4 Ordered mesoporous silica: synthesis and applications

4.1 Introduction

Porous materials were initially defined in terms of their adsorption properties, and thus distinguished by their pore size range. Pore size usually refers to pore width, i.e., the diameter or distance between opposite walls in a solid. According to the IUPAC definition [1], porous solids are then divided into 3 classes: microporous (< 2 nm), mesoporous (2–50 nm) and macroporous (> 50 nm) materials. Additionally, the term “nanoporous”, which refers to pores in the nanometer size range (< 100 nm), is increasingly being used.

Materials with pores in the nanometer range have emerged as key elements for the development of future technologies including miniaturized electronics, magnetic and optical devices, environmentally friendly catalysts, materials for pollutant removal, biocompatible implants, and drug delivery systems [2–4]. The nanopore size range offers vast potential for the construction of elaborate functional systems with tailor-made properties. As a few examples, nanoporous materials may be used as highly selective sorbents, permselective membranes, systems for energy storage or energy conversion, recyclable solid catalysts, low \( k \)-dielectrics, sensors, biomaterials for drug/gene delivery or medical imaging, etc. Furthermore, nanoscale pores enable confinement effects which can restrict the growth of crystals and quantum objects, shift the phase behavior of fluids, or create compatible hybrid interfaces. Nano-reactors able to perform size- and shape-selective chemical conversions are also being developed on the basis of nanoporous solids. In such systems, cooperative/complementary chemical processes may be realized in the confined space of the nanopores, acting as spatially-functionalized cavities in analogy to enzymatic active sites. However, it is important to keep in mind that the size and volume of the pores in a given material have a profound influence on the final properties of the solid, such as adsorption-desorption processes, diffusion mechanisms, storage capacity, size exclusion, confinement, density, mechanical stability, etc.

Many types of synthetic nanoporous materials, such as ordered microporous and mesoporous materials, controlled pore glasses, gels, pillared clays, anodic alumina, porous polymers, carbon nanotubes, and so forth, have been intensively studied [5–7]. In general, the main attribute is that nanoporous materials exhibit high surface area, and the only way to generate such materials with the desired surface area is through a structuring of the solid at the nanometer level. In many cases, this is achieved with procedures which rely on structuring through the addition of porogen species or templates, which can be single organic molecules or supramolecular aggregates, most
frequently. In addition, some other methods are based on the use of solid templates, namely the nanocasting techniques [8–10]. All of these templating pathways are used to synthesize nanoporous materials with a high level of control over their structural and textural properties. These categories of solids are generally viewed as high performance materials for applications in catalysis, separation or storage. As discussed by Schüth and Schmidt [11], their regular pore system with its exceedingly high surface area can be used to introduce guests (e.g., molecules, clusters, macromolecules, or particles) that are stabilized by the solid framework and spatially organized, which enables the development of functional materials.

In particular, the use of supramolecular assemblies (i.e., micellar aggregates) as structure-directing agents (SDAs) allowed the synthesis of a new family of mesoporous silica and aluminosilicate compounds, which was designated M41S [12, 13]. These solids were the first examples of solids exhibiting ordered arrangements of mesopores with a narrow pore size distribution. This discovery was a major breakthrough, which then opened up a whole field of research, and great new possibilities in many areas of chemistry and materials science. In this chapter, the authors focus first on general aspects related to the synthesis and functionalization of ordered mesoporous silica (OMS) materials. Then, a few recent developments concerning the use of functionalized mesoporous silica will be presented, with special emphasis on modern drug delivery and separation applications.

### 4.2 Ordered mesoporous silica (OMS)

In the area of ordered mesoporous materials, silica-based systems are still the most widely studied. There are several reasons for this: the great variety of possible structures, the precise control of the hydrolysis-condensation reactions possible due to the lower reactivity (compared to transition metals for example), enhanced thermal stability, and a great variety of functionalization methods available. In addition, mesoporous silica is fairly biocompatible, which is of great importance for biomedical applications (see below, Section 4.5).

The characteristic approach for the synthesis of ordered mesoporous materials is the use of liquid crystal-forming templates which enable the specific formation of pores with a predetermined size. Among the different materials reported in 1992 by the scientists at Mobil Corporation [12], the one named MCM-41 (Mobil Composition of Matter №41) exhibits a highly ordered hexagonal array of cylindrical mesopores with a relatively narrow pore size distribution. This new type of solid is thus characterized by periodic arrangements of pores, but the framework pore walls are built of amorphous silica. In general, the combination of powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and gas physisorption analysis enables reliable characterization of ordered mesoporous materials (Fig. 4.1). In particular, the hexagonal arrangement of uniform pores of MCM-41 can be clearly visualized by TEM (Fig. 4.1(a)).
The Mobil synthesis performed in alkaline medium led to three well-defined structures: MCM-41, MCM-48, and MCM-50. Vartuli et al. [14] showed that the surfactant-to-silica mole ratio is a critical variable in the formation of M41S materials. Using tetraethoxysilane (TEOS) with cetyltrimethylammonium chloride (CTAC, C_{16}H_{33}(CH_{3})_{3}NCl), they found that progressively increasing the surfactant-to-silica molar ratio from 0.5 to 2.0 resulted in hexagonal (<1), cubic $Ia\bar{3}d$ (1–1.5), lamellar (1.2–2), and uncondensed cubic octamer (>2) mesoscale structures. The structure of MCM-48 belongs to the $Ia\bar{3}d$ space group (Fig. 4.1c), which has also been found in the binary water/cetyltrimethylammonium bromide (CTAB) system [15]. This three-dimensional (3D) porous structure is considered to be bicontinuous with a simplified representation of two 3D mutually intertwined networks of rods [16, 17]. The unit cell parameter measured for cubic MCM-48 usually ranges in between 8 nm and 10 nm. MCM-50 is a lamellar mesostructure in the as-synthesized form. However, removal of the template results in the collapse of this layered structure unless the material has previously been stabilized.

Since the discovery of the MCM family in the early 90s, considerable progress has been achieved regarding the synthesis, characterization, and porosity control of ordered mesoporous silica. An impressive diversity of synthesis approaches have been developed, which now enables the formation of various OMS (e.g., MSU [19], SBA-15 [20], SBA-16 [20], FDU [21], KIT-6 [22], etc.) with a great variety of morphological, structural, and textural properties [23, 24]. However, for all the materials, the concepts involved in their synthesis usually remain quite similar and can be seen mainly as a combination of three key features: (1) surfactant, co-surfactant, solvent, and co-solvent types, (2) controlled polymerization of suitable inorganic species, and (3) interactions between the inorganic (silica) precursor and the organic templating agents.

### 4.2.1 Principle of synthesis

For the synthesis of OMS, two main routes are possible. These are based on the interactions between organic moieties, known as structure-directing-agents (SDAs) or templates, and the silica precursors, which ultimately lead to the formation of an ordered hybrid mesophase (as illustrated in Fig. 4.2). After extended polymerization and condensation of the silicates (or poly-silicic acid species for low pH synthesis conditions), mesoporosity is then created through the removal of the template.

While the general concept is similar, there are differences between these two pathways:

- **In pathway A**, i.e., the **cooperative self-assembly route**, the mesophase is created through the addition of the silica precursor to the micellar system. Prior to mixing, no liquid crystalline phase exists; only isotropic micelles are present in the solution. The self-assembly reorganization of the micelles occurs **in situ**, coopera-
Fig. 4.1. (a) Transmission electron microscopy image of MCM-41. Reprinted with permission from [24]. (b) Nitrogen adsorption-desorption isotherms (−196°C) and corresponding NLDFT pore size distribution for calcined MCM-41 silica (BET surface area: 1070 m² g⁻¹; Total pore volume: 0.92 cm³ g⁻¹; NLDFT pore size: 4.1 nm). Reprinted with permission from [18]. (c) Examples of powder X-ray patterns obtained for ordered mesoporous silica mesophases shown with their pore topology. On the left: MCM-41 with p6mm symmetry, on the right: MCM-48 with Ia3d symmetry. Reprinted with permission from [24].

quantitatively with the formation and polymerization of the inorganic network around them, leading ultimately to a highly organized hybrid mesophase.

- In pathway B, i.e., the true liquid-crystal templating (TLCT), a pre-formed liquid crystalline phase is used as a template for the infiltration of the silica precursors. The polymerization of the inorganic network is then triggered around this micellar organization. This synthesis pathway was successfully used by Attard et al. [25] to synthesize OMS with various mesostructures, and especially mesoporous silica monoliths.
Most often, however, the so-called *cooperative self-assembly* takes place between the templating species and the mineral network precursors with synchronized self-assembly and inorganic network formation, yielding highly organized mesoscopic architectures. This cooperative formation mechanism, which was first proposed by Stucky, Schüth and co-workers, is now largely accepted by most researchers as an explanation for the mesophase formation [24, 26–28].

**Fig. 4.2.** The two main synthesis pathways for the formation of ordered mesoporous materials: A, cooperative self-assembly and B, true liquid-crystal templating. Reprinted with permission from [23].

