Chem. Mater. **2001,** *13,* 3184−3195

Non-siliceous Mesostructured and Mesoporous Materials[†]

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Received February 5, 2001

Siliceous ordered mesoporous materials are well-investigated and -covered by several excellent reviews. Less work has been directed to non-siliceous materials, although these could have more wide-ranging applications. This review will address the synthesis and properties of non-siliceous ordered mesoporous materials, covering oxidic, non-oxidic, metallic, and pure carbon frameworks. Organometallic frameworks, which are typically not synthesized in the presence of surfactants, are beyond the scope of this paper.

1. Introduction

Since the discovery of FSM-16[1] and MCM-41,[2] both silica or aluminumsilicate ordered mesoporous materials, much work has been devoted to the study of the synthesis, properties, and possible uses of such materials. These topics are covered in several comprehensive recent reviews.[3−6] Already in 1993 it was suggested, on the basis of mechanistic ideas, that it should be possible to synthesize non-siliceous materials following similar pathways.[7] The first examples have been reported already in 1994.[8] However, for these materials it had not been possible to remove the template and thus no mesoporous materials, but only mesostructured materials, could be obtained. The first mesoporous non-siliceous frameworks were reported in 1995/1996,[9,10] from which rapid development started. However, the field of non-siliceous ordered mesoporous materials has found considerably less attention compared to that of mesostructured silica, and only few reviews are available, which focus exclusively on non-siliceous materials.[11]

The lower research intensity in this field lies in several reasons: One is very simple, in that many of the research groups active in the field of mesostructured materials have their origins in zeolite chemistry and thus are very familiar with the chemistry of silicon and aluminum, but to a lesser extent with other elements. Although the very general principles valid for the synthesis of mesostructured silica can be used also for the synthesis of other systems, each new composition needs adaption of the procedures, depending on the chemistry of the system. More importantly, though, silica and aluminumsilicates are typically fairly stable materials in various respects. Other compositions are often more susceptible to hydrolysis, redox reactions, or phase transitions accompanied by thermal breakdown of the structural integrity, which makes it much more difficult to remove the templates and create porous materials. This, however, is a prerequisite for many of the applications envisaged. These factors make the non-siliceous materials less attractive in the eyes of many researchers, but if the problems mentioned above can be solved, the potential of the non-silica compositions seems to be higher than that of the classical silica MCM-41, FSM-16, or SBA-15.

Because the chemistry of non-silica materials is much more diverse than that of the siliceous ordered mesoporous oxides, the synthetic strategies for their production need to be more diverse. General pathways which can lead to mesostructured composites will be discussed in the next section. A more detailed description of selected examples will then be given in the subsequent sections, which are organized according to the chemical composition of the resulting materials. Organometallic frameworks, which are typically not synthesized in the presence of surfactancts, are beyond the scope of this paper. However, they are also covered in a recent excellent review with a broader perspective.[12]

2. Strategies for the Creation of Non-siliceous Ordered Mesoporous Materials

Table 1 gives an overview over different pathways used for the synthesis of non-siliceous mesoporous materials. As can be seen, various compositions are accessible by now, following different routes. The majority of these routes entail the use of organic precursor species which allow the formation of liquid crystals, such as molecular surfactants or block copolymers. Here two general alternatives exist: (i) the composite forms cooperatively from the species present in solution, which are not in a liquid-crystalline state prior to mixing of the precursors; (ii) a liquid-crystalline precursor phase is used which is infiltrated with the inorganic species (true liquid crystal templating, TLTC[13]).

However, also more unusual routes have been developed, for instance, the use of siliceous mesoporous frameworks as a true mold for other materials, such as metals or carbohydrates, which lead to ordered carbon mesoporous materials after pyrolysis. Finally, pore size distributions similar to those obtained for MCM-41 type materials can be synthesized by a route that is probably

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[†] Dedicated to Prof. Dr. Dr. h. c. Klaus Unger on the occasion of his 65th birthday.

10.1021/cm011030j CCC: $20.00

Table 1. General Pathways Used for the Synthesis of Non-siliceous Ordered Mesoporous Materials

pathway	comments	example	reference for example
monomolecular surfactant templated	various surfactants have been used, ranging from anionic over neutral to cationic	Zr−oxophosphate	10
ligand-assisted		Nb_2O_5	16
polymer-templated	typically relatively disordered pore system	Al_2O_3	39
triblock copolymer templated	various compositions possible, also mixed metal oxides	TiO_2	20
conversion of intercalated layered material		$AlPO_4$	37
true liquid-crystal templated		Pt	17
nanocasted	ordered mesoporous silica used as a mold which is later dissolved	Carbon CMK-1	26
inorganic crystal templated	disordered pore system	$Si(NH)_2$	28

