Selective Modification of Hierarchical Pores and Surfaces in Nanoporous Materials

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Tailor-made ordered mesoporous materials bear great potential in numerous fields of application where large interfaces are required. However, the inherent surfacechemical properties of conventional materials, such as silica, carbon or organosilica, pose some limitations with respect to their application. Surface manipulation by functionalization with chemically more reactive groups is one way to improve materials for their desired purpose. Another approach is the design of high surface-area composite materials. The surface manipulation, either by functionalization or by introducing guest species, can be performed selectively. This means that when several distinct, i.e., hierarchical, types of surfaces or pore systems exist in a material, each of them may be chosen for manipulation. Several strategies can be identified to achieve this goal. Molecules or molecule assemblies can be utilized to temporarily protect pores or surfaces (soft protection), while manipulation occurs at the accessible sites. This approach is a recurring motive in this review and can also be applied to rigid template matrices (hard protection). Furthermore, the size of functionalization agents (size protection) and their reactivity/diffusion (kinetic protection) into the pores can also be utilized to achieve selectivity. In addition, challenges in the synthesis and characterization of selectively manipulated ordered mesoporous materials are discussed.

1. Introduction

Their large surface areas, pore volumes, and adjustable pore sizes have made ordered mesoporous materials (OMM) famous for a wide range of potential applications. [1–9] Starting with ordered mesoporous silica (OMS) materials of the MCM family in the 1990’s, [10–12] the range of porous systems was soon extended to ordered mesoporous carbon (OMC), [13,14] periodic mesoporous organosilica (PMO), [15] mesoporous metal oxides, [16] and others. The properties of these materials are marked not only by their porosity but also by their particle shape and size. [17,18] The possibility to control both the inner and the outer surface of a porous material bears the chance for a selective surface modification.

The intermediate soft template-solid composite material is often referred to the as-synthesized product. At this point, the intra-particle surface is occupied by the template, and, thus, inaccessible. In other words, the pore walls are ‘protected’ against chemical reaction. [24] Therefore, the as-synthesized intermediate bears the opportunity of a selective manipulation of the outer surface of the particle (blue in Figure 1) while the intraparticle surface (green) is mostly inaccessible. In the following, this situation will be referred to as ‘soft protection’ of the pore walls, in analogy to the term ‘soft template’. After the removal of the template (Figure 1B), both the intraparticle and the external surface area are accessible at the same time.

The functionalization of OMS materials is most commonly based on the reaction with silanol groups (Si-OH) at the silica surface. They naturally occur due to incomplete condensation during the silica synthesis. Depending on the template removal procedure (and previous synthetic steps), the amount of silanol groups varies. The thermal decomposition (‘calcination’) of the template will lead to a more hydrophobic surface with a low amount of Si-OH, compared to a template removal by solvent extraction. The polarity can be further increased by subsequent oxidative treatment, e.g., with H2O2 or HNO3. The silanol groups serve as a starting point for further reaction with alkoxysilanes, carboxylic acids, or isocyanates, to name just a few possibilities. The first one is by far the most common. [25–27] To further increase the silanol
density on the silica surface, oxidative treatment is the most
common strategy, often followed by further reactions.\textsuperscript{[28–30]} Also, diazonium compounds are established as functionalization agents.\textsuperscript{[31–35]} Even though a high loading of functional groups is usually desired, it needs to be stressed that an over-functionalization or too harsh reaction conditions may lead to a collapse of the ordered structure.\textsuperscript{[36]}

The soft templating approach applies mainly to silica-based materials. Furthermore, metal oxides with a low tendency to crystallize, such as alumina, titania, and some others, are accessible.\textsuperscript{[23]} Additionally, some carbon phases can be synthesized by soft templating if the template-precursor exhibits suitable interactions to remain the structure after precursor conversion. In most other cases (metal oxides and carbon materials), the hard templating\textsuperscript{[37–47]} approach is often the strategy of choice to obtain materials with high control over porosity and structure at the same time.\textsuperscript{[39,48]} Most often this refers to a repeated templating strategy where an OMM, usually based on silica, is utilized as a rigid framework for precursor infiltration, followed by (thermal) conversion (Figure 2A,B) to create metal oxides or carbon materials. Depending on the type of precursor, the utilized amount and the structure precursor interactions, it is possible to entirely fill the matrix’s pore volume (Figure 2A) or just coat the pore wall (Figure 2B). The latter case is referred to as “surface-casting” and most commonly used for the synthesis of “hollow”/“tube-like” like structures based on carbon\textsuperscript{[49,50]} or metal oxides,\textsuperscript{[51]} which will be discussed in detail throughout this article. The process results in a product-template composite material, and, after selective matrix removal, to the desired product, which is obtained as a replica of pore system of the matrix (Figure 2C).

Similar to the above-described soft protection approach, the composite material again bears an opportunity to manipulate the accessible pores while the rest of the surface area is protected by the matrix. In the following, we will call this situation ‘hard protection’. Especially surface casting-derived ‘hollow’/‘tube-like’ materials such as CMK-5 carbon\textsuperscript{[49]} and CMK-9 carbon\textsuperscript{[58]} offer an opportunity to selectively access the intratubular pore system and the external surface of the carbon tubes. Even when more than one type of surface or pore system, respectively, are accessible at the same time, a selective

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**Figure 1.** Hexagonal structure direction process based on the soft templating approach. Colors indicate inner (green) and outer (blue) surfaces.