**Cooperative self-assembly and hybrid interfaces**

In practice, synthesis starts with the dissolution of an amphiphilic molecule, i.e., surfactant that can be ionic or non-ionic, in water. Here, the surfactant-inorganic hybrid mesophase forms cooperatively from the species present in solution which are not in a liquid crystalline state prior to mixing of the precursors. Quaternary cationic surfactants, $C_nH_{2n+1}N(CH_3)_3Br$ ($n = 8–22$), are the most common for the synthesis of ordered mesoporous silica materials with pores $\leq 5$ nm. The commercially available $C_{16}$TAB is widely used for the synthesis of M41S silicas. In order to synthesize materials with larger pores, swelling agents (SAs) can be used, but they generally lead to poorly reproducible syntheses and low-quality materials due to the heterogeneous dispersion of the SAs in the system. Alternatively, amphiphilic non-ionic triblock copolymers were also proposed as self-assembling SDAs, and these have become more and more popular as they allow the design of OMS with larger pores and thicker walls in acidic or neutral media [19, 29]. Nowadays, the commercially available
Pluronics™ \((\text{EO})_x-(\text{PO})_y-(\text{EO})_x\) are widely used for the syntheses of large pore ordered mesoporous silicas, e.g., SBA-15, SBA-16 or KIT-6 (*vide infra*).

When dissolved in aqueous solutions, if proper conditions are met, ionic surfactants or block copolymers assemble into isotropic micelles due to their amphiphilic behavior. Alkoxysilanes, e.g., TEOS, are then added to this stock solution. Inorganic silica precursors are then catalytically hydrolyzed producing silanol groups due to the non-neutral nature of the media. Silanols further condense, forming polymeric silica-based species which aggregate around the micellar structures. The cooperative self-assembly process eventually leads to a supramolecular templating, which results in the hybrid mesophase formation (Fig. 4.2A).

Achieving a well-defined segregation of the organic and inorganic domains at the nanometric scale plays an essential role in the synthesis of OMS. Indeed, it is the nature of this hybrid interface that governs the assembly process, and thus the overall quality of the resulting material. The key thermodynamic factors affecting the formation of a hybrid interface were identified by Huo et al. [27, 28]. In their model, described as *charge density matching*, the free energy of the mesostructure formation \((\Delta G_{\text{ms}})\) is considered the sum of the free energy contributions of the inorganic-organic interface \((\Delta G_{\text{inter}})\), the inorganic framework \((\Delta G_{\text{inorg}})\), the self-assembly of the organic molecules \((\Delta G_{\text{org}})\), and a contribution of the solution \((\Delta G_{\text{sol}})\). The final hybrid mesophase consists of the ordered arrangement with the lowest interface energy.

As explained previously, in the cooperative assembly route the template concentration may be well below that necessary for obtaining liquid crystalline assemblies or even micelles. Therefore, the creation of a compatible hybrid interface between the inorganic walls and the organic templates \((\Delta G_{\text{inter}})\) is essential for the generation of a well-ordered mesoscopic hybrid structure with appropriate curvature. From the kinetic point of view, the formation of an organized hybrid mesostructure results thus from a well-balanced combination of inorganic polymerization, organization of the SDA, and organic-inorganic phase separation. Hence, two aspects are essential to fine-tune the mesophase formation: the reactivity of the inorganic precursors (polymerization rate, isoelectric point, etc.) and the interactions involved in generating the hybrid interface. Here, a generalized cooperative mechanism of formation can be described based on the specific (electrostatic) interactions between the inorganic precursor \((I)\) and the surfactant head group \((S)\). Soler-Illia et al. [30] summarized six possible cooperative interaction pathways for the assembly of the hybrid mesophase, which were originally proposed by Huo et al. [27, 28] and later extended by Pinnavaia [19, 31]. As presented in Fig. 4.3, in the simplest case, the ionic surfactant and the inorganic species are oppositely charged, leading to electrostatic interactions \((S^+I^-\text{ or } S^-I^+)\). Since the synthesis of MCM-41 and MCM-48 silicas is carried out in strongly alkaline media, silica oligomers have a negative charge that interacts with the positive charge of the cationic CTAB molecules \((S^+I^-\text{ mechanism})\). These two direct routes can be completed by two indirect ones, i.e., interactions between surfactants and inorganic moieties with the same charges through the use of a counter-ion [28]. For ex-
For example, the $S^+X^-I^+$ pathway can explain the mesophase formation under acidic conditions and in the presence of halide anions ($X^-=Cl^-, Br^-$), whereas the $S^-M^+I^-$ route is characteristic of base-catalyzed synthesis in the presence of alkaline metal ions ($M^+=Na^+, K^+$).

Moreover, following the early development of the so-called MSU synthesis which was performed in neutral conditions using non-ionic block copolymers, a novel assembly approach was proposed and denoted $N^0I^0$ [19]. In this pathway, mesophase formation is driven by hydrogen-bonding forces. Later on, Zhao et al. proposed the use of non-ionic triblock copolymers (i.e., the Pluronics) and acidic conditions to synthesize SBA-15 silica and other related large pore materials [20]. However, in this case, as the silicic acid species are positively charged and the block copolymer could also be positively charged, the $N^0I^0$ route was thus derived to a $(N^0H^+)(X^-I^+)$ pathway. Finally, a last concept, the $S^0I^0$ interaction is associated with materials called HMS [31], where silicate species interact with a neutral SDA through hydrogen-bonding between the hydroxyl groups of hydrolyzed silicate species and polar amine head groups.

**Hydrothermal treatment and template removal**

Most common syntheses are carried out in aqueous media at temperatures close to room temperature ($< 60^\circ C$), depending on the type of material. After this step, a hydrothermal treatment (HT) or aging can be performed for over a few hours or up to several days in order to achieve a more complete condensation of the silica frame-
work. Even if this aging step is not always mandatory, it usually greatly improves the quality and organization of the resulting OMS [32, 33]. Moreover, mesophase tailoring can be performed during this treatment [22, 34, 35]. Even mesophase transitions are possible in some cases, because variations in the charge density of the silicate-based framework may occur upon condensation [26]. Furthermore, various organics (i.e., co-surfactants) can also be added to the mother liquid in order to modulate the “soft” mesostructure of the material during this stage [24].

After aging, the resultant product is cooled, recovered by filtration or centrifugation if the particles are nanosized, and properly dried in air. The mesoporous material is finally obtained after the removal of the organic template. The most common method for the elimination of the organic moieties is calcination (at temperatures usually above 500°C)[36]. Calcination allows the complete removal of organic species from surfactant-templated silicas. However, when as-made materials containing large amounts of organics are calcined, some carbon deposits or coke formation may be observed. To avoid this contamination, calcination should be performed under sufficient air flow with slow heating rates (1°C min$^{-1}$) and an extended period of heating once the 500–550°C plateau is reached (4 to 8 h). Calcination is the most efficient and convenient method for the removal of organic templates, but the silanol condensation which occurs during this process has two major impacts on the resulting mesostructure: (1) a pronounced decrease of the unit cell of the material (shrinking), and (2) an increase in surface hydrophobicity. Framework condensation can be limited by adjusting the temperature and the duration of the hydrothermal treatment [36]. Furthermore, for copolymer-templated materials especially (e.g., SBA-type and KIT-6 silicas), a brief extraction step using an ethanol/HCl mixture can be performed prior to calcination, in order to improve efficiency and limit detrimental exothermic effects [37, 38]. In addition, the surface silanol density can be easily restored after calcination by performing controlled acidic (aqueous) treatments [39, 40], in order to carry out more efficient post-grafting procedures [41]. Note that calcination is often recommended when OMS are designed for biomedical applications because it removes all trapped SDA organic species. This aspect is of tremendous importance because residual amounts of free surfactants (e.g., CTAB), which typically remain after liquid extraction, were found to be toxic [42, 43]. On the other hand, calcined OMS were found to be “reasonably” biocompatible [44, 45].

Other methods for template removal include liquid extraction [46], acid treatments [47], $\text{H}_2\text{O}_2$ oxidation under microwave irradiation [48], supercritical CO$_2$ extraction [49] and ozone treatment [50]. Each method causes noticeable variations in the final properties of the porogen-free materials. For example, prolonged (12–24 hours) or multiple liquid extraction steps (e.g., Soxhlet extraction) can be used in the case of organic-inorganic hybrid materials in which some organic functionalities must be preserved after template removal. In contrast, $\text{H}_2\text{O}_2$ oxidation under microwave irradiation cannot be used with functionalized organic–inorganic hybrids, but it enables complete removal of the template while generating porous materials with higher pore
volume and a more hydrophilic surface than calcined counterparts, and this in a very short time (< 15 min) [51].

### 4.2.2 Mesostructure diversity and tailoring

Tailoring of the textural and structural properties of the material, i.e., pore size, pore shape, and connectivity, is essential, especially regarding the potential application of OMS in catalysis, selective sorption, sensing technologies, and so on. Various parameters may be tuned, but the most important are the choice and ratios of reactants, synthesis time and temperature, and the use of additives. By carefully adjusting these parameters, a large diversity of materials can be synthesized. The most frequent ordered mesoporous silica materials are compiled in Table 4.1, along with their structural characteristics.

