

This article was downloaded by:

On: 15 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Experimental Nanoscience

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t716100757>

Recent progress in the synthesis and selected applications of MCM-41: a short review

S. Bhattacharyya^a; G. Lelong^a; M. -L. Saboungi^a

^a CRMD-CNRS, 45071 Orléans Cedex 2, France

To cite this Article Bhattacharyya, S. , Lelong, G. and Saboungi, M. -L.(2006) 'Recent progress in the synthesis and selected applications of MCM-41: a short review', *Journal of Experimental Nanoscience*, 1: 3, 375 – 395

To link to this Article: DOI: 10.1080/17458080600812757

URL: <http://dx.doi.org/10.1080/17458080600812757>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Recent progress in the synthesis and selected applications of MCM-41: a short review

S. BHATTACHARYYA, G. LELONG and M.-L. SABOUNGI*

CRMD-CNRS, 1B rue de la Férollerie, 45071 Orléans Cedex 2, France

(Received November 2005; in final form January 2006)

Recent progress in the synthesis and applications of MCM-41 based mesoporous materials is reviewed. Since the independent discovery in the early 1990s by groups in the Japan and USA of the formation of mesostructured silica using surfactants as structure directing agents, a variety of alternative synthesis routes have been proposed. These include the use of ionic (both cationic and anionic) surfactants, neutral surfactants based on block and star diblock copolymers, non-surfactant organic compounds and the Stöber process for synthesizing silica spheres. The unique properties of MCM-41 based silica materials make them attractive candidates for applications in catalysis, production of novel materials by encapsulating metals, semiconductors and biofluids. Particular attention is given to the use of these composites in biotechnology including biosensors, biocatalysis and drug delivery.

1. Introduction

Over the last 15 years, there has been a dramatic increase in the synthesis of open-framework inorganic materials of well-defined geometry. The number of publications on the topic has increased by a factor 100 between 1993 and 2003. The development of such materials, e.g., silica and carbon, with precise and easily controlled pore shapes and sizes is of great importance in many areas of modern science and technology [1–4]. These materials have important applications in several fields such as heterogeneous catalysis, separation process, host–guest chemistry and very recently in bioadsorption and biocatalysis.

Several excellent reviews on advances achieved in microporous molecular sieves [5–9] and in the recently discovered macroporous solids [10–17] are available in the literature. However, a new area in periodic porous materials emerged stimulated by the discovery of ordered mesophases [18–21]. In this review, we will limit ourselves to the ordered mesoporous silica with a special attention to MCM-41 (Mobil Composition of Matter) based materials. We will adopt the IUPAC definition [22] of mesoporous materials as materials with pore diameters between 20 and 500 Å.

*Corresponding author. Email: mls@cnsr-orleans.fr

In the early 1990s, Kuroda's group in Japan developed new alkylammonium-clay intercalation complexes which have been subjected to hydrothermal treatment followed by calcination. The resulting material produced a highly ordered mesoporous powder with a honeycomb structure referred to as FSM 16 [19, 21]. In parallel, work was carried out at Mobil Oil Corporation on a series of new porous materials grouped under the name of the M41S family, with striking resemblances to the Japanese materials [18, 20]. The process was consequently patented in 1991 and 1992 [23–25]. Surprisingly, in a 1971 US patent, Chiola *et al.* [26] reported the synthesis of low-density silica based on the hydrolysis and condensation of a silica precursor in the presence of a cationic surfactant. The unique mesoporous properties of that silica went unrecognized until 1997 when Di Renzo *et al.* [27] reproduced the experiments described in the patent and showed that the resulting product presents all the characteristics and properties of the MCM-41. Nevertheless, the numerous Mobil discoveries and applications have given a remarkable stimulus to the field as witnessed by the development of new synthetic routes [28–31].

The M41S family has been classified into four main groups, as depicted in figure 1(a). The first one refers to disordered rods and the three others are well defined mesostructures: (i) MCM-41 with a hexagonal array of unidirectional and non-interconnecting pores; (ii) MCM-48 with a three-dimensional cubic pore structure; and (iii) MCM-50 with an unstable lamellar structure. One should not forget to mention the molecular organic octamer which is thermally unstable [32] (figure 1b). MCM-41 could be viewed as the ultimate model for mesoporous adsorbent material for investigating fundamental features of adsorption, such as the effects of pore size, hysteresis, etc., owing to its relatively uniform cylindrical/hexagonal pore channels.

Of the many reviews [1, 6, 16, 33–39] on mesoporous materials, only few are devoted to MCM-41 despite considerable progress achieved in the fabrication methods of MCM-41. It is therefore appropriate to revisit the synthesis of MCM-41 based

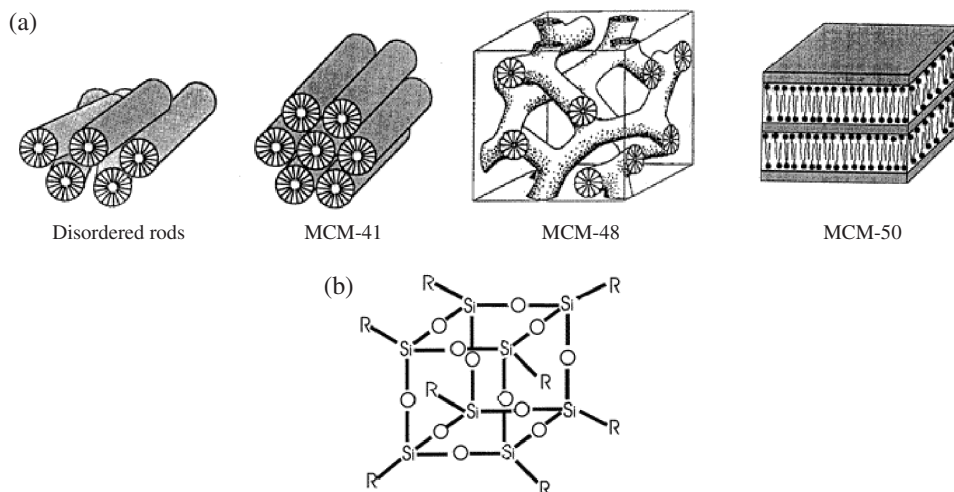


Figure 1a. (a) Four main phases formed from $C_{16}TMA/SiO_2/H_2O$. (b) Surfactant-silica composite unit formed from $C_{16}TMA/SiO_2/H_2O$ (reproduced from ref. [39] with the permission of the American Chemical Society).

materials, and highlight the novel applications especially in host–guest chemistry and bioadsorption.

