, T.; Kleitz, F.; Lindén, M.; Lu, A.-H.; Rosenholm, J.; Schmidt, W.; Taguchi, A. *Stud. Surf. Sci. Catal.* **2003**, *146*, 399–406. (c) Lu, A.-H.; Schmidt, W.; Spliethoff, B.; Schüth, F. *Chem.—Eur. J.* **2004**, *10*, 6085–6092.
(100) Kang, M.; Yi, S. H.; Lee, H. I.; Yie, J. E.; Kim, J. M. *Chem. Commun.* **2002**, 1944–1945.
(101) Wang, L.; Lin, K.; Di, Y.; Zhang, D.; Li, C.; Yang, Q.; Yin, C.; Sun, Z.; Jiang, D.; Xiao, F.-S. *Microporous Mesoporous Mater.* **2005**, *86*, 81–88.
(102) (a) Kim, J. Y.; Yoon, S. B.; Yu, J.-S. *Chem. Mater.* **2003**, *15*, 1932–1934. (b) Kim, J. Y.; Yoon, S. B.; Yu, J.-S. *Stud. Surf. Sci. Catal.* **2004**, *154*, 380–385. (c) Yoon, S. B.; Kim, J. Y.; Yu, J. S.; Gierszal, K. P.; Jaroniec, M. *Ind. Eng. Chem. Res.* **2005**, *44*, 4316–4322.
(103) (a) Roggenbuck, J.; Tiemann, M. *J. Am. Chem. Soc.* **2005**, *127*, 1096–1097. (b) Roggenbuck, J.; Koch, G.; Tiemann, M. *Chem. Mater.* **2006**, *18*, 4151–4156.
(104) (a) Roggenbuck, J.; Schäfer, H.; Tsoncheva, T.; Minchev, C.; Hanss, J.; Tiemann, M. *Microporous Mesoporous Mater.* **2007**, *101*, 335–341. (b) Tsoncheva, T.; Roggenbuck, J.; Tiemann, M.; Ivanova, L.; Paneva, D.; Mitov, I.; Minchev, C. *Microporous Mesoporous Mater.* **2007**, doi: 10.1016/j.micromeso.2007.06.021.
(105) (a) Waitz, T.; Tiemann, M.; Klar, P. J.; Sann, J.; Stehr, J.; Meyer, B. K. *Appl. Phys. Lett.* **2007**, *90*, 123108. (b) Wagner, T.; Waitz, T.; Roggenbuck, J.; Fröba, M.; Kohl, C.-D.; Tiemann, M. *Thin Solid Films* **2007**, *515*, 8360–8363.
(106) Polarz, S.; Orlov, A. V.; Schüth, F.; Lu, A.-H. *Chem.—Eur. J.* **2007**, *13*, 592–597.
(107) Liu, Q.; Wang, A.; Wang, X.; Zhang, T. *Chem. Mater.* **2006**, *18*, 5153–5155.
(108) Lai, X.; Li, X.; Geng, W.; Tu, J.; Li, J.; Qiu, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 738–741.
(109) Lu, A.-H.; Li, W. C.; Schmidt, W.; Schüth, F. *Microporous Mesoporous Mater.* **2006**, *95*, 187–192.
(110) Xia, Y.; Mokaya, R. *J. Mater. Chem.* **2005**, *15*, 3126–3131.
(111) Kang, M.; Kim, D.; Yi, S. H.; Han, J. U.; Yie, J. E.; Kima, J. M. *Catal. Today* **2004**, *93–95*, 695–699.
(112) Fan, J.; Yu, C. Z.; Gao, T.; Lei, J.; Tian, B. Z.; Wang, L. M.; Luo, Q.; Tu, B.; Zhou, W. Z.; Zhao, D. Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 3146–3150.
(113) Fan, J.; Yu, C.; Lei, J.; Zhang, Q.; Li, T.; Tu, B.; Zhou, W.; Zhao, D. *J. Am. Chem. Soc.* **2005**, *127*, 10794–10795.
(114) Yu, C. Z.; Yu, Y. H.; Zhao, D. Y. *Chem. Commun.* **2000**, 575–576.
(115) Yu, C. Z.; Tian, B. Z.; Fan, J.; Stucky, G. D.; Zhao, D. Y. *J. Am. Chem. Soc.* **2002**, *124*, 4556–4557.
(116) (a) Shi, Y. F.; Meng, Y.; Chen, D. H.; Cheng, S. J.; Chen, P.; Yang, T. F.; Wan, Y.; Zhao, D. Y. *Adv. Funct. Mater.* **2006**, *16*, 561–567. (b) Shi, Y.; Wan, Y.; Zhai, Y.; Liu, R.; Meng, Y.; Tu, B.; Zhao, D. *Chem. Mater.* **2007**, *19*, 1761–1771.
(117) Krawiec, P.; Geiger, D.; Kaskel, S. *Chem. Commun.* **2006**, 2469–2470.