**Table 4.1.** Structural parameters of the most common ordered mesoporous silicas (OMS).

<table>
<thead>
<tr>
<th>OMS</th>
<th>SDA system</th>
<th>Type of interaction</th>
<th>Pore mesostructure</th>
<th>Typical pore size (nm)</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>MCM-41</td>
<td>C&lt;sub&gt;n&lt;/sub&gt;(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;N&lt;sup&gt;+&lt;/sup&gt; Br&lt;sup&gt;−&lt;/sup&gt; or Cl&lt;sup&gt;−&lt;/sup&gt;</td>
<td>S&lt;sup&gt;+&lt;/sup&gt;I&lt;sup&gt;−&lt;/sup&gt;</td>
<td>2D hexagonal p&lt;sub&gt;6mm&lt;/sub&gt;</td>
<td>1.5–10.0</td>
<td>[12–14]</td>
</tr>
<tr>
<td>MCM-48</td>
<td>C&lt;sub&gt;n&lt;/sub&gt;(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;N&lt;sup&gt;+&lt;/sup&gt; Br&lt;sup&gt;−&lt;/sup&gt; or Cl&lt;sup&gt;−&lt;/sup&gt;</td>
<td>S&lt;sup&gt;+&lt;/sup&gt;I&lt;sup&gt;−&lt;/sup&gt;</td>
<td>3D cubic Ia&lt;sub&gt;3d&lt;/sub&gt;</td>
<td>1.5–4.6</td>
<td>[14, 26, 37]</td>
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<td>SBA-1</td>
<td>C&lt;sub&gt;n&lt;/sub&gt;(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;N&lt;sup&gt;+&lt;/sup&gt; Br&lt;sup&gt;−&lt;/sup&gt; or Cl&lt;sup&gt;−&lt;/sup&gt;</td>
<td>S&lt;sup&gt;+&lt;/sup&gt;X&lt;sup&gt;−&lt;/sup&gt;</td>
<td>3D cubic Pm&lt;sub&gt;3n&lt;/sub&gt;</td>
<td>1.5–3.0</td>
<td>[27, 28]</td>
</tr>
<tr>
<td>SBA-3</td>
<td>C&lt;sub&gt;n&lt;/sub&gt;(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;N&lt;sup&gt;+&lt;/sup&gt; Br&lt;sup&gt;−&lt;/sup&gt; or Cl&lt;sup&gt;−&lt;/sup&gt;</td>
<td>S&lt;sup&gt;+&lt;/sup&gt;X&lt;sup&gt;−&lt;/sup&gt;</td>
<td>2D hexagonal p&lt;sub&gt;6mm&lt;/sub&gt;</td>
<td>1.5–3.5</td>
<td>[33, 52]</td>
</tr>
<tr>
<td>SBA-12</td>
<td>Brij 76 (C&lt;sub&gt;18&lt;/sub&gt;EO&lt;sub&gt;10&lt;/sub&gt;)</td>
<td>(S&lt;sup&gt;6&lt;/sup&gt;H&lt;sup&gt;+&lt;/sup&gt;)(X&lt;sup&gt;−&lt;/sup&gt;I&lt;sup&gt;−&lt;/sup&gt;)</td>
<td>3D hexagonal (intergrowth)</td>
<td>3.0–5.0</td>
<td>[53, 61]</td>
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<tr>
<td>SBA-15</td>
<td>P123 (EO&lt;sub&gt;20&lt;/sub&gt;PO&lt;sub&gt;70&lt;/sub&gt;EO&lt;sub&gt;20&lt;/sub&gt;)</td>
<td>(N&lt;sup&gt;0&lt;/sup&gt;H&lt;sup&gt;+&lt;/sup&gt;)(X&lt;sup&gt;−&lt;/sup&gt;I&lt;sup&gt;−&lt;/sup&gt;)</td>
<td>2D hexagonal p&lt;sub&gt;6mm&lt;/sub&gt;</td>
<td>4.0–15.0</td>
<td>[20, 37, 61]</td>
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<tr>
<td>SBA-16</td>
<td>F127 (EO&lt;sub&gt;106&lt;/sub&gt;PO&lt;sub&gt;70&lt;/sub&gt;EO&lt;sub&gt;106&lt;/sub&gt;)</td>
<td>(N&lt;sup&gt;0&lt;/sup&gt;H&lt;sup&gt;+&lt;/sup&gt;)(X&lt;sup&gt;−&lt;/sup&gt;I&lt;sup&gt;−&lt;/sup&gt;)</td>
<td>3D cage-like cubic I&lt;sub&gt;m&lt;/sub&gt;3&lt;sub&gt;m&lt;/sub&gt;</td>
<td>4.7–12.0</td>
<td>[35, 54, 61]</td>
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<tr>
<td>KIT-6</td>
<td>F127 + P123</td>
<td>(N&lt;sup&gt;0&lt;/sup&gt;H&lt;sup&gt;+&lt;/sup&gt;)(X&lt;sup&gt;−&lt;/sup&gt;I&lt;sup&gt;−&lt;/sup&gt;)</td>
<td>3D cubic La&lt;sub&gt;3d&lt;/sub&gt;</td>
<td>4.0–12.0</td>
<td>[22, 55]</td>
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<td>FDU-1</td>
<td>B50-6600 (EO&lt;sub&gt;39&lt;/sub&gt;BO&lt;sub&gt;47&lt;/sub&gt;EO&lt;sub&gt;39&lt;/sub&gt;)</td>
<td>(N&lt;sup&gt;0&lt;/sup&gt;H&lt;sup&gt;+&lt;/sup&gt;)(X&lt;sup&gt;−&lt;/sup&gt;I&lt;sup&gt;−&lt;/sup&gt;)</td>
<td>3D cage-like cubic Fm&lt;sub&gt;3&lt;/sub&gt;m</td>
<td>8.0–14.0</td>
<td>[21, 56]</td>
</tr>
<tr>
<td>FDU-12 or KIT-5</td>
<td>F127</td>
<td>(N&lt;sup&gt;0&lt;/sup&gt;H&lt;sup&gt;+&lt;/sup&gt;)(X&lt;sup&gt;−&lt;/sup&gt;I&lt;sup&gt;−&lt;/sup&gt;)</td>
<td>3D cage-like cubic Fm&lt;sub&gt;3&lt;/sub&gt;m</td>
<td>6.0–12.5</td>
<td>[57, 58]</td>
</tr>
<tr>
<td>MSU-H</td>
<td>P123</td>
<td>N&lt;sup&gt;0&lt;/sup&gt;I&lt;sup&gt;0&lt;/sup&gt;</td>
<td>2D hexagonal p&lt;sub&gt;6mm&lt;/sub&gt;</td>
<td>7.5–12.0</td>
<td>[59, 60]</td>
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TMB = trimethylbenzene
Triblock copolymer-templated large pore silica

**SBA-15 (Santa Barbara Acid No. 15).** A breakthrough in the preparation of ordered mesoporous silica was made by Zhao and Stucky in 1998 [20, 61], who used poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymers for the synthesis of the large pore SBA-15 material. The synthesis is simple and based on the use of organic silica sources, such as TEOS or tetramethoxysilane (TMOS), in combination with diluted acidic aqueous solution of a Pluronic-type triblock copolymer (2–7 wt% in water), such as P123 (EO_{20}–PO_{70}–EO_{20}). As discussed above, the hybrid interface formation is here suggested to follow a (N^+H+) (X^-I^+) model, since the block copolymer could be positively charged under the reaction conditions.

Evidently, the use of triblock copolymers expands the accessible range of mesopore sizes. Mesoporous silicas obtained with such copolymers usually exhibit uniform large pores with diameters well above 5 nm and quite thick walls, the latter providing high thermal stability and improved hydrothermal stability compared to OMS synthesized with ionic surfactants, e.g., M41S materials [62]. To compare, MCM-41 materials usually showed a wall thickness of about 1 nm. SBA-15 silica can be synthesized with pore sizes ranging between 5 nm and 12 nm and thick walls (3.0–6.5 nm in width), depending on the reagent ratios, pH, and aging temperature (Figs. 4.4(a), (c); [38]). This material exhibits a large surface area of around 800–1000 m^2^ g^-1 and pore volume up to 1.5 cm^3^ g^-1. A TEM image showing the hexagonal structure of SBA-15 is presented in Fig. 4.4(a).

SBA-15 silica is of growing interest for a wide range of applications (e.g., sorbent, support for catalysts and biomolecules, nanoreactor, solid template, etc.). At first, SBA-15 was thought to be a large pore equivalent of MCM-41, which has unconnected mesoporous cylindrical channels. However, studies showed that the pore size distribution of SBA-15 is rather bimodal, whereby the larger, hexagonally ordered structural mesopores are connected by smaller pores (micropores or small mesopores) located inside the silica walls [37, 63–66]. These pores are not ordered and most probably originate from the penetration of the PEO blocks of the copolymer inside the silica framework. Owing to the interaction of the hydrophilic chains of the P123 copolymer with the polymerizing silica species during the mesophase formation of SBA-15, some EO groups are occluded in the silica walls. After removal of P123, SBA-15 exhibits therefore a secondary pore system in its framework wall (i.e., intra-wall pores). These intra-wall pores are usually in the micropore-small mesopore (~ 2–3 nm) range, but the actual size and associated volume are highly dependent on the details of the synthesis (see below).