**Figure 2.** Hexagonal structure replication process based on the hard templating approach.
surface functionalization is achievable. This requires more elaborate selective manipulation strategies. Obviously, molecules or particles that are too large to access the pores of an OMM can only occupy the outer surface. This situation is often the case with nanoparticles of a specific size of (pre)polymerized compounds. They can still be anchored at the outer surface, but will not penetrate the porous network. Additionally, the reactivity and/or diffusion of functionalization agents can be exploited. The outer particle surface is more easily accessible, and diffusion of the molecules is not restricted by the dimensions of the pore system (i.e., free diffusion vs. Knudsen or even surface diffusion), offering the kinetic control of the manipulation. The interplay between reaction conditions and functionalization can be utilized to achieve a selective surface functionalization. An overview of the soft and hard protection approach, as well as the size (height restriction sign) and kinetically dominated manipulation attempt, is depicted in Figure 3.

It needs to be mentioned that a few of the here summarized studies deal with effects that go beyond the strategies depicted in Figure 3. A short discussion about some special cases is included in this review as well. Besides, a clear differentiation between the distinct selectivity approaches is not possible in some cases.

This review article describes the spatial surface functionalization as well as the selective guest species deposition in multimodal and hierarchical ordered mesoporous materials. Thus this review article is not only referring to the hierarchy of pores but also of surfaces, i.e., internal, external, and interparticular surfaces. It focuses on the four strategies presented in Figure 3; namely, the protection of surfaces by soft and hard templates, referred to as the soft and hard protection approach, as well as size-based protection and a kinetic diffusion/reactivity limited mechanism. By contrast, co-condensation methods and zeolite-based materials are in this review.

In the literature, some review articles are, at least partially, dedicated to the selective functionalization by the soft protection approach, but a detailed discussion is currently missing.

2. Selectivity Strategies

2.1. Template-Based Protection

Depending on the utilized template, such as amphiphilic species (soft templating) or rigid structure matrices (hard templating), various ordered mesoporous materials are synthesizable. The following chapters show the possibility of achieving a spatial surface functionalization or selective deposition of guest species within multimodal and hierarchical ordered mesoporous materials.

2.1.1. Soft Template Protection

The soft protection approach is based on the temporary blockage of intraparticle pores in the as-synthesized product (mostly silica), after its synthesis by utilization of amphiphilic structure-directing templates. The template–silica composite material exhibits pores that are still blocked by the amphiphilic. Therefore, the external surface of the particle is accessible for selective functionalization (Figure 4). This poses the challenge that the functionalization needs to be achieved without accidental loss of the amphiphile. After the subsequent removal of the template, the intraparticle pores are now accessible and can be functionalized with a different functional group. The surface chemistry of OMS materials is dominated by reactions of silanol groups, as mentioned above. Once the external surface is wholly decorated with the first functional group $R_1$, it will no longer be available to the second functionalization agent $R_2$ in the subsequent step.

Vartuli et al. and Stein et al. first described the simultaneous removal of the soft template during the functionalization of ordered mesoporous silica. As-synthesized template-silica composite materials (MCM-41 and MCM-48 silica) were refluxed in trimethylchlorosilane (TMCS) and hexamethyldisiloxane, leading to template removal and surface functionalization, as confirmed by $^{29}$Si solid-state NMR spectroscopy. Even though MCM-based materials
Figure 4. Selective surface functionalization based on the soft protection approach. The intraparticle and external surface area of the OMM can be selectively functionalized while the template still occupies the pores.

exhibit a monomodal pore size distribution, the internal and external surface of the silica particles can still be described as hierarchical.[52]

Stein et al. also used as-synthesized silica materials (MCM-41, FSM-16) and treated them with TiCl₄. They investigated the grafting of titanium species at the silica surface and titania nanoparticle formation. Template-free samples did not withstand the harsh reaction conditions, while the composite material did.[66] Similar approaches were adapted by Jaroniec et al. and Mou et al., who functionalized MCM-41 silica and removed the template (CTAB) at the same time.[67–70]

In 1998, Komarneni and co-workers described the functionalization of MCM-41 with CTAB still being present in the pores.[71] By physisorption analysis, they proved that they obtained a mostly nonporous material (type-III N₂ sorption isotherm, 84 m² g⁻¹). After exposition to propyltrimethoxysilane, phenyltrimethoxysilane, and decyldichlorosilane (primary silylation) in ethanol, the template was removed by extraction with acidified ethanol, and the decyldichlorosilane-functionalized sample was further treated with TMCS (secondary silylation). After the first silylation step, all samples remained nonporous, confirming that the template was not removed inadvertently. However, the pore sizes slightly decreased upon the primary silylation, which indicated that the functionalization agents actually did enter the pore channels to some degree, despite the presence of the template molecules. This observation was also confirmed by H₂O vapor sorption measurements; the water uptake was reduced and shifted toward higher relative pressure with an increasing amount of hydrophobization. This study clearly confirmed that the soft template is literally soft and movable. Hence, accurate control over the reaction conditions (e.g., solvent, template, time, temperature) is crucial for selective functionalization. The aspect of the diffusion of the functionalizing agent, as well as its reactivity,[56,63] will be further discussed in Section 2.2. The second silylation carried out by Kormaneni et al. is the first approach to a binary functionalization at the inner and outer side of MCM-41 particles/pores. Even though these authors could show that the templating silica material exhibits a low porosity, Crudden and co-workers attempted to fill the mesopores in SBA-15 silica completely, to make sure that the larger silica pores (as compared to MCM-41 silica) are entirely filled.[72]