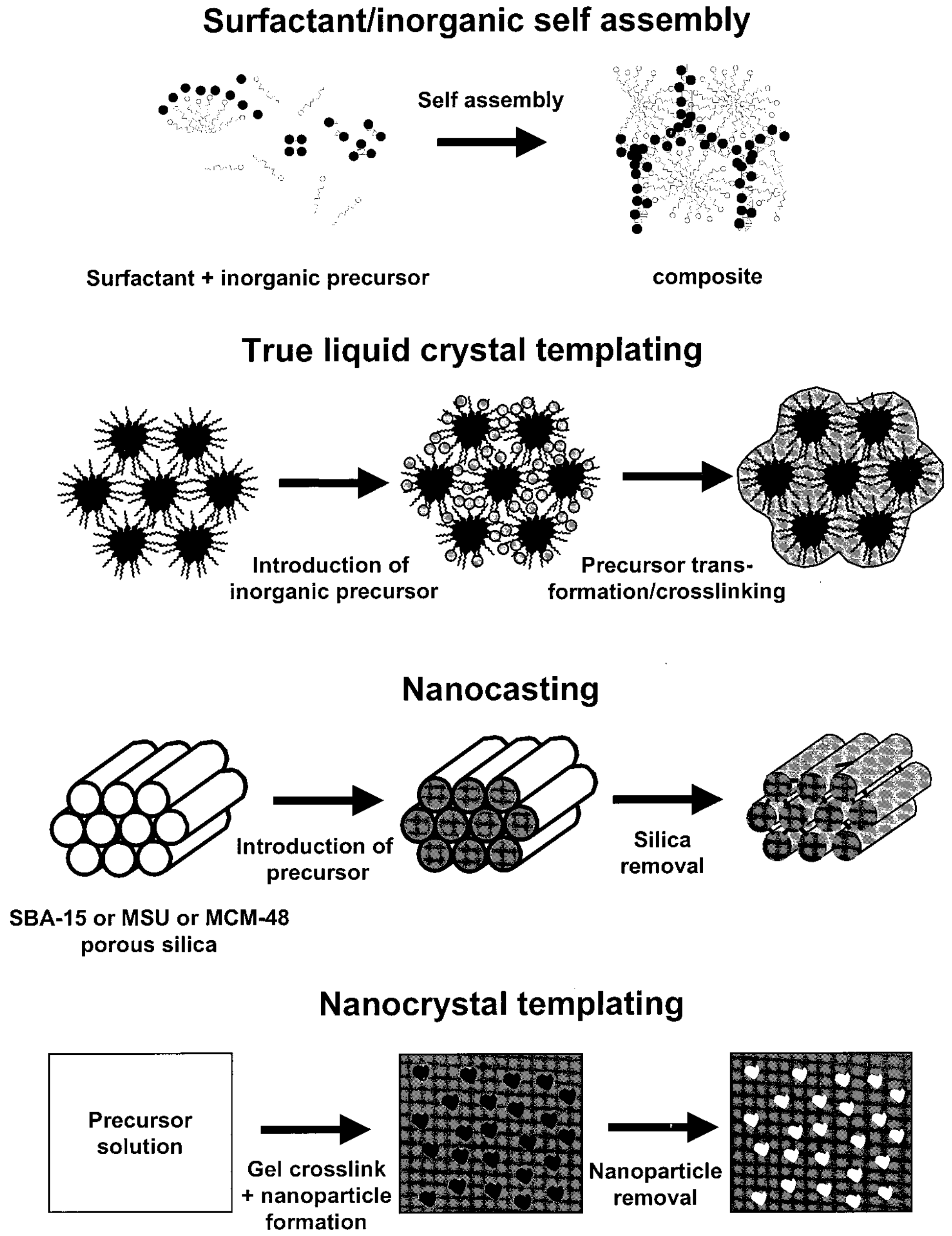


Figure 1. Schematic representation of general pathways leading to mesostructured and mesoporous non-siliceous materials.

an “inorganic crystal templating” pathway, leading to mesoporous imido-nitride frameworks. Figure 1 gives a general schematic representation of these four routes.

2.1. Self-Assembly Driven by Liquid-Crystal Formation. The most obvious method to create non-siliceous materials is the direct adaption of the routes successful in the synthesis of mesoporous silicas. This was in fact used in the first attempts to create ordered mesoporous oxides other than silica. However, if this route is chosen, one has to match the chemistry of the surfactant and the inorganic solution species. The original MCM-41 synthesis is carried out under conditions where the silicate species are negatively charged, interacting with positively charged surfactants. A similar charge interaction or hydrogen-bonding interaction is necessary also when other oxides are being synthesized. In the initial publication reporting the synthesis of non-silica mesostructured materials,[8] four different interaction modes were suggested, S^+I^-, S^-I^+, $S^+X^-I^+$, and $S^-X^+I^-$, with S being the surfactant, I the inorganic species, and X a mediator ion. This list was later on expanded to include also the interaction of inorganic species with neutral surfactants. Thus, depending on the charge of the inorganic species at the solution pH, one has to choose an appropriately charged surfactant. Positively charged surfactants used were mainly quarternary ammonium ions of different types; negatively charged surfactants can be carboxylates, phosphates, phosphonates, sulfates, or sulfonates. However, one has to keep in mind that these negatively charged surfactants only rarely have pK_a values below 2 and will thus be protonated at very low pH. Many of these surfactants are therefore not useful for the mesostructuring of cationic species from highly acidic solutions via the direct S^-I^+ pathways. Despite this limitation, metal ions normally charged positively in solution can be used as precursors to form mesostructured materials following a modified indirect $S^+X^-I^+$ pathway, as has first been used for the formation of mesoporous zirconium oxophosphate from alkylammonium ions and zirconium sulfate, where the sulfate ions coordinate to the zirconium centers and result in the formation of a net negative charge on the inorganic species.[10,14,15]

An extension of these methods, which, however, still resembles the original routes for the formation of mesostructured silica, is the ligand-assisted route introduced by Antonelli and Ying.[16] Here, the inorganic species is linked to a long-chain hydrocarbon ligand in a tighter way, so that already a surfactant–inorganic entity is used as the precursor for the mesophase assembly. It is again decisive to match the chemistry of the inorganic and the surfactant part of the system.

Also, the formation of two unusual compositions, metals[17] and assemblies of CdS nanoparticles,[18] follow synthesis routes that are still very close to the original pathways. Attard et al.[13] introduced the so-called true liquid-crystal templating route, where—other than in the Mobil pathway—surfactant is used at such high concentration that a liquid crystal forms. In this liquid crystal, metal precursors are introduced and reduced, leading to a mesoporous metal replica of the original liquid crystal after template removal. The assembly of the CdS follows a similar approach, but here surfactants with an affinity to the CdS nanoparticles are used, allowing the self-assembly of a CdS mesoporous framework.[18]

There are also several block polymer routes which are highly adaptable and which seem to be very useful and versatile for the formation of non-siliceous ordered mesoporous materials. Wiesner and co-workers[19] used a block polymer, where the hydrophilic part was infiltrated with an inorganic oxide precursor. These composites can be tuned to any structure from the phase diagram of the block polymer via adjustment of the fraction of hydrophilic and hydrophobic parts. The most general pathway so far seems to be the one introduced by Stucky and co-workers.[20] It resembles the route developed for the synthesis of siliceous SBA-15, using the same type of surfactant, that is, triblock copolymers of the EO (ethylene oxide)/PO (propylene oxide)/EO type or diblock copolymers of the EO–BO (butyleneoxide) type. However, while SBA-15 is prepared in an aqueous medium, the key for the synthesis of the non-siliceous compositions is the use of alcohol as a solvent, which leads to essentially nonhydrolytic conditions. It is suggested that the propylene oxide part of the templates binds the metal ions in an essentially crown-ether-like fashion, which, together with the mesophase formation driven by the different polarities of the EO and PO blocks, should lead to the mesostructuring of the inorganic–organic composite. A very wide range of different compositions and structures of the mesophase was accessible following this synthetic route.