**SBA-16.** In the family of copolymer-templated materials, ordered mesoporous silicas consisting of interconnected large cage-like pores are also of significant interest. A silica mesophase related to SBA-15 is the material designated SBA-16 (cubic Im$ar{3}$m symmetry), which is synthesized in a similar way, but using a different nonionic triblock copolymer, e.g., Pluronic F127 (EO_{106}–PO_{70}–EO_{106}). This large pore silica consists of
spherical cavities of 6–11 nm in diameter organized in a body-centered cubic (bcc) array, and the cavities are 3D interconnected through mesoporous openings of 2–4 nm (Figs. 4.4(b), (d)) [54, 61, 67]. Pluronic F127 presents a high hydrophilic to hydrophobic volume ratio (high EO/PO ratio), which is favorable for the formation of highly curved globular micelles under aqueous conditions.

Fig. 4.4. (a) TEM image showing the 2D hexagonal arrangement of the mesopores in SBA-15. Reprinted with permission from [2]. (b) TEM image of cage-like SBA-16 silica aged at 100°C, viewed along the [111] direction. Reprinted with permission from [2]. (c) Nitrogen adsorption-desorption isotherm (−196°C) and corresponding NLDFT pore size distribution for SBA-15 (BET surface area: 875 m² g⁻¹; Total pore volume: 1.26 cm³ g⁻¹; NLDFT pore size: 8.5 nm). Reprinted with permission from [18]. (d) Nitrogen adsorption-desorption isotherms (−196°C) of SBA-16 samples aged at 100°C or 130°C, as indicated. Insert shows a scheme of the pore structure. Reprinted with permission from [54].
KIT-6 (Korea Institute of Technology №6). Another member of the family of triblock copolymer-based silica mesophases is the large pore equivalent of MCM-48 known as KIT-6. One of the easiest methods of generating this interesting mesophase was introduced in 2003 by Kleitz et al. [22, 55], who used a blend of Pluronic P123 and \(n\)-butanol for the structure-direction, along with a fine tuning of the acid concentration. This KIT-6 silica material exhibits a structure with cubic \(Ia\overline{3}d\) symmetry, and the pore network topology can be described as an interpenetrating bicontinuous network of highly interconnected channels (shown schematically in Fig. 4.5; [68]). The mesopore structure of KIT-6 is thus 3D interconnected and built of two continuous ordered channel systems separated by a silica wall which follows the infinite periodic minimal surface (IPMS) called the Gyroid surface (G) [22, 55, 69]. The porosity of KIT-6 is quite similar in nature to that of SBA-15, although subtle differences have been observed [70]. KIT-6 silica has high pore volume and large accessible pores tailored between 5 and 12 nm, with additional intra-wall pores as well [22, 51, 55, 69, 71]. Several other methods of producing a large pore cubic \(Ia\overline{3}d\) silica have been reported [72–74].

![Fig. 4.5. (a) Representative TEM of mesoporous KIT-6 silica. Shown is a view along the [111] direction. (b) Representation of the Gyroid G infinite periodic minimal surface, which is followed by the silica walls in KIT-6. Also shown is an alternative representation of the \(Ia\overline{3}d\) structure, as two interwoven networks of branched cylindrical channels. The G surface separates the two sub-frameworks of rod-like mesopores. Reprinted with permission from [70].](image)

**Some tools for tailoring structure and porosity**

A method of tuning the pore size of surfactant-directed inorganic materials is to simply change the length of the surfactant carbon chain. Usually, a linear relationship is observed between pore size and length of the carbon chain of a molecular template. With \(C_n\)TAB (\(n = 8–18\)), the pore size of the as-synthesized MCM-41 material increases by about 0.45 nm when increasing \(n\) by two carbon atoms. Kruk et al. [75, 76] also confirmed that the pore size of calcined MCM-41 and MCM-48 materials increases almost linearly using \(C_n\)TAB surfactants with chain lengths of 8 to 16 carbons. However, this simple strategy is applicable only as long as the surfactant is soluble and
leads to the formation of a mesophase. It seems that the shortest chain surfactant from which a mesophase could be created is with \( n = 8 \). On the other hand, long-chain surfactants (\( n > 20 \)) are not easily available and are practically insoluble in water, and the mesophases obtained are sometimes rather poorly ordered \([12, 13, 77]\). Similarly, changes in molecular geometry and chain length of nonionic block copolymers permit fine tuning of the pore size of large pore mesoporous silica. There, the adjustment of pore size can be continuously performed by varying the concentration of SDA and changing the composition of the copolymer or the block size \([61, 78, 79]\). Indeed, the ratio of hydrophilic to hydrophobic blocks (EO/PO) in the block-copolymer can be decisive for the nature of the mesostructure. In general, lowering this ratio results in the formation of lamellar mesostructures, while higher ratios favor the packing of spherical micelles into cubic mesophases \([79]\). For instance, triblock copolymers possessing long hydrophilic chains (i.e., high EO/PO ratio), such as F127, lead to materials with highly curved cage-like pores (e.g., SBA-16, KIT-5; \([58]\)). In these cases, simultaneous tailoring of the cage dimensions and pore openings of these cage-like silicas is also feasible by using copolymer blends (P123 mixed with F127), both under control of synthesis temperature and time \([35]\). The EO/PO ratio of the copolymer has a marked influence on pore size and wall thickness of the resulting materials. Alfredsson et al. investigated the influence of the variation in blockcopolymer composition in the synthesis of SBA-15 \([79, 80]\). Their results established that, for synthesis conditions where a hexagonal mesostructure is obtained, an increase in PO chain length resulted in larger pores. On the contrary, an increase in EO chain length led to thicker walls.

Another convenient way to tailor the pore size of an OMS is to vary the temperature and duration of the HT. Applying aging treatments at different temperatures and for prolonged periods (from 24 hours up to several days) can efficiently modulate the nature of the mesophase. This type of treatment can either be performed directly in the mother liquid or at a different pH in fresh solutions (typically water or alcohol). For instance, MCM-41 silica could be restructured at elevated temperatures in its mother liquid, resulting in pore size expansion from 3.5 to 6 nm \([34, 81]\). Moreover, this approach usually results in a material with enhanced stability and higher structural quality owing to denser walls \([82]\). This improved stability could arise from increased condensation of the silanols within the silicate framework, i.e., better silica polymerization, leading to less silanol groups, thus less shrinkage occurring during calcination, and thicker walls. In the case of large pore OMS prepared with triblock copolymers, such as SBA-15 or KIT-6, both synthesis and aging temperature strongly influence the mesostructure formation of these OMS, and this by altering micelle hydrophobicity and silica condensation. The solution reactions leading to mesophase formation are usually performed within a range of 35°C to 45°C depending on the block copolymer. Increasing the synthesis temperature within this range and beyond renders the EO groups more hydrophobic, leading to micelles with larger hydrophobic core volume and smaller hydrophilic regions \([78]\). The temperature and duration of
the hydrothermal aging, which is then applied after this first synthesis step, are also critical. The aging temperature is usually between 40°C to 150°C (often 90–100°C). The mesopore size of SBA-15 is easily tailored from about 5 nm up to 12 nm simply by increasing the aging temperature from 60°C to 140°C. Also, substantially larger pore volumes are obtained and the nature of the intra-wall porosity is drastically modified, depending on the HT temperature applied (Fig. 4.6, [22, 55, 63, 66, 83–89]). It is proposed that SBA-15 prepared with aging between 35°C and 60°C exhibits micropores with no apparent connection between mesopores. In contrast, at 100°C, SBA-15 shows both the presence of micropores and larger connections between the ordered mesopores. At 130°C, the material shows no more micropores, but much larger pore interconnections are present [66]. Note that an aging of 12 hours to several days is normally required to produce silica materials with satisfying quality. Similar to SBA-15, the mesopore size of the cubic \( Ia\bar{3}d \) KIT-6 silica can be varied within a comparable range of diameters [22]. Also, the size of the spherical mesopores of cage-like materials (e.g., SBA-16, FDU-1, KIT-5) can be tailored by applying different aging temperatures and times. However, in this case, not only the main mesocage is enlarged, but the pore openings of the cages also become wider upon prolonged hydrothermal treatment.

Fine tuning of pore size and mesostructure can also be performed by adjusting the solution pH upon addition of given amounts of acid or base during synthesis. This is, for example, well-established for MCM-41 and MCM-48 syntheses [90, 91]. It is usually explained by the strong influence that the solution pH has on the degree of condensation and polymerization of the inorganic oligomeric species, on the charge density of the polyelectrolyte inorganic species involved, and on the micellar organization. Indeed, as reported by Ryoo, adjusting the pH of the reaction mixture in situ during the synthesis of MCM-48 favors the formation of cubic mesophase [92]. Moreover, the materials (MCM-type) prepared with careful monitoring and adjustment of the pH often demonstrate a high degree of long-range order [91]. For block copolymer-templated syntheses, usually performed in acidic media, pH also has great importance. For SBA-15, it is the key parameter to control the overall kinetics of the synthesis. SBA-15 can be synthesized in various acid concentrations [38, 93, 94], however, some noticeable differences in the structural order, particle morphology, and porosity features of the resulting solids have been observed. Syntheses performed with acid concentration \( \geq 1.5 \text{ mol}\text{l}^{-1} \) led to very rapid precipitation [61]. Furthermore, high acid content may somewhat influence the micellar organization [95], although little effect on the micelle shape has been observed, before addition of TEOS, with [HCl] up to 2 moll\(^{-1}\) [93].