2. Synthesis of MCM-41: toward a control of porosity and shape

2.1. Principles of synthesis

A typical synthesis of MCM-41 requires a minimum of four reagents: a solvent (water and/or ethanol), a silica precursor (tetraethyl orthosilicate (TEOS), tetramethyl orthosilicate (TMOS), tetrabutyl orthosilicate (TBOS)), an ionic (anionic or cationic) or non-charged surfactant and a catalyst. Depending on the protocol, the reaction could occur in an acidic or basic medium, with different silica/surfactant ratios. The mixture is stirred, aged at room temperature or around 100°C and placed in a static autoclave for several hours. The surfactant template is removed by calcination. Novel routes have been proposed based either on a non-surfactant templated method [40, 41] or on a polyelectrolyte/hexadecyltrimethylammonium bromide method [42].

An alternate route [43, 44] involves a microwave treatment of a precursor gel first heated by microwave radiation around 100–150°C followed by conventional heating. The advantages of the microwave-assisted preparation over the conventional hydrothermal method is the significant decrease in reaction time, and a more homogeneous heating which led to a better control of the texture and morphology. However, it has been superseded by faster methods which produce within a few hours the same if not better quality materials.

As mentioned above, templating could be achieved, either by using an ionic or neutral surfactant or without any surfactant. These three methods are described below.

2.1.1. Ionic surfactant templated method. The formation mechanism has been discussed in terms of a liquid-crystal templating (LCT) [37, 45, 46] where an organic species functions as a central structure, surrounded by inorganic oxides forming a framework. As illustrated in figure 2, long-chain surfactant molecules arrange themselves assisted by a micelle self-assembly to form liquid-crystalline phases. Silicate species deposit between surfactant ‘rods’ and then condense to form an inorganic network, with a hexagonal ordering dictated by the interaction between the

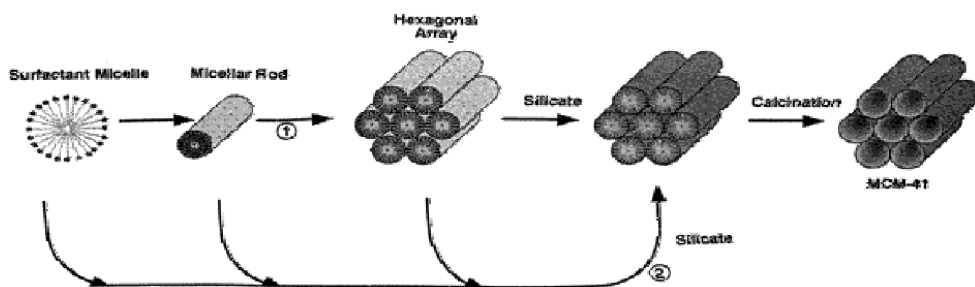


Figure 2. Possible mechanistic pathways for the formation of MCM-41: (1) liquid-crystal phase and (2) silicate-anion (reproduced from ref. [39] with the permission of the American Chemical Society).

surfactant and silicate species. After removal of the surfactant templates, a mesoporosity is obtained with pore size of 2–10 nm. In general, the overall LCT mechanism is governed by two factors: (i) the dynamics of surfactant molecules to form assemblies, micelles, and ultimately crystalline structure, functioning as template; and (ii) the ability of the inorganic oxide to undergo hydrolysis and polycondensation reactions leading to a network surrounding the organic template.

A wide variety of ionic surfactant molecules with different sizes, shapes, functionalities and charges has been shown to be able to effectively function as pore structure directing agents. These surfactant molecules can be classified based on their head group chemistry and charge as follows:

- *Cationic surfactants*: the hydrophilic group carries a positive charge, e.g., tetraalkylammonium salts $(C_nH_{2n+1})(CH_3)_3NX$, $n = 6, 8, 9, 10, 12, 14, 16, 18, 20, 22$; $X = OH, Cl, Br, HSO_4$; and $(C_nH_{2n+1})(C_2H_5)_3N$, $n = 12, 14, 16, 18$.
- *Anionic surfactants*: the hydrophilic group carries a negative charge, e.g., sulfates $(C_nH_{2n+1}OSO_3)$ with $n = 12, 14, 16, 18$, sulfonates $(C_{16}H_{33}SO_3H)$ and $(C_{12}H_{25}C_6H_4SO_3Na)$, and phosphates $(C_{12}H_{25}OPO_3H_2, C_{14}H_{29}OPO_3K)$.

2.1.2. Neutral surfactant templated method. The nature and relative amounts of various ingredients used for the synthesis of MCM-41 can vary greatly, thus offering a high degree of flexibility for the design of new materials. Zheng *et al.* [47, 48] produced a family of highly-ordered mesoporous silica (20–300 Å) using non-ionic alkyl poly(ethylene oxide) (PEO) oligomeric surfactants and poly-(alkylene oxide) block copolymers (PO) in acidic media. The PEO/PO ratio of the copolymers was used to control the nature of the silica mesophase: lowering this ratio promotes the formation of lamellar mesostructured silica, while increasing it favours cubic mesostructured silica. Cubic mesoporous structures could be generated when star diblock copolymers are used as structure-directing agents via a hydrogen-bonding (S^0H^+)(X^-I^+) pathway. Spherical hexagonal mesoporous silica (HMS) has been formed by the neutral assembly pathway in water–alcohol co-solvent systems, using dodecylamine and TEOS as starting materials [49]. Finally, an improvement was achieved in the ordering of silica templated from semi-fluorinated nonionic surfactants by introducing organic additives [50]. It is necessary to point out that in neutral surfactant templating systems where strong electrostatic interactions are absent, the LCT mechanism may not explain the mesophase formation. Instead, Tanev and Pinavaia [51, 52] proposed the neutral S^0I^0 templating route, in which the $Si(OC_2H_5)_{(4-x)}(OH)_x$ species, generated by the hydrolysis of the silica precursor, interact via hydrogen bonding with the head groups of the neutral surfactants (figure 3). These hydrogen bonds change the head-to-chain volume ratio and facilitate the assembly of rod-like micelles. As the reaction advances, further hydrolysis and condensation of the silica precursor take place, enhancing the formation of micelles which in turn create the framework walls.