In 2000, de Juan and Ruiz-Hitzky treated the as-synthesized MCM-41 composite material with TMCS in isopropanol and HCl (reflux, 2 h).[73] After (partial) template removal by treatment with n-heptane/ethanol/NH₄Cl,[74] another functionalization step followed under the same synthetic conditions as in the first step, but with phenylpropyldimethylchlorosilane. The idea was that after initial silylation, all silanol groups at the outer surface of MCM-41 silica are occupied, and only the silanol groups at the inner surface of the pores can react further. This approach resulted in a trimethylsilyl coverage of ≈1.2 × 10⁻³ mol g⁻¹ and a phenylpropyldimethyl coverage of ≈0.15 × 10⁻³ mol g⁻¹, respectively. When they carried out the functionalization in the opposite order (phenyl inside, alkyl outside), the authors reached a larger coverage with phenyl (1.15 × 10⁻³ mol g⁻¹), which they attributed to the fact that the external surface area is more easily accessible. The description clearly indicates that even though a soft templating approach was described, the selectivity strategies most often overlap when it comes to the description of experimental results, which will be further discussed for some more examples within this review. Likewise, Soler-Illia and co-workers synthesized ordered mesoporous silica films (by using Brij 58 as the template) and functionalized the film at the outer side with TMCS, followed by selective amination at the pore surface. By contact angle measurements, EDS, and XPS, they could show that their utilized selective functionalization process was successful.[75]

A more advanced approach was used by Yang et al. in 2007 (Figure 5). SBA-15 exhibits a hierarchical pore system with primary mesopores connected by smaller meso- or micropores.[76] The poly(ethylene oxide) block of the P-123 block copolymer used for the synthesis occupies the interconnecting pores, while the poly(propylene oxide) blocks are mainly located in the primary mesopores. Depending on the synthetic conditions, the size of both pore systems, and thus the hierarchy, can be tuned, which can be crucial for the success of the structure replication in the above-described nanocasting process, as well as for the functionalization or guest species deposition.[76,77]

The primary mesopores can be vacated by treatment with H₂SO₄, leaving the smaller pore system still blocked. TMCS was used to hydrophobize the accessible mesopores. After subsequent complete removal of the template, the smaller pores became accessible for further functionalization with trivinyliclorosilane to create a complex after exposure to dichlorobis(acetonitrile)palladium. After the reduction of the anchored complex, Pd nanoparticles (np) are fully accessible.
within the micropores. These nanoreactors with topological functionalization were successfully utilized as a catalyst for the Heck reaction between bromobenzene and styrene. A more complete overview of studies dealing with the soft-protection approach is given in Table 1.

2.1.2. Hard Template Protection

The first approach of a hard-template selective deposition was introduced by Hyeon and coworkers in 2001. They coated SBA-15 silica with methyl methacrylate (MMA) and polymerized it (PMMA) with benzoyl peroxide, followed by evacuation. They create a PPMA tube within the mesopores of SBA-15 that is later referred to as intratubular pores. Then pyrrole (PY) was loaded and polymerized (PPY). The process is depicted in Figure 6. After etching with hydrofluoric acid, wire-like structures were obtained that were pressed into a film by a compression molder. Since PPY is an electrical conductor, the authors suggested using these materials as isolated nanowires.[133]

Another approach to fill the pores of SBA-15 silica with a polymer was performed by Schüth et al.[135] They completely filled the pores of SBA-15 silica to deposit magnetic cobalt nanoparticles outside of the material selectively. They described a three-step process (Figure 7) that involves the protection of the silica pores by PMMA, followed by nanoparticle deposition and thermal removal of the polymer, as shown in Figure 6. The authors applied a similar approach based on CMK-3 and CMK-5 carbon materials, decorated with Co and Pd nanoparticles, leading to a potent catalyst for the hydrogenation of octane hydrogenation.[34]

The 'tube-like' structure of CMK-5 separates the carbon surfaces in two distinct regimes. Within the carbon tube, the concave surface is often referred to as intra-tubular pore, while the convex surface at the outside of the carbon tube is called an intertubular pore system. The same applies to related structures such as CMK-9 carbon.

The selective intratubular functionalization of CMK-5 carbon was first described by Tüysüz and Schüth in 2012.[136] They coated the surface of SBA-15 silica with a thin carbon layer (typically ~1.5–1.8 nm), as shown in Figure 8.[137] In the carbon–silica composite material (CMK-5@SBA-15), the intratubular carbon pores are accessible. In the example, the authors propose oxidation with HNO₃ to create oxygen-containing functional groups such as carboxylate. These can be activated by using thionyl chloride, followed by amine-treatment, to create amides.