Some general considerations are valid for all synthesis pathways described above in choosing the right precursors or synthetic conditions: (i) The nature of the inorganic species and the surfactant has to be such that a favorable interaction between the two is possible. This means that either a strong Coulomb interaction needs to be present, that strong hydrogen-bonding forces act between the inorganic and the surfactant part of the composite to be formed, or that hydrophilic/hydrophobic interaction leads to the formation of the mesostructure. If these interactions are not sufficiently strong, there will be a high tendency for phase separation, with an inorganic species precipitating and the surfactant remaining in solution. This tendency will be especially strong if the inorganic species can form a stable crystalline structure with high lattice energy. It is thus not surprising that siliceous mesostructured materials are most easily accessible because the tendency of silicon to form amorphous silica networks strongly favors the formation of mesostructured materials. (ii) The inorganic species needs to have a sufficiently high tendency to condense to extended frameworks under the synthetic conditions. Otherwise, structures will collapse after removal of the surfactant template. This is, for instance, a problem if mesoporous materials of group 6 elements are desired because molybdenum and tungsten have a pronounced tendency to form very stable polyanions. This was shown for a tungsten-based mesophase,[21] which later turned out to be rather a salt-like structure with noncondensed Keggin ions[22] and could thus not be obtained as a mesoporous material. (iii) Template removal has to be possible without structural collapse. The most common method to remove the surfactant templates is calcination. However, if the framework is redox unstable, calcination will lead to reduction/reoxidation because first there is no access for oxygen to the pores and thus the template hydrocarbon chains act as reducing agents. As soon as the pores are empty, oxygen can penetrate and reoxidation can occur. Most frameworks will loose their structural integrity during such cycles. This problem can be solved by removing the surfactant by extraction processes, which are best suited for nonionic surfactants. If ionic surfactants shall be extracted, the extraction typically has to be combined with an ion exchange because the surfactant also compensates framework charges. (iv) If mesoporous materials shall be used at higher temperatures, even for redox stable frameworks, problems can arise during thermal treatment if a thermally induced crystallization of the walls occurs. All the ordered mesoporous materials reported so far have amorphous wall structures or at most nanocrystalline particles embedded in an amorphous matrix, as for instance shown for titania.[20] The presence of the mesostructure and crystallinity of the walls are typically not compatible because crystalline materials can in most cases not accommodate the type of curvatures present in the mesostructures. Thus, as soon as recrystallization of the walls to bulk oxides occurs, the mesostructures collapse, as has been observed in many cases.

2.2. "Nanocasting" from Ordered Mesoporous Silica Molds for Other Framework Compositions. The possibility of using ordered mesoporous silica as molds for other materials, especially polymers, has already been realized relatively early.[23-25] However, only recently ordered mesoporous carbons[26] and metals[27] were synthesized by "nanocasting" in mesoporous silica molds. Because a 3-D structure is necessary in the mold to maintain a stable replica, only experiments with MCM-48, MSU-1, and SBA-15 were successful. SBA-15 in principle has an unidimensional channel system. However, micropores seem to connect the linear hexagonally packed mesopores, thus providing the cross-linking necessary for obtaining a stable replica. MCM-41, on the other hand, proved to be less suitable for the production of porous carbons or metals.

The carbons are prepared by infiltrating the pore system with a suitable carbon precursor and subsequent pyrolysis of the precursor to give pure carbon. Suitable precursors were sucrose in the presence of sulfuric acid, furfuryl alcohol, or a phenol-formaldehyde resin, dependent on the exact nature of the system. The metals are prepared by chemical vapor infiltration with volatile metal precursor complexes and subsequent pyrolysis. Both for the carbons and the metals the silica framework is then dissolved either by NaOH solution or with HF.

It is at present not clear how general these pathways are because they have only recently been discovered. It is clear, though, that they will only be suitable for framework compositions which are stable under the conditions used to dissolve the mold, that is, stable in relatively concentrated NaOH or HF in the case of silica. One might, however, go one step further and use the carbons cast by this technique again as a mold for yet another framework and then remove the carbon by calcination to increase the flexibility. It is to be expected that the precision of the nanocasting will decrease with every additional step, but this might be tolerable, depending on the system envisaged.

2.3. Crystal Templating for Silicon Imido Nitride. Very recently, it was discovered that mesoporous silicon imido nitride with a very sharp pore size distribution similar to that of MCM-41-type materials can be synthesized by ammonolysis of silicon halides in aprotic solvents.[28] The authors suggest a pore templating by the hydrolysis product NH_4X ($X = Cl, Br, I$), which is released upon heat treatment and leaves behind pores corresponding to the size of the previous ammonium halide nanocrystals. Because the pore system is disordered, the material does not directly resemble MCM-41, but rather has a structure similar to MSU-type materials introduced by Prouzet and Pinnavaia.[29] The process leading to the material is not really a supramolecular templating, but because the properties are very similar to supramolecularly templated mesoporous solids, these materials should be briefly mentioned here.

3. Compositions

3.1. Oxidic Frameworks. A variety of different framework compositions has been synthesized over the last several years, which not many would have foreseen in the first half of the 1990s, when MCM-41 and related silica or aluminumsilicate materials where first reported and synthesized. In the following the different compositions accessible today and the most salient features of these materials will be discussed, organized going from oxides to sulfides, nitrides, metals, and carbons.

3.1.1. Aluminum Phosphate. Extension of the synthesis of mesostructured silica to aluminum phosphates seemed to be the most straightforward idea because of the similarities between zeolite chemistry and aluminum phosphate chemistry, with various isotypic structures. However, this proved to be much more difficult than expected. Although mesophases could be obtained for aluminum phosphates and silicon aluminum phosphates, removal of the template without structural breakdown was not possible for the products from these initial attempts.[30-32] An interesting, supposedly inverted, hexagonal aluminum phosphate structure was reported to form in an alcoholic system, which, however, was also not stable upon heating.[33]

Stable mesostructured silicon aluminum phosphate synthesized at pH 2.5 in the presence of cetyltrimethylammonium bromide (CTAB) was reported by Chakraborty et al.[34] However, the synthesis conditions should not lead to interaction of the inorganic species with the surfactant, and the pore sizes obtained from sorption experiments and the lattice parameters are not compatible, so that it remains questionable whether really an ordered mesoporous material was obtained in this case. Zhao et al.[35] described a series of aluminum phosphates and silicon aluminum phosphates stable upon calcination which were obtained with cetyltrimethylammonium at pH 9.5. These materials have surface areas close to 1000 m^2/g, but the pore structure is much less ordered than that for the silica. Relatively disordered pore systems for samples synthesized with cationic surfactants under various different reaction conditions were also reported by Zhimyak and Klinowski.[36] These materials were typically supermicroporous with pore volumes around 0.4 mL/g. Very similar textural parameters have been reported by the group of Kuroda, where the hexagonal mesostructure was obtained by the conversion of a layered aluminum phosphate/surfactant intercalate.[37] This last material is probably the one with the best long-range order reported so far. The TEM shows a fairly well-developed hexagonal pattern, and the first three XRD reflections are still visible after calcination. Also, an anionic surfactant (sodium dodecyl sulfate, SDS) can be used to mesostructure aluminum phosphate, if the Al_{13}–Keggin ion is used as aluminum precursor.[38] The initial precipitate is then treated with phosphate solution to give the mesostructured aluminum phosphate. The template is removed by extraction/ion exchange to result in a porous material with relatively ordered hexagonal structure and specific surface areas exceeding 600 m^2/g.