The addition of electrolyte salts, such as NaCl or KCl, obviously affects surfactant packing and the interactions between surfactant molecules and silica. The surface charge density of the surfactant micelles can be modified by adsorbed counter-ions. The surfactant molecules may then self-assemble into a mesophase with, for example, a lower surface charge density, and mesophase transitions could take place upon modification of the surface curvature. Usually, inorganic salts have a strong influence
The effects of hydrothermal aging temperature on the pore structure of SBA-15-type materials: (a) low temperature aging (35–60°C); main mesopores: 5–6 nm – wall thickness: 4 nm – micropore volume: $\sim 0.3 \text{ cm}^3\text{g}^{-1}$; (b) aging at 80–100°C; main mesopores: 7–9 nm – wall thickness: 3.2 nm – micropore volume $\sim 0.1 \text{ cm}^3\text{g}^{-1}$; (c) high temperature aging (> 120°C); main mesopores: $> 9$ nm – wall thickness: 2 nm – no micropores. Reprinted from [70].

on the values of CMC (critical micellar concentration) and CMT (critical micellar temperature) of the triblock copolymer micelles, which can both be decreased or increased upon salt addition. Salting-out electrolytes (lyotropic ions) such as KCl, NaCl or K$_2$SO$_4$, are not adsorbed in the copolymer micelles. These salts dehydrate the hydrophilic portion of the block copolymer, inducing a pronounced reduction in the preferential interfacial curvature of the micelles. On the other hand, salting-in electrolytes (hydrotropic ions) are adsorbed in the micelles and tend to inhibit their growth, which could thus increase the preferential interfacial curvature [73, 96]. The Zhao group was the first to use the salting-out effects caused by the addition of electrolytes to triblock copolymer solutions to produce various well-defined mesostructures [97]. It should be kept in mind, however, that not only the aggregation behavior of the copolymer micelles is affected by salt additions, but the presence of electrolytes will influence hydrolysis and condensation, and the kinetics of aggregation of the inorganic species.
Dissolving hydrophobic additives inside the core of the micelles is largely exploited to increase the pore size of mesoporous silicas. They can alter the interface energy of the system, ultimately leading to changes in numerous features, e.g., micelle shape and size, mesophase transition, enlargement of mesopores and/or variation in the morphology of the final products [23, 24]. Trimethylbenzene (TMB) has been one of the most widely used additives [33, 98], although aliphatic hydrocarbons such as hexane have been used as well [99]. For example, it was shown that the pore size of MCM-41 can be altered in a controlled manner between 2 nm and 10 nm by addition of TMB [13]. An almost linear relationship was found between TMB concentration and final pore size. Hydrocarbons or hydrophobic aromatics are regarded as swelling agents that are preferentially solubilized in the core of the micelles. In contrast, co-surfactant molecules, such as short-chain n-alcohols or n-amines, are accumulated in the palisade layer of the micellar aggregates and therefore induce more intricate effects, whereby both the mesophase behavior and the d-spacing of the mesoscopically ordered material can be affected [100]. The MCM-48 syntheses performed by Ryoo et al. [101] (addition of EtOH) and by Schumacher et al. [102] (addition of triethylamine) are good illustrations of the complex roles of these additives.

The use of TMB to swell the pores of the triblock copolymer-based OMS is also widespread. SBA-15 materials with pore sizes of 15–16 nm can be obtained with this additive. However, the quantity introduced has to be cautiously controlled for retention of the ordered mesoporous mesostructure [103–105]. The silica materials exhibiting pores reaching 30 nm which were obtained by addition of TMB to the synthesis mixture were in fact disordered foam-like structures [105]. Also, additives and HT modulation (time and temperature) can be synergistically combined to tailor porosity of SBA-15 [85]. TMB can also be used to control the phase transition in the triblock copolymer F127 system, leading to large pore OMS [106]. Similarly, for block copolymer-templated OMS synthesized in acidic media, the use of co-surfactant additives can lead to complex systems [107, 108]. The synthesis of KIT-6 silica is a perfect example. This material is uniquely obtained in very high phase purity by carefully controlling both the addition of a co-surfactant (n-butanol) and the acidity of the mother liquid ([HCl] < 0.8 M) [22]. In fact, in these syntheses using n-butanol, the adjustment of the HCl concentration to 0.3–0.7 M is a prerequisite for directing the formation of a given silica-based mesophase. In this way, it actually became possible to synthesize several large pore cubic silica mesophases (Ia̅3d, Im̃3m, and Fm̃3m) in a wide range of reagent compositions (see Fig. 4.7 for the diagram of product phases, as a function of reagent ratios; [109]).
Fig. 4.7. Diagrams of mesophase structures synthesized using blends of triblock copolymer and n-butanol. The diagrams are established according to XRD measurements. (a) Each sample is prepared with a molar ratio of 0.017 P123/x TEOS/y BuOH/1.83 HCl/195 H2O. Reprinted with permission from [22]. (b) Each sample is prepared with a molar ratio of 0.0035 F127/x TEOS/y BuOH/0.91 HCl/117 H2O. Reprinted with permission from [109].
4.3 Functionalization of ordered mesoporous silica

The available methods for the functionalization of ordered mesoporous materials are vast, and a considerable number of studies have been dedicated to potential applications of functionalized mesoporous materials, especially in heterogeneous catalysis. This section is not intended to be a comprehensive survey of the topic; instead it should only provide a brief overview of the various strategies which have been developed to modify mesoporous materials.

OMS are promising in many applications because of their unique porous properties. However, in order to be useful, they usually need to be functionalized. Depending on the requirements of the synthesis and/or the targeted application, various strategies to introduce useful functions to OMS can be considered. It is important to note that only the most common methods will be presented in this brief section. As illustrated in Fig. 4.8, there are two main strategies available to integrate (organic or inorganic) functionalities to OMS [41, 110].

- Post-synthetic modification, which is usually performed by grafting or impregnation/adsorption methods on porogen-free OMS. This approach allows functionalization of the pores and the external surface.
- Direct addition of the functionalities during the synthesis of OMS. This “one-pot” process is also described as co-condensation. In this method, both the silica walls and pores can be modified. A variation of this method consists of the sequential addition of organosilanes or metal-precursors at different synthetic stages. This approach may allow control of the spatial localization of the functionalities [111, 112].

Both methods have their own advantages and drawbacks [110, 111, 113]. Post-grafting functionalization relies on the reaction of organosilanes (e.g., amino-, thio-, phosphosilanes, etc.) with the free silanol groups of the pore surface. Indeed, even after calcination at 550°C, the pristine OMS is not fully condensed and some silanols are still available for grafting even if their density is quite low (1–2 SiOH nm⁻²; [24]). Post-grafting is usually performed by treating the OMS powder in organic solutions of the organosilane under reflux for a prolonged period. This method has several advantages: ease of implementation, it does not alter the mesostructure, and it also offers a great versatility in the choice of introduced groups. However, in some cases, a preferential reaction of organosilanes at the pore entrance can be observed, leading to an inhomogeneous distribution of functionalities. If very large molecules are grafted, some pore blocking may occur [110].

In contrast, ordered mesoporous organosilicas can be obtained by co-condensation of tetraalkoxysilanes (TEOS or TMOS) and terminal trialkoxyorganosilanes of the type (R'O)₃Si-R (where R' is either methyl or ethyl, and R is a non-hydrolyzable organic group). Here, the functional groups are most often placed dangling on the surface, but also partly inside the framework walls [114–117]. In fact, the organoalkoxysilane plays...
two roles, since it acts as a building block in the inorganic structure, co-condensing with the tetraalkoxysilane precursor, and it supplies organic functionality. A wide variety of functional groups can be incorporated using this method (e.g., vinyl, phenyl, aminopropyl, imidazole, cyanopropyl, mercaptopropyl, etc.). The mercaptopropyl groups are especially interesting since these groups can subsequently be oxidized with nitric acid and/or H$_2$O$_2$ to yield sulfonic acid groups [118]. However, the choice of a suitable organosilane precursor is usually limited by the conditions of synthesis, and the template removal must be performed by solvent extraction or careful acid treatment.

The impregnation/adsorption pathway is also an important post-synthesis method for modifying OMS with organics or inorganic species. This technique is based on the capillary introduction of a volatile solvent containing the precursors or molecules of interest inside the mesopores of the solid. After evaporation of the solvent, the functional group is then chemically linked (grafted) to the OMS by a subsequent thermal treatment. Different techniques can be used [111, 119], but the incipient wetness, which employs a minimal amount of solvent at the limit of the powder wetness, has been shown to be very effective [120]. As a nice example, Choi et al. have successfully applied this technique to confine polymerization of vinyl monomers (e.g., styrene, acrylates) selectively on the mesopore surface of SBA-15 silica [121]. The incipient wetness
is a very versatile tool which usually leads to a rather homogeneous distribution of functional species inside the pore network of the OMS [120, 122].