The same approach was used by Fuertes and co-workers in 2013, who selectively oxidized the intra-tubular surfaces of CMK-5@SBA-15 and CMK-9@KIT-6 composite materials.[138] They used naphthalene as a carbon precursor and an acidic solution of ammonium persulfate as an oxidizing agent. It needs to be mentioned that the oxidation process is challenging: as carbon bonds need to be broken to include oxygen in the structure, an overoxidation that leads to a collapse of the ordered structure must be avoided. Especially the small pores that interconnect the primary mesopores in SBA-15 silica and KIT-6 silica that lead to thin bridges between the inverse replica carbon structures are vulnerable.[36] These failure points in the OMC structure can be protected by the silica, leading to the possibility of achieving a comparably high functionalization of the carbon materials, while maintaining the structure.[139]

The oxidization process leads to various functional groups at the carbon surface; some of them are carboxylic acid (strongly or weakly acidic), carboxyl anhydrides, lactones, phenols, and carbonyl/quinone.

Björk and co-workers recently published a study about CMK-5@SBA-15 composite materials[140] that were functionalized with sulfuric acid to create −SO₃H bonds at the intra-tubular carbon wall.[141] The functionalized composites were investigated as catalysts for the esterification of acetic acid with ethanol. After 1 h, almost 30% conversion was reached, compared to about 5% without any catalyst. A more detailed evaluation of surface nanopatterning and functionalization of silica films can be found in a study by Grosso et al.[142]
Table 1. Silica- and PMO-based materials prepared by soft protection approach.

| Framework | Functional group outside | Functionalization inside and/or guest species | Year | Refs. | (Potential) application |
|-----------|--------------------------|---------------------------------------------|------|-------|------------------------|
| MCM-41, SBA-15 | Si-Ph | CdS | 2001 | [79,80] | Nanocasting |
| SBA-15 | −Si(−C(H)_3) | Cu, Ni | 2002 | [81] | Cu, Ni nanowires |
| SBA-15 | −Si(−C(H)_3) | Si−H | 2002 | [82] | Pt nanowires |
| MCM-41 | Coumarin derivative | Cholestane, phenanthrene | 2003 | [83,84] | Drug delivery |
| MCM-41 | Various NH_{2} | Various NH_{2} | 2003 | [85] | Fundamental research |
| MCM-41 like (thiol containing) | Poly(lactic acid) | Dopamine, glutamic acid, tyrosine | 2004 | [86] | Sensing |
| SBA-15 | −Si(−C(H)_3) | −NH_{2}, CdSe NP | 2004 & 2005 | [87,88] | Fundamental research |
| MCM-41 | Phenytrimethoxysilane | Eu phen complex | 2005 | [89] | Fundamental research |
| SBA-15 | −COOH | Polymer + vancomycin | 2005 | [90] | pH-responsive carrier |
| SBA-15 | Cs_{2.5}H_{0.5}PW_{12}O_{40} | Cs_{2.5}H_{0.5}PW_{12}O_{40} | 2005 | [91] | Catalyst |
| MCM-41 | −F | −NH_{2} | 2006 | [92] | Fundamental research |
| SBA-15, MCM-41, FDU-12 | −Si(−C(H)_3) | −NH_{2} | 2006 | [93] | Ag NP |
| MCM-41 | Rotaxane | Coumarins, Ir(ppy)_3, rhodamine B | 2007 | [94] | Redox-switchable molecular nanovalves |
| SBA-15 | −Si(−C(H)_3) | Au NP, Ag NP | 2005 & 2008 | [95,96] | NP synthesis |
| SBA-3, SBA-15 | −NH_{2}, −COOH | −NH_{2} | 2008 | [97] | Drug delivery |
| Hexagonal OMS | −Si(−C(H)_3) | Ti | 2008 | [98] | Catalysis |
| MCM-41 | Various NH_{2} | 2009, 2011 | [99,100] | Drug delivery |
| MCM-41 | Poly(acrylic acid) | Fluorescein | 2009 | [101] | pH-triggered nanocarrier |
| SBA-15 | −Si(−C(H)_3)−SH | NH_{2}, Au NP, Pd NP | 2009 | [102] | Catalysis |
| MCM-41 | −SH, Herceptin | 2009 | [103] | Drug delivery, cancer cell targeting |
| SBA-15 | −NH_{2}, −SH | −SH | 2010 | [104] | Fundamental research |
| MCM-41 | DMS | Ibuprofen | 2010 | [105] | Drug delivery |
| MCM-41 | Polymer | 2010 | [106,107] | Drug delivery |
| MCM-41 | Various | Doxorubicin | 2011 | [108] | Drug delivery |
| PMO | Various | various | 2011 | [109] | Fundamental research |
| MCM-41 like | −NH_{2} | −SO_{4}H | 2011 | [110] | Catalysis |
| MCM-41 like | −Si(−C(H)_3) | −Si(−C(H)_3) | 2012 | [111] | Fundamental research |
| MCM-41 like | NH_{2}, polymer | Opotecan | 2012 | [112] | Drug delivery |
| PMO | −NH_{2}, −COOH, arginine, glycine, aspartic acid | Fluorescent dye (ATTO-610) | 2012 | [113] | Drug delivery |
| MCM-41 like | −OH | Phosphopeptide | 2012 | [114] | Adsorption |
| MCM-41 | −Si(−C(H)_3) | −NH_{2}, Rh complex | 2013 | [115] | Catalysis |
| MCM-41 | PEG | Doxorubicin | 2013 | [116] | Drug delivery |
| PMO | Macrocycle | 2013 | [117] | Sensing |
| MCM-41 | −Cl, −NH_{2} | −Cl | 2013 | [118] | Fundamental research |
| MCM-41 like | −Cl, R_{2}NH | Aminobenzonic acid | 2014, 2015 | [120,121] | Drug delivery |
| MCM-41 | −F, NH2 | − | 2014 | [122] | Fundamental research |
| SBA-15 | −Si(−C(H)_3)−SH | − | 2015 | [123] | Fundamental research |
| SBA-11 | −Ph−C(−C(H)_3)− | −Si(−C(H)_3)− | 2015 | [124] | Malathion scavenger |
| MCM-41 like | −N_{3} | −Si(−C(H)_3) | 2017 | [125] | Dye separation |
| MCM-41 | −SH | −(C(H)_3)CH_{3} | 2017 | [126] | Fundamental research |
| MCM-41 | −COOH | Doxorubicin | 2018 | [127] | Drug delivery |
In a study published in 2016 by Weinberger et al., a CMK-5@SBA-15 composite was treated with acidic ammonium persulfate solution to create oxygen-containing moieties at the intratubular pore surface.\cite{139} The increase of polarity of the carbon surface was quantified by elemental analysis. Oxygen content of up to 13 wt% was achieved. Furthermore, the effect of the functionalization on the surface polarity was studied by water sorption measurements. With an increasing number of oxygen-containing groups at the carbon surface, the uptake of water in the intratubular carbon pore shifted toward lower relative water steam pressure. At the same time, the uptake of water in the remaining silica pore was unaffected. After the removal of the silica matrix, the ad-/desorption of water was still influenced by the polarity of the carbon surface, but the effect was less pronounced as compared to the carbon–silica composite materials.