3.1.2. Alumina. Many attempts have been made already very early to synthesize ordered mesoporous alumina. The reason for this is, among others, the widespread use of alumina as a catalyst support, which is superior to silica because of the higher hydrolytic stability and the different point of zero charge, which makes it easier to load it with different metal species. It should be noted that, although by now much progress has been achieved in mesostructuring alumina by pathways resembling the synthesis of MCM-41, there is an alternative electrolytic pathway: Anodized alumina can have pore size distributions almost as narrow as MCM-41 with the pore sizes being adjustable over a much wider range.[39] The drawback of this route is the fact that anodic aluminas can only be synthesized in low quantities because it is a surface process as opposed to the bulk solution process used to prepare ordered mesoporous alumina with surfactant templates.

The first successful synthesis of a MCM-41 related mesoporous alumina was reported by Bagshaw and Pinnavaia.[40] The material was prepared with poly(ethylene oxide) and had a pore structure which resembled that of the MSU silica with surface areas of around 400−500 m^2/g. Similar aluminas with "wormhole" pore structures were also prepared by Cabrera et al.,[41] but following a synthesis pathway using a cationic surfactant under conditions, where the aluminum species in solution are anionic. In the alumina system it became also obvious that the use of surfactant-type molecules in an oxide synthesis does not necessarily follow a real templating route. Vaudry et al.[42] prepared a very high surface area alumina ($>700\ m^2/g$) using alkyl carboxlyates, but there was no dependence of the pore size on the surfactant chain length, which excludes a real liquid-crystal templating mechanism. One should always consider the possibility that the surfactant does not act as a porogen, but rather stabilizes small particles, which will—after removal of the organic molecules—have a very high surface area. Yada et al.[43] studied the formation of mesostructured ordered alumina in the presence of SDS. The precipitate could be obtained as a mesostructure in a narrow range of conditions; however, the structure was completely lost after calcination. It was, however, possible to obtain stable materials for alumina as well as for gallium oxide by doping with yttria.[44−46] Later, Valange et al.[47] also achieved materials which were stable after calcination, after they had investigated several routes to synthesize ordered mesoporous aluminas at pH values below the isoelectric point of alumina of around 8−9. This means that the syntheses essentially started from cationic species such as $[Al(H_2O)_6]^{3+}$ or Keggin-type alumina clusters, depending on pH. Mostly anionic surfactants were used, but some syntheses were carried out with neutral surfactants or mixtures of anionic and cationic surfactants. The materials were thermally stable and pore sizes could be tuned by the conditions of the synthesis. However, although the pore size distributions were typically quite narrow, the long-range order, judging from the diffraction data, was rather low for these materials.

Concerning various compositions, one of the most fruitful approaches was the one developed in the Stucky group using triblock copolymer templates in alcoholic solution,[20] as described above. Alumina was accessible following this route which has a disordered pore structure and pore sizes exceeding substantially those reported for the other materials described in this section. The pore size distribution appears to be bimodal with the strongest contribution from pores 14 nm in size.

3.1.3. Transition-Metal Oxides and Related Compositions. Because of their redox activity and possible use in catalysis, transition-metal oxides seemed to be among the most attractive targets for mesostructuring. However, the desired feature of redox activity immediately presents the problem of template removal because a redox-active framework will in most cases collapse during the calcination, with reducing conditions predominating initially in the template-filled pores and oxidizing conditions later on during the calcination, when most of the template has already been removed.

When considering mesoporous transition-metal oxides, on first glance one might not be too impressed with the relatively low specific surface areas compared to those of the silica materials and the other framework compositions discussed above. However, one has to keep in mind that the density of the oxide wall enters the calculation of specific surface areas and pore volumes. For the same structural parameter a wall density which is by a factor of 2 higher reduces all specific parameters by a factor of 2. Assuming identical oxide densities as in the crystalline bulk (which is a reasonable approximation for this comparison, the real wall densities are probably somewhat lower than bulk densities), 1000 m^2/g for silica (density of quartz 2.6 g/cm^3) corresponds to 605 m^2/g for titania (density of rutile 4.3 g/cm^3) and 440 m^2/g for zirconia (density of zirconia (baddeleyite) 5.9 g/cm^3). When comparing specific surface areas and pore volumes for materials with a density strongly deviating from that of silica, this fact has to be considered.

After the first attempts failed to remove the surfactants from the mesostructured transition-metal oxides,[8,21,48] it took another 2 years before the first mesoporous transition-metal oxide was synthesized, which was notably not one of the redox-active ones, but titania.[9] Also in the following, mostly relatively redox-stable compositions have been synthesized, such as zirconium-based materials[10,14] or vanadium (phosphorus) oxide,[49] niobium oxide[16,50] and tantalum oxide.[51] For these compositions, often a remarkable structural perfection is observed, as can be seen in Figure 2 for a zirconium-based mesostructure. For the niobium oxide and the tantalum oxide, the redox stability problem was circumvented by using the ligand-assisted templating pathway with subsequent extraction of the template, thus avoiding the problems with calcination. For all these materials, specific surface areas of up to 500 m^2/g have been reported. Several reports have appeared following these initial papers, where similar or related compositions have been synthesized, although different templating routes have been chosen, ranging from ionic surfactants[52−57] over neutral surfactants[58,55] and triblock copolymers[20] to the ligand-assisted pathway.[59] Table 2 lists the compositions synthesized thus far.

Figure 2. TEM of a calcined hexagonally ordered zirconium oxophosphate. Reprinted with permission from ref 3. Copyright 1999 Elsevier.