2.1.3. Non-surfactant templated method. An alternative method based on a non-surfactant templated sol–gel route has been proposed [40, 41, 53–57]. Unlike the surfactant template pathway, the non-surfactant organic compounds, such as glucose, maltose, urea and dibenzoyltartaric acid, were used as templates or pore structure

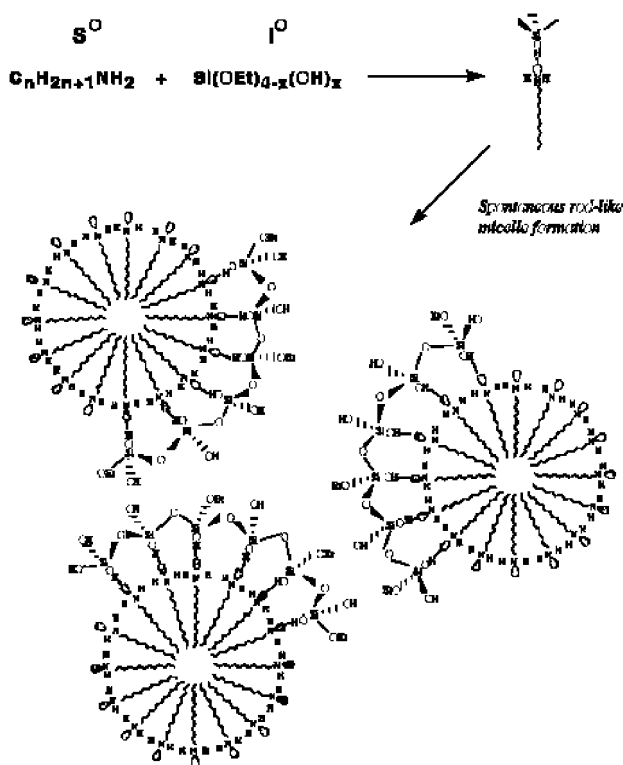


Figure 3. Schematic representation of the $S^\ominus I^\ominus$ templating mechanism (reproduced from ref. [52] with the permission of the American Chemical Society).

directing agents during a sol-gel process at room temperature. The template can be easily removed by solvent extraction. The resulting materials with a surface area of $\sim 1000\text{ m}^2\text{ g}^{-1}$ exhibit mesoporosity with pore diameter of $\sim 2\text{--}6\text{ nm}$, which is controllable by simply varying the non-surfactant content in the solution. While the pore structure is not highly ordered, it remains similar to that produced by neutral surfactant templated method. A framework filled with interconnected worm-like pores is observed. Initially, the non-surfactant template pathway involved the formation of silica mesophases under acidic conditions but subsequent efforts have shown that these structures could be obtained in basic or near neutral media.

It has been proposed that during the non-surfactant templated sol-gel process, non-surfactant aggregates and the aggregate assemblies may function as organic templates. At low template content, the formation of aggregates is inhibited due to the presence of large amount of silanols. With increased template content, aggregates start forming leading ultimately to a mesophase [57]. Nevertheless, the presence of a critical concentration above which the template molecules crystallize from the gel shows that the ability to control the pore diameter by varying the template content is limited. It remains that a systematic study of the synthesis mechanism is lacking.

2.2. Tailored synthesis

2.2.1. Nanospheres. Following the discovery of mesoporous materials, the synthesis of hierarchically ordered structures on different length scales such as beads of controlled sizes has generated a great deal of effort from both a fundamental and practical points of view. Controlling the internal pore structure is a challenge in the synthesis of mesoporous M41S based nanospheres [58–66].

Grün *et al.* [67] first demonstrated the suitability of adapting the Stöber synthesis [68] of silica spheres for the production of spherical MCM-41 particles under basic conditions. Freshly distilled TEOS is combined with a dilute surfactant solution and ammonia as catalyst in a rapid room temperature preparation. The resultant silica solids are calcined at 550°C in air to produce mesoporous solids that exhibit the characteristic low angle X-ray diffraction pattern associated with MCM-41, and the familiar reversible type IV nitrogen isotherm typical for these materials [69]. Scanning electron microscopy (SEM) reveals the spherical morphology of these solids. Since then, various assembly pathways have been used to produce mesoporous silica spheres [70–76] based on a procedure where TEOS is used as silica source, hexadecyltrimethylammonium bromide (C₁₆TMABr) as surfactant, alcohol as solvent and aqueous ammonia as catalyst. It is to be noted that spheres can also be obtained in acidic medium by substituting HCl to ammonia [77]. Although various morphologies have been achieved, the formation mechanism and the control of the morphologies of MCM-41 spheres are not well mastered yet. Different morphologies and textures can be obtained by varying the amount of surfactant and solvents. Huo *et al.* [78] produced marble like spheres of about 1 mm in diameter using TBOS based on emulsion biphasic chemistry which usually produces hollow mesoporous silica micro-spheres. Under basic conditions, TBOS undergoes hydrolysis to give butyl alcohol (BuOH), which is immiscible with water. The oil-in-water emulsion formed during the early reaction stage thus contains BuOH and partially hydrolysed TBOS as the oil phase. The quaternary ammonium surfactants play an important role for the stabilization of this emulsion. Hydrogen bonding between the BuOH and water molecules provides a diffusion pathway for the surfactant and water to penetrate the TBOS/BuOH oil droplets and promotes the hydrolysis of TBOS. The resulting silicate polymerizes under the influence of the structure directing surfactant, and transforms into solid spheres via a soft silicate gel. Very recently, the formation processes of spherical mesoporous silica were studied [79] in the case of a biphasic system containing an hydrophobic siloxane (TBOS) and an alkali solution with the presence of a surfactant. The water pools in the TBOS phase were shown to be connected to each other, and a regularly arranged nanostructure was formed by the self-assembly of surfactant. Thus, the nanostructure of spherical mesoporous silica was determined to be the reverse of MCM-41, in which continuous mesopores were developed.

The effect of alcohol on the morphology of the spheres was investigated [80–82]. Increasing the ethanol concentration in the TEOS-C₁₆TMABr-ammonia-water system at room temperature led to the formation of a succession of mesophases in the order MCM-41 (hexagonal phase), MCM-48 (cubic phase) and MCM-50 (lamellar phase). Such phase succession is the result of the co-surfactant behaviour of the ethanol. At lower alcohol concentration, SEM shows only undefined or barely spherical structures; when the alcohol concentration is further increased, it will mainly act

as a co-solvent producing spherical particles. It was suggested that increasing the alcohol amount changes the surfactant packing parameter, g [83, 84], given by:

$$g = \frac{V}{a_0 \cdot l}$$

where V is the total volume of the surfactant chain plus any co-solvent molecules between the chains, a_0 the effective headgroup area at the organic–inorganic interface, and l the surfactant chain length. The parameter g directs the phase configuration in the synthesis of mesoporous materials. Small values of g stabilize more curved surfaces such as MCM-41 ($1/3 < g < 1/2$), while larger values stabilize structures with less curvature such as MCM-48 ($1/2 < g < 2/3$). The proposed mechanism of pore formation is shown in figure 4. The MCM-48 crystal core exhibits a truncated octahedron shape, where each facet plays the role of a substrate for the growth of cylindrical pores in an epitaxial manner (figure 4a). The epitaxial pores are forced to adopt the pore packing of the MCM-48 crystal facet surface. The pores growing on the $\{111\}$ facets adopt a packing close to the hexagonal MCM-41, and those on the $\{001\}$ facets an intermediate packing between MCM-48 and MCM-41.