Apart from the selective intratubular surface functionalization, i.e., decoration of the pore walls with organic moieties, it is also possible to deposit guest species such as metal oxides inside the carbon tubes of CMK-5. A similar approach as for the organic functionalization can be used. A suitable precursor is infiltrated into the CMK-5@SBA-15 composite. After thermal decomposition to the desired product, the silica matrix is selectively removed by etching, leading to a guest@intraCMK-5 composite material. Lu and co-workers presented this in 2010 for $\gamma$-Fe$_2$O$_3$ as the guest species.\cite{143} They achieved an iron loading of up to 12.2%. The addition of the metal oxide led to a reduction of the BET surface area (by 34%) and pore volume (by 52%). The residual porosity was still high because of the intertubular pores that remained unfilled. The iron oxide-loaded material was shown to exhibit high catalytic activity in the thermal decomposition of ammonia. In another study, Schüth and his group increased the polarity of the intratubular carbon surface of CMK-5 carbon to achieve a more targeted distribution of cobalt(II) nitrate that was subsequently converted to Co$_3$O$_4$.\cite{144} After selective removal of the silica matrix, they obtained Co$_3$O$_4$ selectively deposited within the intra-tubular pore system of CMK-5 carbon. This approach seems quite promising for utilization in lithium-ion batteries. The confinement in the carbon pore serves as a rigid structure to maintain the morphology of the electrode material after cycling between the charged and discharged state.\cite{145-150} It is essential to mention that during the lithiation and delithiation process in batteries, the volume changes can be drastic, which is a major cause of poor cycling stability in many such systems.\cite{150-152} Thus, the local confinement may be advantageous for increased cycling stability.

Weinberger et al. synthesized SnO$_2$@intraCMK-5 composite materials as well as S@intraCMK-5 composite materials with varying amounts of the guest species. They showed that hydrophobic sulfur preferably occupies the intratubular CMK-5 carbon pore, while silica pores (that remained carbon-free due to incomplete infiltration of the carbon precursor, and shrinkage of the precursor during thermal conversion) remained unoccupied (except for high loadings with sulfur), as shown in Figure 9.\cite{149} The distribution of the guest species is different in the case of SnO$_2$. The
deposition was achieved by the incipient wetness approach utilizing an acidic solution of SnCl₂. The hydrophilic solution occupies the smaller but more hydrophobic carbon pores (3.6 nm) compared to the small amount of larger silica pores (7.8 nm), showing an interesting interplay between the influence of capillary forces and the polarity of the pore wall. These results highlight that not only capillary forces are crucial when it comes to the deposition of a guest species. Furthermore, the pore wall polarity can be influenced by functionalization before guest species infiltration. This approach enables a more controlled operating principle. In extreme cases, it might be possible to completely omit the deposition in small pores when the host–guest interactions are properly balanced.[153]

Moreover, TiO₂, Mn₃O₄/Mn₃O₄, NiO, and CoFe₂O₄ loaded CMK-5 samples were synthesized.[148,149] The distribution of the metal oxides can be observed by transmission electron microscopy, as shown in Figure 10. The location of Fe₃O₄ in the hollow carbon tubes is clearly visible by the image contrast as the electron density of carbon walls, and the metal oxide is so different. A summary of all discussed materials is shown in Table 2.