Table 2. Ordered Mesoporous Materials Based on Transition or Rare Earth Metals[a]

composition	structure	references
TiO_2	cubic	**20**
	hexagonal	**9**, **52**
	disordered	**20**, 56, **58**, **101**, **108**
	lamellar	52
Ti−oxophosphate	hexagonal	**53**
	disordered	**54**
ZrO_2	cubic	104,**105**
	hexagonal	**20**
	disordered	56
	lamellar	59
ZrP_xO_y	disordered	**55**, **59**
Zr−oxophosphate	hexagonal	**10**, **14**, **15**, **57**, **109**
HfO_2	disordered	**103**
V_2O_5	hexagonal	63
	disordered	20
	lamellar	63
V−P−oxide	cubic	49
	hexagonal	60, 61, 62
	lamellar	61
Nb_2O_5	hexagonal	**16**, **20**, **50**, **98**, **99**, **100**
	disordered	56
Ta_2O_5	hexagonal	**20**, **51**, **102**
MoO_3	lamellar	8
WoO_3 (salt-like with Keggin ions)	hexagonal	8, 21, 22
Mn-oxide	hexagonal	64, 65
	lamellar	8, 64, 65
ReO_2	disordered	67, 20
Fe_2O_3	lamellar	8
CoO	lamellar	8
NiO	lamellar	8
ZnO	lamellar	8, 48
	?	20
$HZnPO_4$	lamellar	8
Y_2O_3	lamellar, hexagonal	**106**
rare earth metal oxides	lamellar, hexagonal, disordered	**107**
CdO	?	20

[a] References printed in bold font refer to porous materials. Oxidation state of the metal ion is not exactly known in all cases. Several other transition-metal-based materials have been reported which have been synthesized in the presence of surfactants. However, in many cases the pores are interparticle pores and not part of the solid structure. These compositions are not listed in the table.

The zirconium-based materials are good examples for discussing the problems related to the stability of the frameworks. For these materials the inorganic species and the surfactant had to be adapted to each other. Coassembly of cationic zirconium solution species which are present in $ZrOCl_2$ or $ZrCl_4$ solution having a pH close to zero with anionic surfactants proved to be not possible because the surfactants are protonated under these solution conditions. Zirconium sulfate proved to be an ideal precursor because the negatively charged solution species interact favorably with the cationic surfactants.[14] However, the presence of sulfate groups in the inorganic framework prevents full condensation, on one hand, and leads to major framework disruption because of sulfate removal upon calcination, on the other hand. Exchange of the sulfate groups against more suitable species, such as phosphate, improved the stability of the materials substantially so that easily calcinable samples which retain the mesoporosity could be obtained. Similar approaches were later on chosen for the stabilization of other types of zirconia[57] and titania.[53]

An interesting type of material from a catalytic point of view could be the vanadium-based systems, especially the vanadium phosphates. However, although several attempts have been made, it appears that no thermally stable well-developed ordered mesoporous vanadia or vanadium phosphate has been synthesized as yet.[49,60−63] However, a mesostructured vanadium phosphate could be an interesting precursor for the VPO catalyst used for butane oxidation to maleic anhydride.[62]

As stated above, most transition-metal oxide compositions are from the early transition metals with a relatively high redox stability. A notable exception has been reported by Suib and co-workers[64,65] who synthesized mesoporous manganese oxides also having semiconducting properties. For the synthesis of these materials the redox state of the manganese has to be carefully adjusted to allow the formation of the mesostructure, similar to that observed by the same group for the synthesis of the so-called octahedral molecular sieve (OMS) type materials.[66] The synthesis can start from Mn^{2+}, where the manganese is precipitated as $Mn(OH)_2$ and reacted with CTAB. This precipitate needs to be oxidized to induce the formation of the mesostructure. Alternatively, one can start from Mn(VII), where the manganese has to be reduced. The nature and structure of the pore system is not fully clear yet because the sorption isotherms[65] are very different compared to those reported for other types of ordered mesoporous materials. The walls of these materials consist of nanocrystallites of different manganese ox-

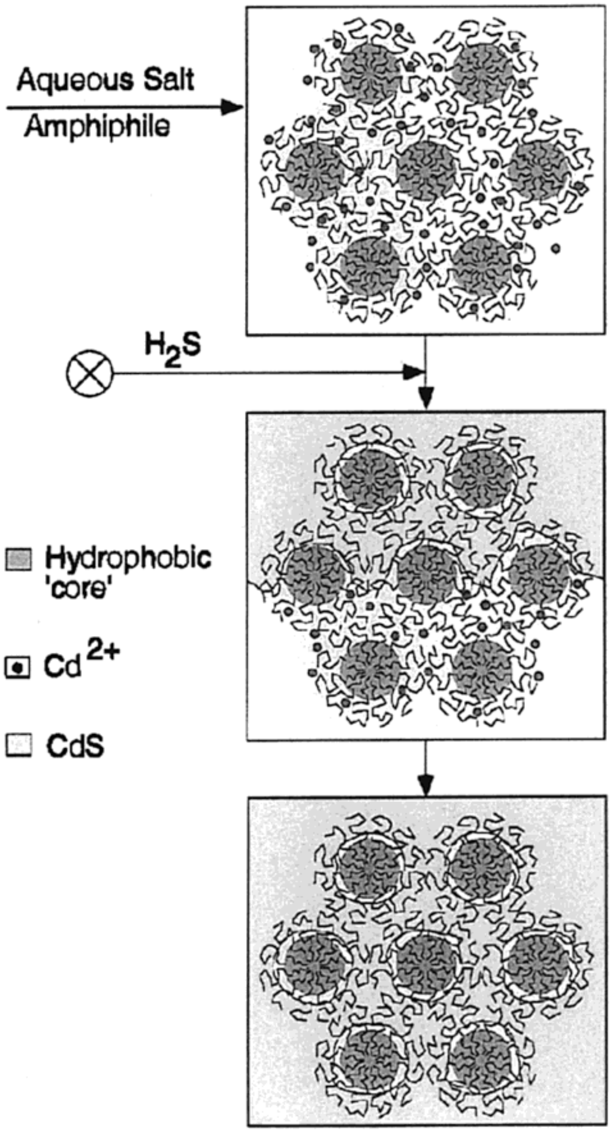


Figure 3. Schematic representation of the process used to synthesize hexagonally ordered metal chalkogenide nanocrystals. Reprinted with permission from ref 69. Copyright 1997 American Chemical Society.

ides, resulting in an average oxidation state between 3 and 4; the conductivity is on the order of 10^{-6} S/cm. Another group 7 element which can be mesostructured is rhenium. However, the structure formed is disordered, and the alkylamine template cannot be removed.[67]

3.2. Chalkogenide Frameworks. The investigation of chalkogenide frameworks mesostructured by surfactants started with the work of Stupp and coworkers.[18,68−70] However, these materials differ substantially from those described in the previous sections in that they are composed of chalkogenide nanocrystals as opposed to the essentially amorphous continuous wall structures described above. Also, the synthesis pathway differs because the approach used by Stupp resembles the true liquid-crystal templating (TLTC) introduced by Attard et al.[13] (Figure 3). A lyotropic liquid-crystalline phase from polymers is formed in aqueous solution; this phase is loaded with a metal ion precursor solution and then exposed to hydrogen sulfide gas. This results in the formation of metal sulfides in the liquid crystal by which the metal sulfide is mesostructured. Instead of hydrogen sulfide, hydrogen selenide can be used which results in the formation of hexagonally ordered metal selenide nanocrystals. Following this route, mesostructured CdS, CdSe, and ZnS could be obtained, while attempts to synthesize mesostructured Ag_2S, CuS, HgS, and PbS failed.[70] This led the authors to the conclusion that a specific interaction between the metal ions and/or the precipitate and the liquid crystal is necessary.