Another route should be mentioned, the synthesis of silica spheres with a spray-drying route. After Lu *et al.* [85] demonstrated the feasibility of this synthesis route, recent results on the preparation of high-quality mesoporous silica spheres by the

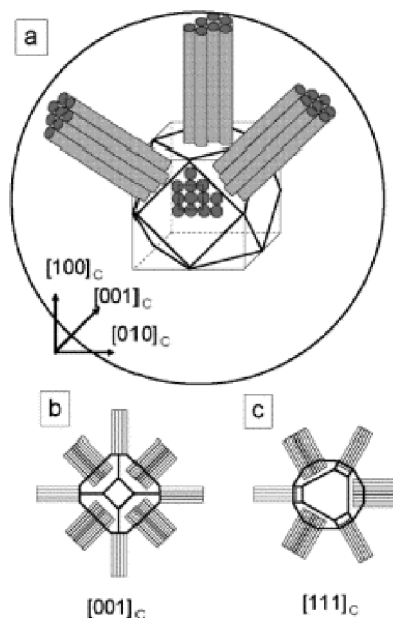


Figure 4. (a) Schematic representation of a spherical particle consisting of a nucleus of cubic MCM-48 and bundles of cylindrical pores grown epitaxially on the $\{111\}_c$ and $\{001\}_c$ facets. (b), (c) Two projections of the particle, viewed along $[001]_c$ and $[111]_c$, are also presented (reproduced from ref. [82] by permission from Elsevier).

Evaporation Induced Self Assembly (EISA) process [86, 87] have been reported [77, 88–90]. A sol, composed generally of a precursor of silica (TEOS), a cationic surfactant ($C_{16}TMABr$) and/or block copolymer (PEO-PPO-PEO), a solvent ($iPrOH$, Ethanol) and water in an acidic medium, is atomized inside a drying chamber at a constant inlet temperature. Parameters such as $C_{16}TMABr/Si$ molar ratio, pH, solvent quantity and drying temperature influence the texture and the morphology of the final product. Very recently, Alonso *et al.* [90] have proposed a scheme for the formation of spheres through spray-drying alcoholic sols. Using ^{29}Si and 1H solid state NMR experiments, the formation mechanism is first composed of a droplet fragmentation due to the fast solvent evaporation, followed by aggregation and self-assembly of the surfactant molecules with the oxo-oligomers. The resulting mesophase extends inside the particles and forms ordered textures.

2.2.2. Other structures: nanorods, thin films and monoliths. Alternatively to nanospheres, various morphologies and shapes have been achieved keeping intact all pore structure [70, 91]. We will limit our discussions to the mesoporous silica rods, thin films and monoliths.

Well-ordered mesoporous rods-like MCM-41 were generated in a water/ethanol basic medium in the presence of $C_{16}TMABr$ [92–94]. The temperature control and the alkalinity were shown to play a crucial role in the control of both morphology of the particles and the mesoporosity.

Ogawa *et al.* [95, 96] have reported a rapid spin-coating procedure for making transparent mesoporous films. Following these publications, a series of reports appeared on supported mesoporous thin films prepared on various substrates by liquid deposition techniques (e.g. dip-, spin-, or spray-coating) [87, 97–103]. Very recently, Grosso *et al.* [104] have provided an overall view of the mechanism of mesoporous silica film formation with the EISA process.

It is worthwhile adding that mesoporous monolithic silica have been produced recently [105–107]. The lack of external surfaces makes them ideal substrates for macromolecular separation. In the case of the remarkable work of El-Safty *et al.* [108], mesoporous and optically transparent silica monoliths have been produced using lyotropic and microemulsion liquid crystalline phases of P123 copolymer as a template.

3. Applications

Very little if any recent progress has been achieved in the area of catalysis and we will refer the readers to existing excellent reviews on the catalytic applications of MCM-41 based materials [109–135]. We summarize below some of the other important applications of MCM-41 based silica materials.

3.1. Nanomaterials

Quantum structures obtained via confinement allow to probe the relations between size and physical, magnetic and chemical properties [136, 137]. Among various preparation routes of nanostructured materials, the ‘host–guest’ synthetic method

provides satisfactory control of both the size and shape of the confined guest materials. The porosity of MCM-41 makes it an ideal candidate for the loading and encapsulation of metals, metal oxides and semiconductors as well as molecular liquids, e.g. water [136, 138–146]. We should also mention the fascinating materials formed by the encapsulation of graphite-type [139] or polyaniline [141, 144] wires in the hexagonal channels of MCM-41. Different pathways have been reported for synthesizing metallic particles within mesoporous silica: impregnation from solution followed by a reduction process (heat-treatment, irradiation, chemical reduction), supercritical fluid inclusion, gas phase deposition and chemical vapour deposition. Inclusion chemistry is by far the most used route and improvements have been made to increase the amount of loaded material via a functionalization of the mesopores [147]. The functionalization can be achieved by introducing positive charges in the intrachannel surface of the host silica for the accommodation of negatively charged metal complexes. Supported high density stable arrays of highly crystalline nanowires can be produced inside the mesoporous matrix. In the case of the noble metals (Au, Pt, Pd), bundles of nanowires were observed with a diameter ranging from 2.4 to 3 nm depending on the kind of MCM used [148]. Recently, Guo *et al.* [149] reported Pt nanorods, and nanonetworks in mesoporous silica MCM-48. One of the interesting results was the single-crystal-like platinum nanowire networks formed in one of the asymmetric bicontinuous channels of MCM-48. Adhyapak *et al.* [150] synthesized Ag nanowires by a controlled reduction of silver nitrate with sodium borohydrate within the channels of MCM-41. The presence of the surface plasmon absorption peak of silver, red-shifted compared with that of silver nanoparticles due to agglomeration of silver clusters, and room temperature photoluminescence spectra, exhibit interesting optical properties. In a different direction, Hornebecq *et al.* [151] produced silver nanoparticles by γ -irradiation of silver solution in mesoporous silica. The silver/silica heterostructure thus obtained is stable in the presence of oxygen and exhibits interesting luminescence as observed for direct-band-gap semiconductor heterostructures [152, 153]. The luminescence properties of Ag/silica composites are examples of the quantum confinement effects found in low dimensional materials which give rise to unique and unusual optical and electronic properties [154]. Due to their possible magnetic applications, iron [155–161], iron–cobalt [162] and iron oxide [163–165] nanoparticles are the subject of a large number of investigations. Recently, Eliseev *et al.* [156, 157] have demonstrated the feasibility of highly ordered iron nanowires presenting an anisotropic structure by thermal reduction of a $\text{Fe}(\text{CO})_5$ solution embedded within the pores. They reported an increase in the coercive force reaching 650 Oe at 4 K and 80 Oe at room temperature, a highly encouraging result for future data storage devices. Supercritical fluid inclusion offers an attractive new route for the synthesis of metallic nano-objects. For example, Crowley *et al.* [166] succeeded in synthesizing cobalt, copper, and iron oxide magnetite (Fe_3O_4) nanowires by this new method (figure 5).