Schüth et al. recently presented a technique to synthesize hollow metal oxide tubes that resemble the structure of CMK-5 carbon.[51] They increased the surface polarity of SBA-15 and KIT-6 silica by treatment with HNO₃/H₂O₂. The resultant silanol-rich silica materials were then impregnated with zirconyl chloride. After calcination, the silica surface was decorated with a fragile layer of ZrO₂. After careful removal of the silica matrix, hollow metal oxide tubes could be obtained. In case of the hexagonal pore system, the nanocasting success was proven by X-ray diffraction and electron microscopy.

Figure 7. Selective deposition of cobalt nanoparticles outside of the porous framework of SBA-15 silica. Reproduced with permission.[335] Copyright 2007, American Chemical Society.

Figure 8. Proposed synthetic strategy of intratubular selective surface functionalization in ordered mesoporous CMK-5 carbon. Reproduced with permission.[336] Copyright 2012, Elsevier.
The results for the cubic system were more challenging in comparison to the first example, because of the more complex 3-D structure compared to the hexagonal materials. The strategy emphasizes the importance of investigation of the host–guest interactions when it comes to structure replication on the nanometer scale. Weak interactions might lead to a poor distribution of the guest species within the porous host, leading to a frail replica. Too strong interdependencies may result in blockage of the pores, and thus, to a poor replica structure, as discussed by Zhao et al. In general, this approach may open the door to novel composite materials with a shell of metal oxides and a core with various guest species. In case of an intratubular deposition of a guest species, the structure might even be supported. Possible applications include catalysis and energy conversion.

In case of ordered mesoporous silica materials, a double functionalization (inside the pores, i.e., at the pore walls, and at the outer particle surface) approach has already been established, as discussed above. For ordered mesoporous carbon materials, however, this is not yet the case. The approach is depicted in Figure 11. After the initial intratubular functionalization step, the intratubular pores are temporarily blocked by filling with a guest species that serves as a ‘protecting agent’ (e.g., sulfur or PMMA), leaving the intertubular surface exposed for a second functionalization. The protecting agent is later removed, either by thermal decomposition (provided that the functional groups \(R_1, R_2\) are stable enough, or by solvent extraction (e.g., THF, acetone).

The class of materials (not necessarily limited to carbon) introduced in Figure 11 might be interesting for drug delivery systems. Silica-based materials are already well investigated. An outer particle functionalization makes it easier to pass certain areas in the body, while the intrapore surface functionalization can be utilized to increase the loading with a drug. Furthermore, heterogeneous phase transfer catalyst systems might be another field of application. By choosing the right combination of solvents, reactants, and functional groups, adjusting the solvent–catalyst interactions might be possible.

### 2.2. Kinetic Protection

When more than one kind of surface or pore system are exposed simultaneously, selectivity can also be achieved by exploiting constrained accessibility and the space confinement of the pore system. For example, silanol groups at the external surface of a silica particle are easily accessible for a functionalization agent, while a diffusion barrier exists for the interior of the pores. Using a kinetically driven reaction may lead to a functionalization selectively at the most accessible reaction centers. Shephard et al. reported the passivation of the outer particle surface of MCM-41 silica with \(\text{Ph}_2\text{SiCl}_2\) and subsequent functionalization of the pore walls with \((\text{MeO})_3\text{Si(CH}_2)_3\text{NH}_2\). The latter served for the immobilization of a Ru-based catalyst.
in the confined pore environment.\cite{158} The same authors also selectively functionalized MCM-41 silica with Ph$_2$SiCl$_2$ at the outer side of the particle while anchoring a ferrocene-based chiral complex at the pore walls. Utilizing the heterogeneous catalyst in the allylicamination of cinnamyl acetate, they achieved high conversion rates and exceptional ee values over 99%. In comparison to commercially available silica particles, the confinement effect of the MCM-41 silica enables a targeted catalytic conversion to the desired product.\cite{159} The same group obtained similar results in two-step hydrogenation of nicotinate to ethyl nipecotinate.\cite{160}

Salmio and Brühwiler investigated in detail how the structure of aminopropylsilanes affects their functionalization behavior.\cite{161} The highest degree of functionalization was achieved with monoaminosilanes, whereas dipodal aminosilanes preferably occupied the most accessible sites at the outer surface and pore entrance. Another way to selectively modify the site selectivity is the variation of the solvent. Better spatial distribution of aminosilanes was shown to be possible by choosing solvents with high polarity to reduce clustering. Such adjustment of the synthetic conditions facilitates the tailoring of the materials.\cite{64,162,163} An even distribution of functional groups or even a complete blockage of the pore system can be achieved if the functional groups mainly occupy the pores or pore entrances.\cite{164} Another detailed investigation was performed by Anwander et al., who analyzed the site-selective functionalization of mesoporous SBA-1 (space group Pn3m) and MCM-41 silicas.\cite{165} They identified three distinct sites of silanol groups in the cage-like structure of SBA-1, namely intra-particle, extra-particle, and at the cage/pore entrance, as shown in Figure 12. The size of the pore entrance is rate-determining for the silylation with monosilazanes (Me$_2$NSiMe$_2$R). For large alkyl groups (e.g., C$_8$H$_{17}$), an excess of functionalization agent can lead to clogging of the pores. Less reactive chloro- and alkoxy-silanes led to a more uniform/random distribution throughout the material. In the tubular pores of MCM-41 silica, silylation was found to be kinetically controlled for monosilazanes. The diffusion of the sterically more demanding intermediate surface species rather than the free diffusion of the silazane itself was rate determining. The study confirmed that monosilazanes exhibit a higher silylation efficiency than chloro- and alkoxy-silanes.\cite{165}