The first sulfides with a connected framework were reported for tin,[71,72] which were both lamellar. Subsequently, also ZnS-based materials[73] were described. The best investigated system, however, seems to be the germanium/sulfur system, where the first mesostructured compound, a layered material, was reported by Fröba in 1997.[74] In more recent work, primarily by the groups of Kanatzidis[75−78] and Ozin[79,80] mesostructures were assembled from the well-defined adamantane-like Ge_4S_{10} units. These units are linked with each other to an extended framework by transition-metal ions, such as nickel or cobalt. The problem of the low solubility of the precursors was solved by using formamide as the solvent instead of water. Because of the high dielectric constant of formamide, surfactant phase diagrams in this solvent are often quite similar to the ones in water.[81] Kanatzidis, however, also succeeded in synthesizing similar compounds from an essentially aqueous system.[78] An interesting expansion of this synthetic approach was reported in a recent publication, where the Ge_4S_{10} units were coassembled with biologically relevant Fe_4S_4 clusters, resulting in a well-ordered hexagonal mesostructure.[82] The presence of intact iron−sulfur clusters was demonstrated by several analytical techniques, such as Mössbauer and IR spectroscopy.

So far, no porous structure has been obtained with a chalkogenide framework, but the semiconducting properties of metal chalkogenides, if they should prove to be useful, can probably also be exploited when the surfactants are still present.

3.3. Nitridic Frameworks. Although nitrides can have remarkable stability, not much work has so far been devoted to the synthesis of porous nitride frameworks. The first nitride structures resembling zeolites were synthesized by the group of Schnick,[83,84] which have, however, typically no accessible pore system. In principle, a silica analogous nitride sol/gel chemistry should be possible, thus opening also the route to microporous and mesoporous imides and nitrides because the NH fragment in silicon imides and amines corresponds to the oxygen in silicon dioxide and alkoxides. It was therefore attempted to synthesize mesostructured and mesoporous silicon imides and nitrides by using silicon amine precursors in the presence of ammonia and different nonaqueous solvents together with surfactants. Although pore sizes could be adjusted by the alkyl chain length of alkylamines,[85] the resulting imides are supermicroporous and not mesoporous and show a low degree of order so that probably no liquid-crystal templating takes place.

Alternatively, a very cost-efficient pathway has been introduced recently. Silicon halides are ammonolyzed in different hydrocarbons. The ammonolysis results in the formation of ammonium halide nanocrystals, which are subsequently removed by calcination in an ammonia

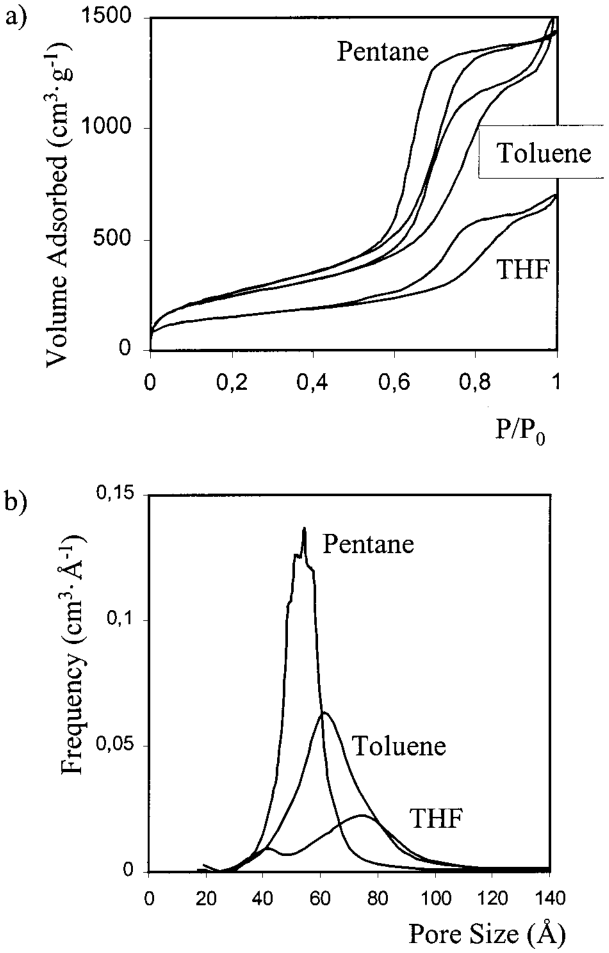
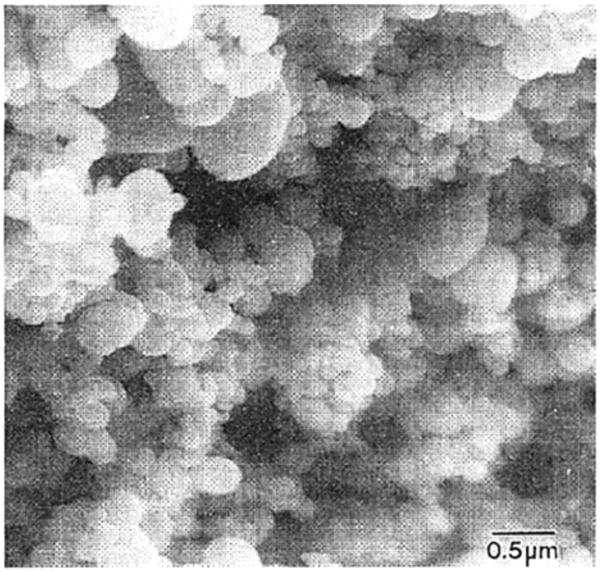


Figure 4. (a) Nitrogen physisorption isotherms of mesoporous silicon imido nitride synthesized via ammonolysis of $SiCl_4$ in different solvents. (b) Corresponding BJH pore size distributions calculated from the desorption branch. Reprinted with permission from ref 86. Copyright American Chemical Society.

atmosphere. Because the homogeneous ammonolysis leads to a narrow particle size distribution of the ammonium halide, the resulting pores also have a narrow size distribution in exactly the range which is typically covered by MCM-41-type materials (Figure 4). By proper choice of the hydrocarbon and the silicon halide, the pore sizes can be adjusted in a similar range as for ordered mesoporous silica.[28,86]

3.4. Metals. The possibility to synthesize nonsiliceous covalent inorganic frameworks was predicted on the basis of the mechanistic ideas developed in the early 90s.[7] However, at this time it was not foreseen that also metals could be synthesized in a mesostructured or mesoporous form because there the synthesis pathway obviously had to be quite different. Nevertheless, relatively early Attard, Göltner, and co-workers succeeded in the synthesis of hexagonally ordered noble metals which could be obtained in a mesoporous form.[17,87] The basis for these syntheses was the use of the TLTC approach, where a lyotropic liquid-crystalline phase was loaded with the metal precursor ion and then reduced within the liquid crystal. As a reducing agent, either large lumps of less noble metals were used or dissolved agents, such as hydrazin.[17] The surfactant, for instance, octaethylene glycol monohexadecyl ether, was removed by washing in acetone, water, and HCl.