The encapsulation of metal nanowires in mesosilicates is known to induce confinement effects on the structural properties. Hierarchically well-ordered CdS nanowires were reported in mesoporous silica with hexagonal mesostructure and a high degree of cubic zinc blende crystallinity, a crystalline structure which is not observed in bulk CdS [167].

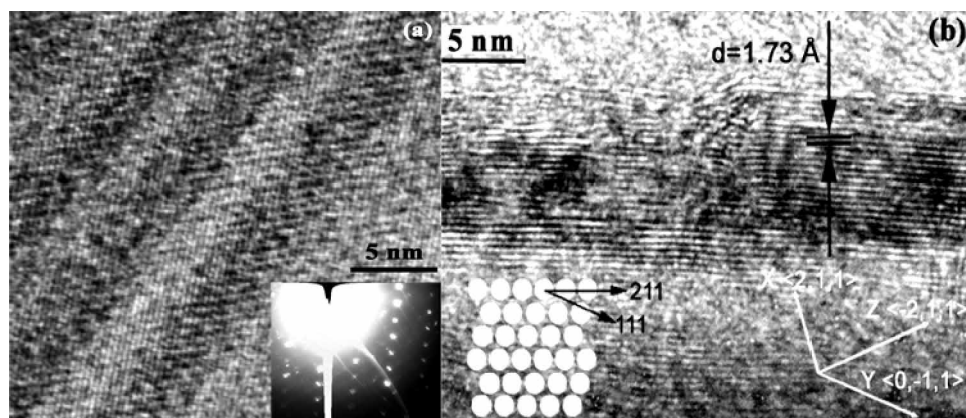


Figure 5. HRTEM image of (a) a series of parallel cobalt nanowires. The inset shows the SAED pattern of the cobalt nanowires. (b) An individual Fe_3O_4 nanowire synthesized in mesoporous silica at 450°C and 345 bar. The d spacing of 1.73 \AA shown is assigned to the crystal spacing of (422) planes. Also shown is the relationship of the equivalent (211) directions to a vicinal (110) direction and the (211) crystal plane projected onto the $(0, 1, -1)$ plane (reproduced from ref. [166] with the permission of the American Chemical Society).

A non-exhaustive list of different metals and semiconductor nanostructures have been successfully synthesized within the pore channels of MCM-41 based mesoporous silica template, such as Ag [168], AgI [169], Ag_2Se [170], Au [171], CdS [167, 172], CdSe [173, 174], $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ [175], Co [166], Cu_2Te [176], CuO [177], Ge [178], Pd [179], Pt [171, 180, 181], Se [182], Si [183], WO_3 [184], $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ [185], ZnS [186, 187], ZnO [188].

Incorporation of ions in the silica matrix has been reported for rare earth trivalent ions such as Eu^{3+} . The composite exhibits an intense photoluminescence in the visible region (around 620 nm) [189]. In the case of copper and silver, composites were reported with monolithic silica with a good propene–propane selectivity ratio and a high propene adsorption capacity [190]. More recently, Ni-MCM-41 and Co-MCM-41 produced by the same route [191, 192] are used as catalytic templates to synthesize single-wall or multi-wall nanotubes of uniform diameter [193–198]. Ciuparu *et al.* [199] were the first to synthesize pure boron single-wall nanotubes inside mesoporous silica. This was achieved by reacting BCl_3 with H_2 over an Mg-MCM-41 catalyst with parallel, uniform diameter (36 \AA) cylindrical pores. The nanotube diameter was approximately that of the pore of the mesoporous molecular sieve template, suggesting a physical templating process.

3.2. Biotechnology

Enzymes, proteins and biocatalysts with high selectivities have been widely used in the food industry. Encapsulated enzymes and other proteins within inorganic host materials [200] and especially in controlled porous glasses (CPG) represent one of the most rapidly growing fields over the past few years. It has been already established that biomolecules immobilized in inorganic matrices retain their functional characteristics to a large extent. However, the main disadvantages of CPG materials for adsorption

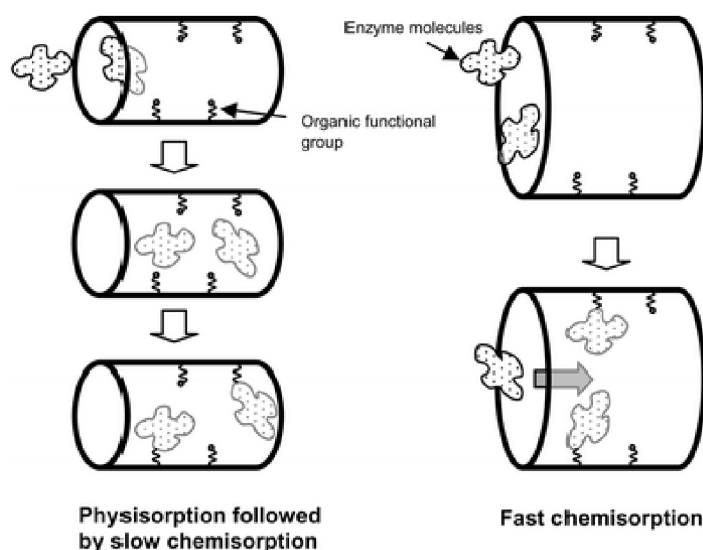


Figure 6. Illustrations showing two possible mechanisms of protein binding on to the functionalized surface of mesoporous silica (reproduced from ref. [203] by permission of the Royal Society of Chemistry).

studies are their high cost and the rapid decrease of the surface area with increasing pore size (30–200 nm). A comprehensive review by Hartmann [201] outlined the advantages of mesoporous MCM-41 based materials for bioadsorption. For the immobilization of biomolecules, the general procedures can be broadly categorized into two types depending on the interaction between the biomolecules and host: covalent binding and adsorption or encapsulation.