(118) Parmentier, J.; Patarin, J.; Dentzer, J.; Vix-Guterl, C. *Ceram. Int.* **2002**, *28*, 1–7.
(119) Yang, Z.; Xia, Y.; Mokaya, R. *Chem. Mater.* **2004**, *16*, 3877–3884.
(120) Krawiec, P.; Weidenthaler, C.; Kaskel, S. *Chem. Mater.* **2004**, *16*, 2869–2880.
(121) Lu, A.-H.; Schmidt, W.; Kiefer, W.; Schüth, F. *J. Mater. Sci.* **2005**, *40*, 5091–5093.
(122) (a) Dibandjo, P.; Chassagneux, F.; Bois, L.; Sigala, C.; Miele, P. *J. Mater. Chem.* **2005**, *15*, 1917–1923. (b) Dibandjo, P.; Bois, L.; Chassagneux, F.; Toury, B.; Cornu, D.; Babonneau, F.; Miele, P. *Stud. Surf. Sci. Catal.* **2005**, *156*, 279–286. (c) Dibandjo, P.; Bois, L.; Chassagneux, F.; Cornu, D.; Letoffe, J. M.; Toury, B.; Babonneau, F.; Miele, P. *Adv. Mater.* **2005**, *17*, 571–574.
(123) (a) Vinu, A.; Ariga, K.; Mori, T.; Nakanishi, T.; Hishita, S.; Golberg, D.; Bando, Y. *Adv. Mater.* **2005**, *17*, 1648–1656. (b) Vinu, A.; Terrones, M.; Golberg, D.; Hishita, S.; Ariga, K.; Mori, T. *Chem. Mater.* **2005**, *17*, 5887–5890.
(124) Gao, F.; Lu, Q.; Zhao, D. *Adv. Mater.* **2003**, *15*, 739–742.
(125) Liu, X. Y.; Tian, B. Z.; Yu, C. Z.; Tu, B.; Liu, Z.; Terasaki, O.; Zhao, D. Y. *Chem. Lett.* **2003**, *32*, 824–825.
(126) Wang, Y.; Yu, A.; Caruso, F. *Angew. Chem., Int Ed.* **2005**, *44*, 2888–2892.
(127) (a) Sakthivel, A.; Huang, S.-J.; Chen, W.-H.; Lan, Z.-H.; Chen, K.-H.; Kim, T.-W.; Ryoo, R.; Chiang, A. S. T.; Liu, S.-B. *Chem. Mater.* **2004**, *16*, 3168–3175. (b) Sakthivel, A.; Huang, S.; Chen, W.; Kim, T.; Ryoo, R.; Chiang, A. S. T.; Chen, K.; Liu, S. *Stud. Surf. Sci. Catal.* **2004**, *154*, 394–399.
(128) Yang, Z. X.; Xia, Y. D.; Mokaya, R. *Adv. Mater.* **2004**, *16*, 727–732.
(129) Kim, S.-S.; Shah, J.; Pinnavaia, T. J. *Chem. Mater.* **2003**, *15*, 1664–1668.
(130) Holland, B. T.; Abrams, L.; Stein, A. *J. Am. Chem. Soc.* **1999**, *121*, 4308–4309.
(131) Seiyama, T.; Kato, A.; Fujiishi, K.; Nagatani, M. *Anal. Chem.* **1962**, *34*, 1502–1503.
(132) Stetter, J. R.; Penrose, W. R.; Yao, S. *J. Electrochem. Soc.* **2003**, *150*, S11–S16.
(133) Yamazoe, N. *Sens. Actuators, B* **2005**, *108*, 2–14.
(134) Tiemann, M. *Chem.—Eur. J.* **2007**, *13*, 8376–8388.
(135) Franke, M. E.; Koplin, T. J.; Simon, U. *Small* **2006**, *2*, 36–50.
(136) Korotcenkov, G. *Sens. Actuators, B* **2005**, *107*, 209–232.
(137) Wagner, T.; Roggenbuck, J.; Kohl, C.-D.; Fröba, M.; Tiemann, M. *Stud. Surf. Sci. Catal.* **2007**, *165*, 347–350.
(138) Rolison, D. R.; Dunn, B. *J. Mater. Chem.* **2001**, *11*, 963–980.
(139) Lee, J.; Yoon, S.; Hyeon, T.; Oh, S. M.; Kim, K. B. *Chem. Commun.* **1999**, 2177–2178.
(140) Hu, Y. S.; Adelhelm, P.; Smarsly, B. M.; Hore, S.; Antonietti, M.; Maier, J. *Adv. Funct. Mater.* **2007**, *17*, 1873–1878.
(141) Trong On, D.; Desplantier-Giscard, D.; Danumah, C.; Kaliaguine, S. *Appl. Catal., A* **2001**, *222*, 299–357.
(142) Taguchi, A.; Schüth, F. *Microporous Mesoporous Mater.* **2005**, *77*, 1–45.
(143) Rolison, D. R. *Science* **2003**, *299*, 1698–1701.

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