### 4.4 Morphology control

Morphology control is indispensable in many of the advanced applications envisioned for functional mesoporous materials [123]. Perm-selective membranes, microspheres or monoliths are important for sorption, separation and chromatography purposes. Porous thin films or fibrous structures are relevant for electronics, optics, low $k$-dielectrics, and sensing applications. Colloidal particles or nano-spheres are preferred for biomedical systems to be used in drug delivery or magnetic resonance imaging (MRI) with contrast agents. The first ordered mesoporous materials which were synthesized were typically finely divided powders consisting of small particles (< 10 μm) with no well-defined morphology. Since then, a wide variety of shapes, including thin films, (nano)spheres, fibers, tubes, macroporous-mesoporous monoliths, and many other complex morphologies have been described for ordered mesoporous materials (Fig. 4.9; [124–135]). Mesoporous solids with controlled macroscale morphology can either be designed by processing conditions such as dip-coating, spin-coating or emulsion templating, or alternatively, formed spontaneously through self-organization processes which are mostly based on kinetic regimes. Due to the amorphous nature of the silica walls, simultaneous modulation of both the mesoscale (hybrid mesophase) and macroscale (particle size and shape) is possible during synthesis. However, it has to be kept in mind that formation of the mesophase and growth of the morphology influence one another and cannot be seen as separate aspects [23]. With the ongoing emergence of complex nanostructures, controlling both mesopore structures and morphologies of MSNs at the nanoscale is not straightforward and requires a thorough understanding of the chemistry involved [136].

Mesoporous particles with spherical morphology are easily synthesized under alkaline aqueous conditions. For instance, Huo and Schüth [137] reported in 1997 the preparation of hard transparent spheres from an emulsion at room temperature. Ingeniously, Grün and Unger modified the Stöber synthesis of monodisperse spheres performed in the presence of ethanol and ammonium hydroxide [138] and could successfully prepare almost monodispersed mesoporous MCM-41 and MCM-48 spheres [102]. Also, pseudomorphic transformation of commercially available pre-shaped spherical silica particles (5 to 800 μm) can also be used to produce ordered mesoporous MCM-41 and MCM-48-like particles with a spherical morphology. In this latter method, amorphous silica is progressively and locally dissolved under mild alkaline conditions and re-precipitated at the same rate in the presence of the surfactant, without modifying the global spherical morphology [139, 140]. Finally, the synthesis of hollow particles is achievable, for example, by spray-drying techniques, based on very rapid solvent evaporation and retention of the pre-formed shapes [141].
Among these, morphologies, spheres, and especially nanospheres, are most interesting for the biomedical world because these objects may interact well with cells and do not exhibit sharp edges or preferential faces [142]. Most of the current mesoporous spherical particle syntheses are actually derived from the seminal work of Grün, which described the synthesis of colloidal spheres of MCM-41 and MCM-48 [102, 143]. In 2001, Cai et al. [144] and Mann et al. [145] both reported the first successful syntheses of individualized MCM-41 nanoparticles. However, the term Mesoporous Silica Nanoparticles (MSNs) was popularized in 2003 by Victor Lin, who published the first facile preparation of functionalized MCM-41 nanoparticles for drug delivery applications [146]. This synthesis provided homogeneous spherical particles with a diameter ≤ 200 nm and good porosity features, making them excellent candidates for cellular applications. Following this breakthrough, many efforts were devoted to developing MSNs with controllable particle and pore sizes [136]. In particular, in 2008, Kim et al. reported the first synthesis of MCM-48 nanospheres with high pore ordering and highly uniform particle size (Fig. 4.10(c); [147]). By using a modified version of the Stöber synthesis, and Pluronic F127 as a “particle-designer” agent in alkaline media again, they successfully formed monodisperse MSNs with controllable sizes within the range of 70–500 nm [148].

However, the main drawback of the most common MSN protocols remains the relatively small pore sizes of the synthesized particles. Indeed, because almost all
syntheses are performed with CTAB-like molecules as SDAs, a maximum pore size of 4–4.5 nm is achieved. Swelling agents can be used to reach larger pores, but as for the classical OMS, they lead to a decrease or a loss in mesostructure ordering [149]. However, this latter aspect is not necessarily of critical importance for most biomedical applications. Triblock copolymers may also be suggested as SDAs to produce particles with larger pore size, while keeping mesoscopic ordering. Unfortunately, obtaining MSNs in acidic medium is more difficult than in alkaline medium (more complex interactions occurring during synthesis, and difficulties associated with kinetic control). In this area, He et al. [150] and Kim et al. [151] recently proposed two different pathways leading to pellet-shaped SBA-15 silica (large pores) of 300–600 nm (see Fig. 4.10). Both methods are based on restricting the growth of the SBA-15 particles. The first group used Zr$^{IV}$ multivalent metal ions to “cut” the micellar aggregates \textit{in situ}, whereas the latter employed Pluronic P104 as SDA, and specific synthesis conditions to favor initial nucleation and growth of primary particles while limiting further aggregation [152]. Alternatively, by mixing fluorocarbon-surfactant (e.g., FC-4) with the classical Pluronics, Han et al. successfully synthesized a new family of large pore MSNs which were called IBN [153]. These new materials could have great potential for biomedical applications as they exhibit spheroidal shapes with required particle dimensions (Fig. 4.10(c)) and fairly large pores (> 8 nm; [154, 155]).

![Fig. 4.10](image.jpg)

\textbf{Fig. 4.10.} TEM images of large pore ordered MSNs: (a) SBA-15 pellets obtained using the protocol described by He et al. [150], (b) Kim et al. [151] (images: R. Guillet-Nicolas, F. Kleitz, U Laval), and (c) IBN-like material obtained by Hartono et al. Reprinted with permission from [155].

\subsection*{4.5 Selected applications of functionalized ordered mesoporous silica}

Applications of mesoporous materials have been considered in many areas, including catalysis, optoelectronics, sensors, sorption, biomedical materials, environmental remediation, green chemistry, and most recently, energy storage and conversion [5, 156–159]. In this chapter, emphasis is placed on recent developments in the area of sorbents and materials for chromatographic extraction, as well as new innovative drug delivery systems.
4.5.1 Functionalized MSNs as controlled drug delivery platforms

Targeted drug delivery is one of the greatest challenges in modern medicine. To address the limitations of conventional drug delivery systems, mesoporous silica nanoparticles (MSNs) are considered robust inorganic alternatives to polymeric nanoparticles, owing to their high porosity, biocompatibility, and ease of modification. MSNs have thus captivated a lot of interest worldwide and have emerged as promising carrier materials for controlled and vectorized delivery of drugs [160–175]. Their stable mesoporous structure and well-defined surface properties make mesoporous silicas good matrices to host a wide variety of drugs and biologically active species for local and controlled drug delivery applications [149, 176–179]. Another attractive advantage is that amorphous silica is fairly degradable in aqueous solution, and thus problems related to the removal of the material after use can be avoided. Moreover, there are large numbers of silanol groups covering the mesoporous silica walls which are susceptible of undergoing chemical or biochemical functionalization, which is one of the key aspects for the prospect of biological applications of these materials.

An ideal drug delivery system should enable efficient healing at the lowest drug concentration and dosage frequency, while being both patient-friendly and safe. Owing to their outstanding features, which allow both the loading of various drugs or bioactive species and the adequate functionalization needed for in vitro and in vivo purposes, stimuli-responsive MSNs can be seen as truly promising carriers for delivering precise doses of drugs to targeted sites. Moreover, by combining diagnosis and therapeutic tools, theranostic MSN-based platforms may be designed [164, 166].

The concept of controlled drug delivery comprises 4 major steps:

1. The fabrication of a biocompatible device that will efficiently encapsulate high loading of the desired drug(s).
2. No premature release prior to reaching the target location is needed in order to protect the healthy organs and/or cells, i.e., avoidance of side effects due to non-specific interactions, and prevent the decomposition/denaturing of the drugs.
3. Efficient and sustained release of the drug at the targeted location.
4. Easy clearance of the biocompatible and/or biodegradable carrier by natural pathways.

Such a strategy is expected to enhance the drug efficiency while minimizing the required quantities owing to enhanced bioavailability at the key location [180–182]. Nevertheless, the key challenge still remains to simultaneously achieve precise targeting and proper colloidal stability, especially in real physiological media [122, 183]. To achieve these goals, several controlled drug delivery systems (CDDS) have been proposed based on various external or internal stimuli, e.g., temperature, time, chemical reactions, enzymes or pH, to name a few [184–189].

With MSNs, the sequestration of the drug inside the porous network is usually realized through the functionalization of the inner and/or outer pore surface with var-
Various barriers acting as “gates”, such as proteins, polymers, macrocycles, or even nanoparticles. These “gatekeepers” respond to a specific chemical or environmental stimulus which will induce their (reversible) removal upon exposure, hence triggering the drug release. Barriers are of prime importance as immediate drug release is commonly observed after administration in sink conditions, when drugs are simply adsorbed into non-modified MSNs [177, 190]. However, the release behavior of pristine MSNs should be considered with great care as it is also dependent on the conditions chosen to simulate the different body fluids [191]. The main MSN-CDDS are summarized in Table 4.2. Among these, the systems based on drug release triggered by pH variations have been widely investigated. Indeed, since the pH variations within the body and/or cells are well-known, they can be advantageously used for target drug delivery. For example, the pH difference between normal and cancer cells may be used for the specific targeting of tumor cells using MSNs [192].