Kleitz and co-workers recently described the functionalization of the outer surface of MCM-48 silica with diethylenetriaminopentaacetic acid and polyethylene glycol (PEG). They utilized a low concentration of the functionalization agent. Besides the high molecular weight, a slow diffusion could be achieved, leading to an outside functionalization of the OMS. Even though an efficient grafting process was achieved, the
porosity remained high (90% of the initial value). Thus, it was concluded that pore-blocking did not occur, which again shows the enormous potential of such custom-made materials as drug carriers or for other medical applications.[166–174]

2.3. Size Protection

The choice of large, bulky functionalization agents provides an excellent opportunity for a size-selective protection approach. Species that cannot enter the pores for steric reasons will selectively cover the outer particle surface. Furthermore, they may be used to deliberately block the pore entrances. If this blockage can be controlled by external stimuli, a ‘gate’ function for controlled loading and release of guest species from the pores is possible (‘gate-keeper’ or ‘stopcock’ principle).[57,60,175–180]

Zhao et al. used poly(N-isopropyl acrylamide) based polymer with azobenzene and 2-nitrobenzyl groups as light-responsive gates for drug delivery purposes (Figure 13).[181] Flourescein was used as a traceable guest molecule. Only a low degree of leakage was observed within 24 h after loading the particles. UV irradiation led to an opening of the molecular gates, and most of the fluorescein was released in the following 24 h. Slowing and co-workers discussed the combination of a size and accessibility protection strategy at OMS based on Pluronic P104 that were decorated at the outer particle surface with glycidoxypropyl groups, followed by the addition of enzymes (alcohol oxidase and catalase). The pore surface was functionalized carrying propylamine groups.[182] They used the catalysts for the subsequent conversion of alcohols with low molecular weight to aldehydes with longer alkyl chains. The spatial separation of the enzyme and the amino group were necessary to avoid interactions between them. PEG is biocompatible and thus often used to coat extrinsic materials into an in-vivo environment.

2.4. Other Strategies

Apart from the above-described main strategies for implementing selectivity, some studies also identify other causes for selective deposition of a guest species in OMM. One example is the distribution of Pd nanoparticles in the primary and secondary pores of SBA-15 silica, as described by Kiwi-Minsker et al.[183] The location of the noble metal nanoparticles depends on the atmosphere during the thermal conversion of the precursor, Pd(CH$_3$COO)$_2$. Conversion under air atmosphere at 550 °C leads to nanoparticles that are located in the primary mesopores of SBA-15. Interconnecting micro/mesopores in the silica pore walls can be filled by a reductive treatment in H$_2$ at 300 °C, followed by oxidative treatment as described above. The distribution was clearly indicated by physisorption measurements as well as transmission electron microscopy images in Figure 14. The authors explain this phenomenon by the mobility of the precursor in the pore systems. In the presence of (surface-bound)

Figure 13. Grafting large strains of poly(N-isopropylacrylamide)-based polymers block the pore system of MCM-41 silica. After UV irradiation, the pores open up, and a guest molecule are released. Reproduced with permission.[181] Copyright 2010, The Royal Society of Chemistry.

Figure 14. Transmission electron microscopy images displaying the distribution of Pd nanoparticles in a) the mesopore system and b) the intrawall micropores of SBA-15 silica. Reproduced with permission.[183] Copyright 2004, American Chemical Society.
water in the mesopores, Pd$^{2+}$–hydroxyl complexes easily migrate into the mesopores, and the silanol groups facilitate the clustering. By contrast, after the formation of Pd nanoparticles after reductive treatment, Pd probably forms palladium silicides (Pd$_n$Si), mostly located in micropores.$^{[183,184]}$ It is noteworthy that metal and metal oxide nanoparticles can be mobile within the mesoporous framework depending on the species, the surrounding atmosphere, and the chemical nature of the guest species.$^{[143,185,186]}$ It is not surprising that capillary forces and polarity in nanochannels influence the location of guest species.$^{[187]}$ This effect was investigated for titania clusters entrapped in the micropores of SBA-15 silica. Three impregnations with small amounts of titanium isopropanoxide in isopropanol were performed, leading to a filling of the microporosity while the mesopores were not affected.$^{[188]}$ Again, the synthetic conditions, such as matrix pretreatment, seem to have a substantial influence on the guest species distribution. One main reason might be the amount of silanol groups, which depends on the temperature the material has been exposed to.$^{[189,190]}$

### 3. Characterization Techniques

While the selective surface functionalization or deposition of a guest species is an ambitious goal, the characterization and proof of selectivity is particularly challenging. Some studies provide convincing and conclusive evidence by applying various analytical methods. Some examples have already been mentioned above.