3.2.1. Covalent binding. In general, it consists of the functionalization of the support for efficient immobilization of the biomolecules via covalent bonding with the tunable silanol groups. These silanol groups are readily available and can be used as the reactive sites for functionalization, thus providing a controlled immobilization of biomolecules. Functional groups like thiols, carboxylic acids, alkyl chlorides, amines are amongst the most useful ones [202]. The covalent binding gives a better stability to the immobilized biomolecules and particularly for enzymes. Wang and coworkers [203] observed that α -chymotrypsin immobilized on mesoporous silicas functionalized with trimethoxysilylpropanal exhibited a >1000 fold higher half life than the native enzyme, both in aqueous solution and organic solvents (Figure 6). Pandya *et al.* [204] found that higher thermal and pH stabilities can be achieved by immobilizing α -amylase on amino-functionalized MCM-41 supports than the free enzyme.

We must keep in mind that the harsh reaction condition which is generally used during the covalent binding can alter the properties of immobilized biomolecules.

3.2.2. Adsorption or encapsulation. This is a simple process which requires no further chemical treatment of the host. The lack of complex chemical treatment gives the

encapsulation or adsorption process a great advantage over the covalent bonding because denaturation of biomolecules can be easily avoided. In addition, a high loading can be achieved due to high specific areas of the MCM-41 based materials.

3.2.3. Selected examples. One of the earliest reports on immobilization by adsorption of globular enzymes, cytochrome c (bovine heart), papain (papaya latex) and trypsin (bovine pancreas), in the mesoporous molecular sieve MCM-41 was made by Diaz *et al.* [205]. The efficiency of papain and trypsin immobilization was found to be pH dependent and favourable at pH values <7, while immobilization of cytochrome c was more efficient at pH >7 and less susceptible to pH changes. The adsorption of vitamin B2 (riboflavin) onto MCM-41 and MCM-48 was studied by Kisler *et al.* [206]. The observation that MCM-41 shows significantly higher adsorption of vitamin B2 than MCM-48 (0.015 vs. 0.005 $\mu\text{mol/g}$) was suggested to result from the difference in pore sizes. Adsorbed vitamin B2 has a maximum size of $\sim 60\%$ of the MCM-48 pore size, and thus steric hindrance is believed to play an important role. Desorption experiments revealed that some vitamin B2 remains adsorbed, showing that the adsorption is not completely reversible. Recently, Farzaneh *et al.* [207] found that Vit-B12/MCM-41 successfully catalyses the oxygen transfer of *tert*-butylhydroperoxide (TBHP) to norbornene and *trans*-2-hexene-1-ol and formation of the corresponding epoxides with 90% reactivity and 100% selectivity.

Adsorption properties of host material are very important for the purification of biomolecules. It was reported that MCM-41 is a good candidate as a high surface area adsorbent for biological molecules such as amino acids [208]. The basic amino acid, lysine, adsorbs on siliceous MCM-41 following a Langmuir-type isotherm with a maximum capacity at pH 6 of 0.21 mmol/g. The extent of adsorption depends on the solution pH and ionic strength, with a combination of electrostatic interactions and ion exchange governing the uptake of lysine.

MCM-41 was tested as drug delivery system for the controlled release of ibuprofen [209]. A maximum uptake of 0.3 g of ibuprofen per g of C₁₂-MCM-41 was observed. Thereafter, the drug-charged material was shaped into disks to improve the drug-release process (Method 1). The release curve was obtained by immersing the sample into a defined volume of simulated body fluid (SBF). It has been found that initial release is fast, reaching 60% after 24 h, and reached a maximum value of 70% after 32 h. If ibuprofen is loaded into MCM-41 after disk formation (a C₁₂-MCM-41 wafer is immersed into the ibuprofen solution in *n*-hexane, Method 2), the delivery rate is almost similar, but the release reached 100% of the adsorbed ibuprofen. Recently, the same group has demonstrated the delivery rate of drugs occluded in MCM-41 matrixes by functionalizing the pore wall with silane derivatives [210]. In the case of ibuprofen, which contains an acid group, the functionalization of well-ordered MCM-41 matrixes with aminopropyl moieties allows decrease of the delivery rate. It has been shown that the functionalization procedure is determinant in both the adsorption of the drug and its release profile. These preliminary studies demonstrate the feasibility of designing drug-release systems by suitable choice of support and drug.

Various proteins such as cytochrome c [211–216], lysozyme [217, 218], trypsin [219–222] have been successfully immobilized or absorbed onto MCM-41 based

mesoporous materials and their activities studied. The physical immobilization of whole microbial cells of *Arthrobacter* sp., *Bacillus subtilis*, and *Micrococcus luteus* on the mesoporous molecular sieve MCM-41 was studied by Tope *et al.* [223]. Recently Lin *et al.* showed that well-ordered mesoporous silica nanoparticles could be used as cell markers [224]. Some general trends can be deduced from the adsorption studies published so far. Adsorption is dominated by weak physical forces, i.e., Van der Waals or dispersion forces. It is shown in some studies that proteins tend to adsorb better when strong electrostatic (charge) interactions occur between the silica surface and the protein. Near the isoelectric point (pI), the coulomb forces derived of the positive charges from the ionized protein and the negative charges at the silica surface are small. Under these circumstances, hydrophobic interactions between the protein and the adsorbent become more important.

4. Conclusions

In this brief review, we have tried to convey the enormous potentials of MCM-41 based mesoporous materials for applications in production of new materials and biotechnology. The increasing number of synthesis routes under development will greatly facilitate the preparation of materials with tailored properties suitable for a specific application. It is remarkable that this explosion in the range of synthetic routes and targeted applications has taken place in little over a decade since the original discovery of the material [18–21].

Acknowledgements

Helpful discussions and suggestions by Dr. T. Steriotis (Demokritos, Athens, Greece) are gratefully acknowledged. We thank Region Centre for the fellowship SOLEIL given to G. Lelong.