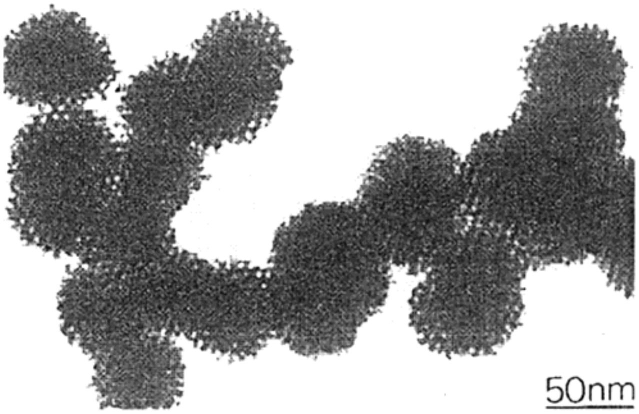


Figure 5. SEM image of a mesoporous Pt sample obtained via the true liquid-crystal templating pathway (top) and TEM of such a sample (bottom). Reprinted with permission from ref 17. Copyright 1997 Wiley.

The materials are typically obtained as powders composed of particles with sizes of some hundred nanometers. The metals are hexagonally ordered; the pore sizes are around 3 nm, with almost equal wall thicknesses (Figure 5). Specific surface areas are around 20 m^2/g and thus comparably low, which is due to the relatively thick walls and the very high density of the noble metals.

The technique proved to be effective for the synthesis of powders but it could also be used for the electrodeposition of mesostructured metallic thin films.[88,89] For these syntheses the lyotropic liquid crystalline phase of octaethyleneglycol monoalkyl ether was formed in the presence of a high fraction of a platinum salt and then used as an electrolyte for the electrodeposition of platinum on a gold electrode. The resulting platinum films are mesostructured in a similar manner as corresponding powders, where the reduction of the platinum was induced chemically. For such a platinum film an electrochemically active specific surface area of 22 m^2/g was determined, compared to 4.5 m^2/g for a film deposited in the absence of surfactant. Similar mesostructured films can also be obtained with tin.[89]

While the mesostructured metals described so far were obtained by the TLTC pathway, recently an alternative pathway was used, the nanocasting using MCM-48 as a mold.[90] In this case a slightly volatile palladium precursor, Pd(hfac)$_2$ (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate), was sublimed into the empty pores of the mold structure. Pyrolysis of the Pd(hfac)$_2$ precursor in the pores of SBA-15 at 150 °C in flowing hydrogen/nitrogen then leads to the formation of encapsulated metals. Pore volumes and surface areas are only decreased slightly, which suggests that the palladium is not distributed homogeneously over the entire host structure. TEM revealed that the metal accumulates in about 35−40-nm small domains. Dissolution of the silica host with 20% HF leaves a black powder, which consists of ball-shaped, 35−40-nm-sized palladium particles, having the replicate structure of the MCM-48 pore system.

3.5. Carbons. The second pathway described above for the formation of metals by the "nanocasting" process is the only route developed so far to produce ordered mesoporous carbons. This route was pioneered recently by Ryoo and co-workers.[26] Here again MCM-48 was used because a mold with a 3-D pore system is necessary to obtain a stable material, named CMK-1, after removal of the mold. In a subsequent publication, however, the same group could show that also SBA-15 with a one-dimensional pore system could be used to produce a hexagonally ordered mesoporous carbon, named CMK-3.[91] This work incidentally proved that the mesopores in SBA-15 are most probably interconnected through the walls via micropores because otherwise the stability of the carbon replica could not be explained.

In general, the pores of the silica matrix are filled with a carbon-containing material which is then pyrolized. An aqueous solution of sucrose and sulfuric acid proved to be a suitable precursor. Typically, the silica mold is impregnated with such a solution, dried, and heated at 433 K, and then this cycle might be repeated to obtain a more complete pore filling. Final pyrolysis is carried out at 1173 K under vacuum. Removal of the silica mold is possible by treatment with HF or NaOH. Sucrose is not the only possible precursor; furfuryl alcohol was also found to be effective[92] as well as a phenol/formaldehyde resin formed in situ in the pore system.[93] The mold for the latter material was an HMS-type mesostructure; the resulting carbon was called SNU-1.

These carbon materials show remarkable structural and textural properties. The replica of the original structure is surprisingly perfect, on the nanometer scale, that is, on the level of the pore system, as well as on the micrometer scale, that is, on the level of the crystallite (Figure 6). The values of the specific textural parameters exceed those for the silica molds used in their synthesis because of the very low density of a carbon framework, which probably has a similar local structure as activated carbons. BET surface areas up to 1800 m^2/g and pore volumes up to 1.3 mL/g have been reported for these materials. However, other than for the silica molds, it is difficult to tailor the pore sizes of the carbon materials. Because the pores are formed by dissolution of the silica framework, the sizes of the pores are governed by the silica wall thickness. This is much more difficult to control in the synthesis of MCM-48 and SBA-15 than the pore size in these materials, and ranges reported in the literature for the wall thickness are much more narrow than ranges reported for the pore sizes of the silicas.