Because of the extreme importance of cancer therapy, most of the research involving MSNs has so far been dedicated to the release of compounds in an acidic environment, i.e., cancer cells where pH is mildly acidic [166, 182, 189]. However, MSN-CDDS could also be synthesized for drug delivery applications where release is triggered at neutral or physiological pH. This feature is, for instance, of high interest for oral delivery applications because the pH in the human gastrointestinal tract naturally varies, i.e., the stomach is highly acidic (pH = 1.2) compared to the small intestine (pH = 6.5–7.0) and colon (pH = 7.0–8.0), making a neutral pH-triggered approach a smart strategy for oral delivery of drugs into the intestine. This is highly desirable as it improves patient compliance and convenience [193, 194].

In 2007, Kawi reported a simple and fast method for encapsulating protein-loaded \( \text{NH}_2-\text{SBA-15} \) with polyacetic acid, creating a smart pH-responsive protein delivery system for the first time [195]. This material exhibited almost no premature release in pH = 1.2 (less than 2%) during the first five hours, being compatible with the United States Pharmacopeia and the National Formulary (USP–NF) guidelines for gastro-resistant compounds, i.e., less than 10% drug release after 2 hours in gastric conditions [196]. However, in this example, protein release at pH = 7.4 was only 40% after 35 hours, limiting somewhat the efficiency of this system. This low release in physiological conditions was linked to the poor colloidal and chemical stability of the materials. Another method of generating pH-responsive MSN-CDDS is to incorporate positive charges into the mesopore channels of MSNs by means of trimethylammonium (TA) groups [197]. These groups allow efficient adsorption of anionic molecules and minimize their release under acidic pH owing to unfavorable electrostatic interactions. At neutral pH the strong electrostatic repulsions then trigger a sustained release of the loaded drug. This original system showed excellent drug sequestration ability in an acidic environment and appreciable drug release in physiological media. However, if such materials are not coated or properly encapsulated, the drug loaded inside the pores might be denatured by the acidity of the stomach environment, ultimately altering the bioactivity of the molecule once released in the intestine.
Some controlled drug delivery systems (CDDS) using MSNs, reported in the literature. Adapted with permission from [172].

<table>
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<th>Class</th>
<th>Examples</th>
<th>Schematic structure</th>
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<td><strong>Structure I</strong></td>
<td><strong>Nanoparticles</strong></td>
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<td>Au Nps</td>
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<td>ZnO Nps</td>
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<td><strong>Structure II</strong></td>
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<td>Cyclodextrin (CD)</td>
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<td>Dibenzo-24-crown-8 (DB24C8)</td>
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<tr>
<td><strong>Structure III</strong></td>
<td><strong>Linear molecules</strong></td>
<td><strong>Linear molecules</strong></td>
</tr>
<tr>
<td>3</td>
<td>Linear polyamine derivative</td>
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<tr>
<td></td>
<td>Saccharide derivative</td>
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<tr>
<td></td>
<td>Linear polymer</td>
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<td></td>
<td>Peptide sequence</td>
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<tr>
<td><strong>Structure IV</strong></td>
<td><strong>Multilayer shell coating</strong></td>
<td><strong>Mesoporous silica</strong></td>
</tr>
<tr>
<td>4</td>
<td>Polymer layers</td>
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<tr>
<td></td>
<td>Biomolecules</td>
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<tr>
<td></td>
<td>Polyelectrolyte multilayers</td>
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<tr>
<td><strong>Structure V</strong></td>
<td><strong>Pore modification</strong></td>
<td><strong>Functional molecule</strong></td>
</tr>
<tr>
<td>5</td>
<td>Functional molecule</td>
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<td></td>
<td>Polymer</td>
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<td>Azobenzene derivatives impeller</td>
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Furthermore, this approach can only be used with anionic compounds. In 2011, the Cheng group [198] improved this system by introducing a hydrazone bond to synthesize MSN–hydrazone–TA materials. The TA groups can further be eliminated through the progressive hydrolysis of hydrazone bonds in gastric pH conditions, leading to a rapid and complete release of the drug only once the intestine has been reached. This time-dependent and pH-sensitive MSN-CDDS was shown to enable accurate delivery of therapeutic drugs to the targeted tissue (colon), while limiting premature release during gastric emptying. Here, high biocompatibility was found and no cytotoxicity, even at a high nanoparticle concentration, i.e., 500 μg ml$^{-1}$. In another example, Sun et al. [199] also developed a pH-responsive oral delivery system, this time by exploiting coordination between an anti-tumor-active poly-oxo-metalate and amino-functionalized MCM-41 mesoporous silica nanosphere. Their results indicate zero premature release in stomach and small intestine conditions, whereas release was observed in colon conditions due to the pH increase. In this system, the gating effect is believed to be based on the rupture of the coordinate bond between the metal...
centers and the amino groups in mildly basic conditions. Importantly, no cytotoxicity was observed with healthy human amniotic cells. Unfortunately, the polyoxometalate clusters only showed modest inhibition when tested on human malignant tumor cell lines derived from different tissues.

From the perspective of delivery of active compounds through the gastrointestinal tract, the use of nanocapsules or coatings would be highly beneficial to completely isolate and protect the active compound from the acidity of the stomach. As such, one could argue that focus should be placed on the development of simple, efficient, biocompatible and/or biodegradable materials. Furthermore, in vivo colloidal and chemical stability of functionalized MSNs is a critical aspect of this technology. In this case, addressing the issue of premature release of bioactive compounds loaded in the nanocarriers is extremely critical, especially with costly drugs. In most reported cases, the drug is just physically adsorbed into the pores, which may cause undesired leaching of the cargo before it reaches the target site making these systems less effective in therapeutic targeting. In this context, Kleitz and Qiao described a new system in which an azo prodrug is covalently bound to MSNs and the drug is released via reduction of the azo bond by the enzyme azoreductase, which is present in the microflora of the colon. Hence, enzyme-responsive MSNs have been designed for a site-specific delivery to the colon, which is achieved by a combination of passive targeting via the nanoparticles and selectivity of the cargo itself towards the colonic azoreductase. In this system, sulfasalazine (SZ, a prodrug first-line therapy for inflammatory bowel disease (IBD)) was covalently attached to the mesopore surface of MCM-48 silica nanospheres acting as the enzyme-responsive carrier, and the molecule could then be reduced to 5-ASA and sulfapyridine by the azo-reductase bacteria inside a simulated colon medium (see Fig. 4.11). The chemical binding of the prodrug on the pore surface prevents premature release of the drug. Monodisperse MCM-48 nanospheres (∼ 150 nm) were chosen as an inorganic scaffold due to their proven superiority in adsorption and release, owing to their 3D continuous pore network and their very high surface area. This system responded very well to the enzyme and no release was observed before the particles were exposed to the simulated colon medium. The covalent attachment of SZ onto nanoparticles thus clearly ensures zero release in stomach (pH 1.2) or intestine (pH 7.4), and at the same time this system also has great potential for delivering therapeutics to the right locations i.e., inflamed tissues or cancer cells, therefore reducing side effects and improving bioavailability of the drugs. With this type of carrier, one could hope that high concentrations of drug-loaded nanoparticles will reach the inflamed tissues and cells, with high in vivo efficacy ensured by zero premature release.

Leading candidates for the next generation therapeutic carriers may also be pH-responsive systems. As discussed above, this approach has received a lot of attention for cancer treatment application, owing to the noticeable pH difference between normal and cancer cells [197, 200, 201]. Particularly interesting are strategies based on the use of proteins as stimuli-responsive gating systems [202, 203]. Among their advan-
Fig. 4.11. (a) Synthesis of the enzyme-responsive drug delivery system based on mesoporous silica nanoparticles with 3D pore structure. (b) Representation of the process of enzymatic release of 5-ASA and sulfapyridine from the nanoreactors in the presence of azoreductase bacteria. Reprinted with permission from [188].

Advantages, these materials are characterized by high biocompatibility and biodegradability, abundance of reactive groups which can be used for chemical modifications, i.e., grafting [204, 205]. Similarly, being able to enhance colloidal stability in the desired release media constitutes a major improvement, as it will lead to a more homogeneous and efficient delivery of the active compound to the target location.

In this area, our laboratory evaluated the potential of the nutraceutical MSN conjugates as a new pH-responsive oral drug delivery system showing low toxicity and sufficient colloidal stability (Fig. 4.12; [206]). In this work, nutraceutical-functionalized mesoporous silica particles have been developed for the protection and site-specific release of gastro-sensitive compounds via the oral route. This innovative approach makes use of the fully biocompatible and biodegradable nutraceutical β-lactoglobulin, which serves as a pH-responsive gating device. This nano-conjugation led to significantly enhanced colloidal stability (a prerequisite for most drug delivery or cell tracking applications), while the functionality of β-lactoglobulin was fully preserved, i.e., the gelation and gating effect was observed, and thus it could be used for protecting and/or delivering bioactive components (i.e., via pH-controlled delivery). Nutraceutical proteins, such as β-lactoglobulin (a member of the albumin family, present in cow’s milk) or soy protein isolates, clearly offer the advantages of low cost
and excellent biocompatibility. By using bio-conjugation chemistry smartly, it was possible to synthesize a pH-responsive system showing limited premature release in acidic media (mimicking stomach acidity). In contrast, when the particles where suspended in physiological intestine conditions (pH 7.4), sustained release was observed for 24 hours, together with enhanced colloidal stability over 48 hours. Moreover, the differences in drug release which were observed at pH = 5 could also make this system very attractive from the perspective of cancer therapeutics. In addition, since β-lactoglobulin is a major by-product of the dairy industry, its production is quite cost-effective compared to other complex and expensive systems. As such, this approach is hence also inscribed in a strategy of smart recycling of industrial waste.