Obviously, physisorption analysis is one of the major techniques to characterize porous materials.$^{[191]}$ Selective functionalization of the outer particle surface will not affect the pore size, which can be easily verified by measuring the pore size distribution before and after functionalization.$^{[71,186]}$ In addition to using standard sorptive gases, such as N$_2$ and Ar, water sorption studies may provide additional information, as the sorption behavior of H$_2$O at room temperature strongly depends on both the porosity and the surface chemical properties (i.e., polarity) of the sample.$^{[192–194]}$ This effect can be exploited for distinguishing nonfunctionalized surfaces and surfaces that are decorated with (e.g., nonpolar) moieties.$^{[71,119]}$

X-ray diffraction is another standard tool for the characterization of ordered mesoporous materials. In particular, low-angle diffraction or measurements at even smaller angles (small-angle X-ray scattering, SAXS) is frequently used for studying periodic order at the nanometer length scale, such as ordered mesoporosity.$^{[195,196]}$ While this is mostly used as a fingerprint method for identifying the symmetry of a pore system, a more elaborate analysis of electron density distributions offers

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Figure 15. Calculated diffractograms of CMK-5 (left, adapted with permission.$^{[154]}$ Elsevier) and CMK-9 (right, adapted with permission.$^{[206]}$ Elsevier) carbon-based materials with sulfur deposited in the intratubular pore systems. Interconnecting carbon bridges are not shown.

Figure 16. Confocal laser scanning microscopy measurements of ordered mesoporous silica nanoparticles (pores parallel to the long axis) functionalized with various amino-containing silanes (3-aminopropyltrimethoxysilane APTMS, 3-(2-aminoethylamino)propyltrimethoxysilane AEAPTMS, N$_1$-(3-trimethoxysilylpropyl)diethylenetriamine TMPTA, 3-Aminopropyl(diisopropylamino)trimethoxysilane ADPipes, bis(triethoxysilylpropyl) amine BTESPAs and 3-aminopropyltris-(methoxymethoxy ethoxy)silaneAPTMEES). Reproduced with permission.$^{[207]}$ Copyright 2011, The Royal Society of Chemistry.
an opportunity to extract more detailed information.[197] For example, in the case of hollow carbon materials such as CMK-5 and CMK-9, the diffraction diagrams are strongly influenced by the wall thickness of the corresponding material.[49,50,137,198–205] Guest species deposited selectively in the intratubular pores of either CMK-5 or CMK-9 carbon will cause significant changes in the diffraction patterns, which provides conclusive evidence of the selective deposition. The reason for this is that in the \( p\overline{6}mm \) space group (CMK-5 carbon) and \( Ia\overline{3}d \) (CMK-9 carbon), the crystallographic positions in the center of the hollow carbon ‘tubes’ contribute the strongest to the typically most intense 10 10 patterns with a reasonable intensity.[143,144,149,154] Thus, sulfur is an ideal guest species for this purpose.[149,154,206] In the case of metal oxides, the electron density of the guest species is much higher as compared to the surrounding framework.

It has to be mentioned that OMC materials exhibit microporosity to a certain extend. The proportion with respect to the mesoporosity depends on the utilized precursor and synthetic conditions. In case of the carbon materials mentioned above, the precursor solution is based on furfuryl alcohol leading to a comparably neglectable microporosity compared to sucrose or resol. In case of a substantial amount of microporosity, the distribution of guest species, e.g., sulfur, can be monitored by small-angle X-ray scattering as investigated by Mascotto et al.[195,196]

Functionalization of mesoporous materials can generally also be studied by microscopic methods. Zucchetti and Brühwiler presented an impressive example of using optical confocal laser scanning microscopy.[207] They used various alkoxysilanes to amino-functionalize OMS materials by a co-condensation method and verified that the spatial distribution of the functionalities, as shown in Figure 16.[182,208]

The location of functional groups or guest species can also be monitored by electron microscopy. Figure 17 shows a scanning electron microscopic study by She et al., who investigated CMK-5 carbon with CoFe\(_2\)O\(_4\) in the intratubular pores. Energy-dispersive spectroscopic mapping reveals the lateral distribution of iron, cobalt, and oxygen in the intra-tubular pores, while the inter-tubular pores are empty.[148] Also, electron energy loss spectroscopic (EELS) mapping was used by Pellicer et al. to show that a silica material could be homogeneously coated with a metal oxide precursor during a nanocoating synthesis.[209]

4. Conclusion

In summary, this review gives an overview of research work dedicated to the selective manipulation of hierarchical surfaces in multimodal ordered mesoporous materials. Historically speaking, the soft protection strategy evolved shortly after the first discovery of ordered mesoporous materials. While the pore system is still blocked by the structure-directing agent or by a hard matrix backbone, the outer surface or the pore entrances of a material can be functionalized. When several distinct functionalization sites are exposed, the reactivity/diffusion of a functionalization agent can be used for targeted surface manipulation. Obviously, the size of the guest species/reagent also plays an essential role, as access to the pore system may be hindered or prevented entirely. A variety of characterization techniques were developed and refined to actually prove a selectivity in the synthetic approach of manipulating ordered mesoporous materials. Selective functionalization or loading with guest species may lead to improved functional materials for such applications as adsorption/separation, energy conversion, or catalysis. Also, numerous studies have shown the potential of functionalized mesoporous materials in biomedical applications and drug delivery systems.

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Conflict of Interest

The authors declare no conflict of interest.

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carbon, functionalization, ordered mesoporous, selective, silica
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