References

- [1] T.J. Barton, L.M. Bull, W.G. Klemperer, D.A. Loy, B. McEnaney, M. Misono, P.A. Monson, G. Pez, G.W. Scherer, J.C. Vartuli, O.M. Yaghi. Tailored porous materials. *Chem. Mater.*, **11**, 2633 (1999).
- [2] Y. Ma, W. Tong, H. Zhou, L. Suib. A review of zeolite-like porous materials. *Microp. Mesop. Mater.*, **37**, 243 (2000).
- [3] A.K. Cheetham, G. Férey, T. Loiseau. Open-framework inorganic materials. *Angew. Chem., Int. Ed. Engl.*, **38**, 3269 (1999).
- [4] P. Behrens. Mesoporous inorganic solids. *Adv. Mater.*, **5**, 127 (1993).
- [5] J.L. Casci. The preparation and potential applications of ultra-large pore molecular sieves: a review. *Stud. Surf. Sci. Catal.*, **85**, 329 (1994).
- [6] A. Corma. Microporous to mesoporous molecular sieve materials and their use in catalysis. *Chem. Rev.*, **97**, 2373 (1997).
- [7] M.E. Davis. Zeolites and molecular sieves: not just ordinary catalysts. *Ind. Eng. Chem.*, **30**, 1675 (1991).
- [8] J.V. Smith. Topochemistry of zeolites and related materials: I. Topology and geometry. *Chem. Rev.*, **88**, 149 (1988).
- [9] A. Corma. Inorganic solid acids and their use in acid-catalyzed hydrocarbon reactions. *Chem. Rev.*, **95**, 559 (1995).
- [10] A. Imhof. Ordered macroporous materials by emulsion templating. *Adv. Mater.*, **10**, 697 (1995).

- [11] H. Yan, C.F. Blanford, B.T. Holland, W.H. Smyrl, A. Stein. General synthesis of periodic macroporous solids by templated salt precipitation and chemical conversion. *Chem. Mater.*, **12**, 1134 (2000).
- [12] G.A. Ozin. Morphogenesis of biomineral and morphosynthesis of biomimetic forms. *Acc. Chem. Res.*, **30**, 17 (1997).
- [13] R.A. Caruso, M. Giersig, F. Willig, M. Antonietti. Porous 'coral-like' TiO₂ structures produced by templating polymer gels. *Langmuir*, **27**, 6333 (1998).
- [14] D. Zhao, Q. Huo, J. Feng, J. Kim, Y. Han, G.D. Stucky. Novel mesoporous silicates with two-dimensional mesostructure direction using rigid bolaform surfactants. *Chem. Mater.*, **11**, 2668 (1999).
- [15] D.M. Antonelli. Synthesis of macro-mesoporous niobium oxide molecular sieves by a ligand-assisted vesicle templating strategy. *Microp. Mesop. Mater.*, **33**, 209 (1999).
- [16] M.E. Davis. Ordered porous materials for emerging applications. *Nature*, **417**, 813 (2002).
- [17] F. Schüth, K.S.W. Sing, J. Weitkamp (Eds). Ordered mesoporous oxides. In *Handbook of Porous Solids*, p. 1311, Wiley-VCH, Weinheim.
- [18] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature*, **359**, 710 (1992).
- [19] T. Yanagisawa, T. Shimizu, K. Kuroda, C. Kato. The preparation of alkyltrimethylammonium-kanemite complexes and their conversion to mesoporous materials. *Bull. Chem. Soc. Jpn.*, **63**, 988 (1990).
- [20] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olsen, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker. A new family of mesoporous molecular sieves prepared with liquid crystal templates. *J. Am. Chem. Soc.*, **114**, 10835 (1992).
- [21] S. Inagaki, Y. Fukushima, K. Kuroda. Synthesis of highly ordered mesoporous materials from a layered polysilicate. *J. Chem. Soc., Chem. Commun.*, **1993**, 680 (1993).
- [22] J. Rouquerol, D. Avnir, C.W. Fairbridge, D.H. Everett, J.H. Haynes, N. Pernicone, J.D. Ramsay, K.S.W. Sing, K.K. Unger. Recommendations for the characterization of porous solids. *Pure Appl. Chem.*, **66**, 1739 (1994).
- [23] J.S. Beck. Method for synthesizing mesoporous crystalline materials. US Patent 5,057,296 (1991).
- [24] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli. Composition of synthetic porous crystalline material, its synthesis. US Patent 5,102,643 (1992).
- [25] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli. Synthesis of mesoporous crystalline material. US Patent 5,102,643 (1992).
- [26] V. Chiola, J.E. Ritsko, C.D. Vanderpool. Process for producing low-bulk density silica. US Patent 3,556,725 (1971).
- [27] F. Di Renzo, H. Cambon, R. Dutartre. A 28-year-old synthesis of micelle-templated mesoporous silica. *Microp. Mater.*, **10**, 283 (1997).
- [28] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky. Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 Å pores. *Science*, **279**, 548 (1998).
- [29] Q. Huo, D.I. Margolese, U. Ciesla, P. Feng, T.E. Gier, P. Sieger, R. Leon, P.M. Petroff, F. Schüth, G.D. Stucky. Generalized synthesis of periodic surfactant/inorganic composite materials. *Nature*, **368**, 317 (1994).
- [30] P. Feng, X. Bu, G.D. Stucky, D.J. Pine. Monolithic mesoporous silica templated by microemulsion liquid crystals. *J. Am. Chem. Soc.*, **122**, 994 (2000).
- [31] C.Y. Chen, S.Q. Xiao, M.E. Davis. Studies on ordered mesoporous materials III. Comparison of MCM-41 to mesoporous materials derived from kanemite. *Microp. Mater.*, **4**, 1 (1995).
- [32] J.C. Vartuli, K.D. Schmitt, C.T. Kresge, W.J. Roth, M.E. Leonowicz, S.B. McCullen, S.D. Hellring, J.S. Beck, J.L. Schlenker, D.H. Olsen, E.W. Sheppard. Development of a formation mechanism for M41S. In *Zeolites and Related Microporous Materials: State of Art*, J. Weitkamp, H.G. Karge, H. Pfeifer, W. Höderich (Eds), p. 53, Elsevier, Amsterdam (1994).
- [33] U. Ciesla, F. Schüth. Ordered mesoporous materials. *Microp. Mesop. Mater.*, **27**, 131 (1999).
- [34] V. Ajayan, H.K. Zakir, A. Katsuhiko. Recent advances in functionalization of mesoporous silica. *J. Nanosci. Nanotech.*, **5**, 347 (2005).
- [35] A. Sayari. Periodic mesoporous materials: synthesis, characterization and potential applications. *Stud. Surf. Sci. Catal.*, **102**, 1 (1996).
- [36] A. Sayari, P. Liu. Non-silica periodic mesostructured materials: recent progress. *Microp. Mater.*, **12**, 149 (1997).
- [37] J.Y. Ying, C.P. Mehnert, M.S. Wong. Synthesis and applications of supramolecular-templated mesoporous materials. *Angew. Chem., Int. Ed.*, **38**, 56 (1999).
- [38] X.S. Zhao, G.Q.M. Lu, G.J. Miller. Advances in mesoporous molecular sieve MCM-41. *Ind. Eng. Chem. Res.*, **35**, 2075 (1996).
- [39] P. Selvam, S.K. Bhatia, C.G. Sonwane. Recent advances in processing and characterization of periodic mesoporous MCM-41 silicate molecular sieves. *Ind. Eng. Chem. Res.*, **40**, 3237 (2001).