**Fig. 4.12.** Schematic representation of the post grafting, bio-functionalization, and pH-responsive release of a drug/dye from β-lactoglobulin-modified-MSNs. Reprinted with permission from [206].

### 4.5.2 Functionalized mesoporous materials for extraction chromatography (EXC) applications

Historically, the first system for adsorption of heavy metal ions based on mesoporous silica supports was used for the trapping of mercury [207]. It was proven that silica materials containing thiols (or thiol derivatives) were particularly effective as sorbents for the capture of environmentally harmful Hg^{2+}. Soon after, several other silica materi-
als, modified mainly with amino- or phosphonate-groups, were applied for adsorbing metals, such as Cu$^{2+}$, Zn$^{2+}$, Ni$^{2+}$, or Fe$^{3+}$ [208, 209]. Later it was proposed that silica-based inorganic-organic hybrid sorbents could also be versatile for sequestration/extracting radionuclides [210, 211]. For instance, functionalized MCM-41 materials grafted with acetamide-phosphonate ligands have shown promising properties for Am$^{3+}$ and Pu$^{3+}$ decontamination from acidic aqueous solutions [212].

Evidently, the development of new sequestration materials for the nuclear industry is essential from a health and environmental protection point of view, as they not only provide an appropriate solution to nuclear wastes, but also enable their detection if coupled with the appropriate analytical methodologies. The incident in Fukushima Dai-Ichi, Japan, and the long-term consequences of this event are convincing reminders that sequestration/detection of long-lived radionuclides is critical. The expected consequences of radiological/nuclear events and their aftermath on agriculture, population, and the environment have led the scientific community to rethink its approach to monitoring methods based on radiochemical separation [213]. With this objective in mind, our laboratory described a simple and effective functionalization of large pore 3D cubic mesoporous KIT-6 silica to produce a new family of selective sorbents for radionuclides [214, 215]. Using a simple one-step post-grafting method, phosphonate groups were chemically anchored to the silica surface, providing a highly selective and durable functionalization for the extraction of actinides (see Fig. 4.13).

Extraction experiments performed with this material demonstrated extremely rapid kinetics (< 1 min) and high selectivity towards actinide extraction, especially uranium (VI). The unique spatial configuration of the 3D cubic mesoporous hybrid induced much higher selectivity and adsorption capacity than other sorbents, and the material is applicable over a range of conditions (pH = 4, room temperature) which are relevant for real environmental analysis. In addition to these unique extraction performances, synthesis of the mesoporous hybrid EXC chromatography materials is very simple and easily scalable, which represents a true alternative for the replacement of currently non-recyclable commercial EXC resins at an acceptable cost. The high extraction efficiency of the functionalized KIT-6 sorbent for U (VI) at relatively neutral pH could also lead to alternative analytical strategies for uranium wastewater management, and environmental and biological monitoring from the perspective of anthropogenic contamination. In addition, such materials are mandatory for all aspects of the nuclear fuel cycles, from mining (treatment of wastewater) to fuel reprocessing (separation of impurities).

Well-defined mesoporous materials can also provide opportunities in the highly valuable area of rare-earth elements [216–218]. Nowadays, the importance of rare-earth elements (REEs) in the global economy is booming as they are used in numerous advanced technologies more and more. High purity REEs are needed for the production of magnets, chemical sensors or lasers, computers, plasma screens, cell phones, cameras, and so forth; however, natural REE resources are either very limited or their
extraction/separation processes are not acceptable in terms of sustainable development [219, 220]. Therefore, it is certainly of value to develop efficient sorbents for the extraction and valorization of REEs, also from alternative sources, for instance, industrial and mining wastes. Commercially, extraction and purification of REEs is based on multiple liquid-liquid extraction (LLE) or chromatographic-based resin separations. However, these approaches are hampered by several issues. Because of the subtle dif-

\[ \text{Fig. 4.13.} \text{ (a) Schematic representation of the synthesis of the extracting agent-functionalized SBA-15-P/KIT-6-P materials. (b) Comparison of the extraction capacities of different phosphonate-functionalized materials and photograph of an SPE cartridge assembled with the KIT-6-based sorbent. Reprinted with permission from [215].} \]
ferences between the various REEs, extraction and purification of REEs is very time-consuming and involves multiple extraction/purification steps. In order to substantially improve this process and provide a greener alternative to LLE, novel functional nanoporous hybrid materials were proposed demonstrating enhanced selectivity towards heavier REEs in comparison to commercially available products. In this case, KIT-6 silica was modified with the diglycolylamide (DGA) ligand to generate an efficient sorbent for REEs extraction applications (Fig. 4.14; [221]). For this, the DGA ligand was chemically grafted to the silica surface, which enabled the resulting hybrid materials to be cycled and regenerated, a key feature in the development of sustainable and cost-effective resin-type materials minimizing waste production. The choice of KIT-6 silica was motivated here by the highly interconnected nature of the porous network of this material, which is expected to reduce the risk of pore blocking and to be beneficial for diffusion of liquids through the system, all being obvious advantages in chromatographic processes. Extraction of REEs was tested in a solid-liquid system, and distribution coefficients (named Kd) from batch extraction tests were obtained. Clearly, these new sorbents showed excellent stability upon recycling and demonstrated greater selectivity than commercially available DGA resins under the extraction conditions tested. Most importantly, some of the new sorbents exhibited a much higher affinity for the separation of heavier lanthanides (i.e., yttric earths), being most relevant for the electronics industry. These hybrid sorbents also showed specificity towards Eu and Gd and low competitive behavior with other non-lanthanide trivalent ions and actinides, which are problematic in the commercial extraction of REEs. The perspective for this new system will be to minimize the number of extraction steps used for the purification of REEs as far as possible. Functionalized nanoporous materials with a high surface area and high pore volume can offer high contact efficiency with solutions and high adsorption capacities while preserving adequate flow and transport properties if properly structured. Using such materials may indeed enable the substantial reduction of the number of steps needed for separation of these critical elements, and thus decrease both the required time and the waste production.

4.5.3 Mesoporous organic-inorganic hybrid membranes for water desalination

Nowadays, water scarcity, brought about by population growth and industrialization, is one of the major challenges facing society. Desalination of brackish or seawater is one of the most effectively implemented solutions. However, an alternative process to the conventional desalination technologies, e.g., distillation and reverse osmosis (RO), is the thermally-driven membrane distillation (MD; [222]). Typically, such a membrane maintains water at the pore entrance and allows water evaporation, leaving the non-volatile salts behind [205]. Membrane distillation has some benefits, although its industrial application remains low. This lack of commercial success is mostly the result of the dominance of reverse osmosis processes, mem-
brane flux decay, and the use of macroporous (0.2–0.7 mm), hydrophobic polymeric membranes [224, 225]. These hydrophobic polymeric membranes are often plagued by fouling and pore wetting issues, and thus the development of new membrane materials which will overcome these limitations is necessary. In this area, membranes based on nanoporous, inorganic-organic hybrid materials represent a potential alternative, with adequate chemical and thermal stability and appropriate pore structure [226, 227]. Within this context, the use of nanoporous organosilica thin-film membranes (∼20 cm² in size) with highly ordered pores (∼2 nm) has been suggested (Fig. 4.15; [228]). The mesoporous hybrid membranes were prepared by the dip-coating technique using 1,2-bis(triethoxysilyl)ethane, as a single bridged silicon source, in the presence of Pluronic F68 (E₀₈₀P₀₃₀E₀₈₀). After adequate drying, the films were then calcined in air at 300°C to preserve the organic groups in the framework walls.

These mesoporous films exhibit excellent desalination performance in the case of synthetic salt solutions with feed temperatures between 20 and 60°C (using a vacuum MD process). These membranes produced pure water across a large range of salt concentrations (10–150 g l⁻¹ NaCl) at average temperatures ≤ 60°C, without exhibiting the usual degradation. Furthermore, the results revealed excellent salt rejection (> 99.9%) and good water fluxes (up to 13 kg m⁻² h⁻¹ at 60°C). Here, it was hypothesized that the organic moieties placed within the siloxane framework conferred enough hydrophobicity to the pore walls to form a liquid/vapor interface at the pore entrance, whilst the small mesopore size was crucial in preventing pore wetting. This most recent development could indeed open up a potentially scalable process for fabricating high-performance membranes for efficient water desalination.

Fig. 4.14. On the left: high-resolution SEM image of the functional organic-inorganic hybrid KIT-6. On the right: diglycolylamide (DGA)-modification of the surface of KIT-6 silica to generate the mesoporous rare-earth element (REE) sorbents. Reprinted with permission from [221].
Fig. 4.15. (a) Schematic representation of the water desalination process by membrane distillation using a periodic mesoporous organosilica (the mesoporous structure of the hybrid membrane is shown by TEM). (b) Comparison of organosilica (OS) membrane (square symbols) and pure silica (PS) membrane (cross symbols) in 50 g l⁻¹ feed concentration run at 60°C. Filled symbols represent water fluxes and open symbols represent salt rejection. Reprinted with permission from [228].

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References

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