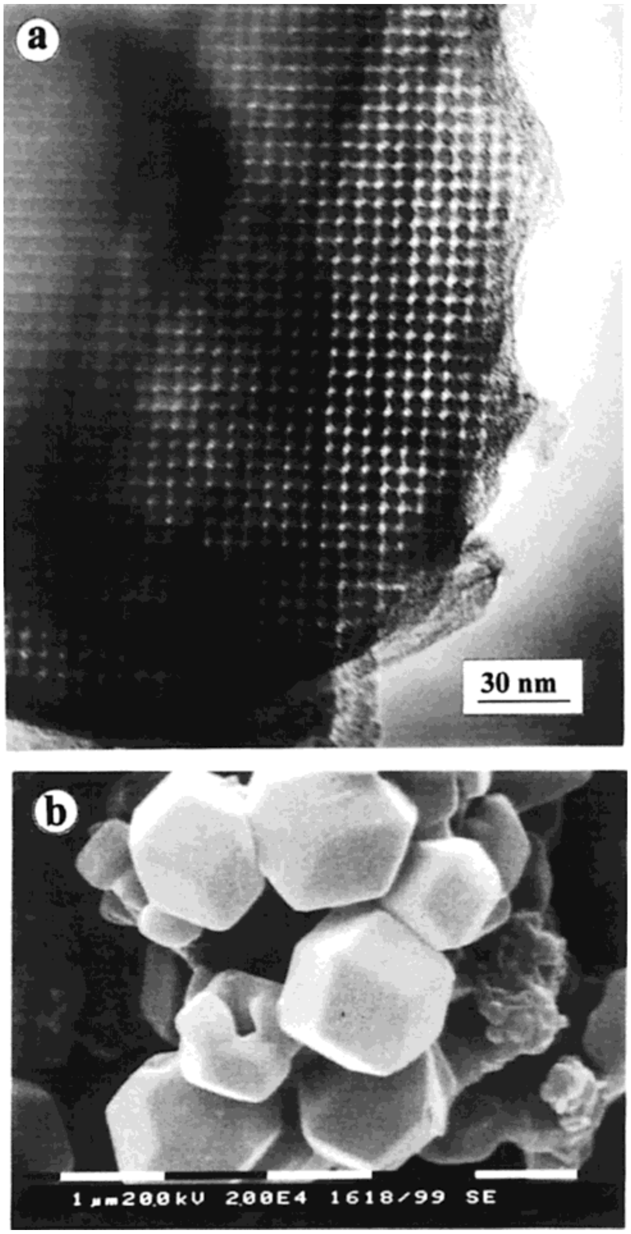


Figure 6. TEM image of an ordered mesoporous carbon CMK-1 obtained from "nanocasting" in a MCM-48 mold (top). SEM image of particles of CMK-1 (bottom). Reprinted with permission from ref 26. Copyright 1999 American Chemical Society.

4. Applications

As not even the siliceous materials, which have been known several years longer than the non-siliceous framework compositions, seem to be used in technical applications today, it cannot be expected that non-siliceous materials are commercially used nowadays. However, because the non-siliceous mesoporous structures cover a much wider range of different properties, it can be expected that also a wider range of possible applications will be accessible.

The most obvious field for use of these materials is catalysis and their use as ion exchangers. Ordered mesoporous silica and aluminum silicates are comparably less attractive in catalytic applications because in these cases cheaper and almost as good alternatives are available. Precipitated silica and aluminum silicate gels can be very easily synthesized with 50% of the surface areas of MCM-41-type materials, and the advantage of the sharp pore size distribution and the regular pore arrangement is not used in most of the possible applications. In contrast to that, there are often no good alternative routes for the synthesis of high surface area transition-metal oxides, and the starting materials are often more expensive than in the case of silica. The added cost incurred by the mesostructuring is thus relatively less important. However, despite these facts favoring the catalytic application of ordered mesoporous non-siliceous materials, so far only a few reports are available on their catalytic performance. The photocatalytic oxidation of 2-propanol to acetone was studied over mesoporous titania or niobia, but quantum yields were orders of magnitude lower than those for dense phases.[94] In some cases phosphated or sulfated zirconias were tested as acid catalysts.[57,59,95,96] However, the performance of the catalysts reported does not justify the high effort needed to synthesize the material. Ion-exchange properties of anionic surfactant templated aluminum phosphates were studied by the group of Stein.[38,97] The material was found to be effective for several organic anionic dyes at capacities comparable to commercial exchange resins. In addition, size-selective uptake of dyes was observed.

Potential applications outside of catalysis and ion exchange have been envisaged in several papers, typically in the last paragraph of the Conclusions section. However, such visions rarely go beyond the mere statement that applications could be possible in optics, electronics, or sensing. Interesting optical properties have been observed for mesostructured gallium or indium thiogermanates, which show an intense green luminescence upon near UV irradiation.[77] However, the origin of this luminescence is not clear yet. For thiogermanates incorporating the Fe_4S_4 cluster it is suggested that such materials could be used as photocatalysts or for artificial photosynthesis.[82] Some materials have attracted interest because of their interesting electrical and electronic properties. Manganese oxides[65] and niobium oxides[98] have a semiconducting framework, with conductivities on the order of 10^{-7} to 10^{-6} S/cm, although this property has not been used for any application. The group of Antonelli used the niobium oxide material as a host for cobaltocene, where depending on the loading level paramagnetic or superparamagnetic behavior is observed,[99] and for bis-benzene chromium which forms supposedly one-dimensional conductors.[100] However, in these studies it is not quite clear how strongly contributions from the external surface of the materials influence the results. Rare earth oxide based materials showed unusual magnetic behavior resembling that of spin glasses.[107]

The mesoporous carbon materials have been evaluated as electrochemical double-layer capacitors.[93] Here, the mesoporous material SNU-1 was found to be superior to a conventionally used activated carbon in that it showed a much steeper current change at the switching potential. This was attributed to the facile reorganization of the double layer in the regular interconnected mesopores as compared to the more irregular micropores in the activated carbon.

Summarizing this section, one can state that non-siliceous ordered mesoporous materials offer several interesting properties, but that applications going beyond laboratory tests are at present out of reach. Claims with respect to applications made at the end of the Conclusion section should always be taken with a grain of salt.

5. Conclusion and Outlook

Non-siliceous ordered (sometimes less ordered) mesoporous materials are by now accessible in a wide range of compositions. The synthesis pathways are even more diverse than those for the siliceous materials because the nanocasting based on siliceous ordered mesoporous solids provides a possibility of creating very unusual framework compositions with a high degree of order. It is probably no great risk to predict that the variety of different materials will steadily increase over the coming years.

As is the case with the siliceous mesostructures, applications—in research, but even more so commercial ones—will lag substantially behind the synthetic achievements. The very feature of ordered mesoporous solids which makes them attractive, their complexity, allowing a tunability of their properties over a wide range, also creates problems with respect to applications. The complexity typically leads to increased costs of production and simultaneously to increased problems concerning reproducibility. The more components are combined, and the more steps a process has before the final product is produced, the higher are the obstacles for eventual commercialization of a material. The coming years will show whether some of the compositions discussed in this article or new ones not even envisaged yet will overcome these obstacles.

Acknowledgment. The research of my group in this field was continuously supported by the Fonds der Chemischen Industrie and grants from the EU (ERB-FMRX-CT96-0084) and the DFG (Schu744/8-1,2), which are gratefully acknowledged.

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CM011030J