- [40] B.J. Pang, K.Y. Qiu, Y. Wei, X.-J. Lei, Z.F. Liu. Facile preparation of transparent and monolithic mesoporous silica materials. *Chem. Comm.*, **6**, 477 (2000).
- [41] B.J. Pang, K.Y. Qiu, Y. Wei. A new nonsurfactant pathway to mesoporous silica materials based on tartaric acid in conjunction with metallic chloride. *Chem. Mater.*, **14**, 2361 (2001).
- [42] C.C. Pantazis, P.N. Trikalitis, P.J. Pomonis, M.J. Hudson. A method of synthesis of silicious inorganic ordered materials (MCM-41 – SBA-1) employing polyacrylic acid- C_n TAB-TEOS nanoassemblies. *Microp. Mesop. Mater.*, **66**, 37 (2003).
- [43] S.-E. Park, D.S. Kim, J.-S. Chang, W.Y. Kim. Synthesis of MCM-41 using microwave heating with ethylene glycol. *Catalysis Today*, **44**(1–4), 301 (1998).
- [44] C.-G. Wu, T. Bein. Microwave synthesis of molecular sieve MCM-41. *Chem. Comm.*, **8**, 925 (1996).
- [45] N.K. Raman, M.T. Anderson, C.J. Brinker. Template-based approaches to the preparation of amorphous, nanoporous silicas. *Chem. Mater.*, **8**, 1682 (1996).
- [46] I. Soten, G.A. Ozin. Assembly and mineralization processes in biomineralization. In *Supramolecular Organization and Materials Design*, W. Jones, C.N.R. Rao (Eds), p. 34, Cambridge University Press, Cambridge (2002).
- [47] J.-Y. Zheng, J.-B. Pang, K.-Y. Qiu, Y.J. Wei. Synthesis of mesoporous titanium dioxide materials by using a mixture of organic compounds as a non-surfactant template. *Mater. Chem.*, **11**, 3367 (2001).
- [48] J.-Y. Zheng, J.-B. Pang, K.-Y. Qiu, Y. Wei. Synthesis and characterization of mesoporous titania and silica–titania materials by urea templated sol–gel reactions. *Microp. Mesop. Mater.*, **49**, 189 (2001).
- [49] H.-U. Lin, Y.-W. Chen. Preparation of spherical hexagonal mesoporous silica. *J. Porous. Mater.*, **12**, 95 (2005).
- [50] Y. Di, X. Meng, S. Li, F.-S. Xiao. Ordering improvement of mesoporous silica materials templated from semi-fluorinated nonionic surfactants by introduction of organic additives. *Microp. Mesop. Mater.*, **82**, 121 (2005).
- [51] P.T. Tanev, T.J. Pinnavaia. A neutral templating route to mesoporous molecular sieves. *Science*, **267**(5199), 865 (1995).
- [52] P.T. Tanev, T.J. Pinnavaia. Mesoporous silica molecular sieves prepared by ionic and neutral surfactant templating: a comparison of physical properties. *Chem. Mater.*, **8**, 2068 (1996).
- [53] Y. Wei, D. Jin, T. Ding, W.-H. Shih, X. Liu, S.Z.D. Cheng, Q. Fu. A non-surfactant templating route to mesoporous silica materials. *Adv. Mater.*, **3**(4), 313 (1998).
- [54] Y. Wei, J. Xu, H. Dong, J.H. Dong, K. Qiu, S.A. Jansen-Varnum. Preparation and physisorption characterization of d-glucose-templated mesoporous silica sol–gel materials. *Chem. Mater.*, **11**, 2023 (1999).
- [55] J.-B. Pang, K.-Y. Qiu, J. Xu, Y. Wei, J. Chen. Synthesis of mesoporous silica materials via nonsurfactant urea-templated sol–gel reactions. *J. Inorg. Organomet. Polym.*, **10**(1), 39 (2000).
- [56] J.-B. Pang, K.-Y. Qiu, Y. Wei. A novel nonsurfactant pathway to hydrothermally stable mesoporous silica materials. *Microp. Mesop. Mater.*, **40**, 299 (2000).
- [57] J.-Y. Zheng, J.-B. Pang, K.-Y. Qiu, Y. Wei. Synthesis of mesoporous silica materials via nonsurfactant templated sol–gel route by using mixture of organic compounds as template. *J. Sol–Gel Sci. Tech.*, **24**, 81 (2002).
- [58] M. Run, S. Wu, G. Wu. Ultrasonic synthesis of mesoporous molecular sieve. *Microp. Mesop. Mater.*, **74**, 37 (2004).
- [59] S. Han, W. Hou, J. Xu, Z. Li. Synthesis of hollow spherical silica with MCM-41 mesoporous structure. *Colloid Polym. Sci.*, **282**(11), 1286 (2004).
- [60] Y. Zhu, J. Shi, H. Chen, W. Shen, X. Dong. A facile method to synthesize novel hollow mesoporous silica spheres and advanced storage property. *Microp. Mesop. Mater.*, **84**, 218 (2005).
- [61] E. Van Bavel, P. Cool, K. Aerts, E.F. Vansant. Morphology variations of plugged hexagonal templated silica. *J. Porous. Mater.*, **12**, 65 (2005).
- [62] Y. Li, J. Shi, Z. Hua, H. Chen, M. Ruan, D. Yan. Hollow spheres of mesoporous aluminosilicate with a three-dimensional pore network and extraordinarily high hydrothermal stability. *Nanolett.*, **3**(5), 609 (2003).
- [63] D. Zhao, J. Sun, Q. Li, G.D. Stucky. Morphological control of highly ordered mesoporous silica SBA-15. *Chem. Mater.*, **12**, 275 (2000).
- [64] S. Huh, J.W. Wiench, J.-C. Yoo, M. Pruski, V.S.-Y. Lin. Organic functionalization and morphology control of mesoporous silicas via a co-condensation synthesis method. *Chem. Mater.*, **15**, 4247 (2003).
- [65] W. Zhao, Q. Li. Synthesis of nanosize MCM-48 with high thermal stability. *Chem. Mater.*, **15**, 4160 (2003).
- [66] A. Sayari, B.-H. Han, Y. Yang. Simple synthesis route to monodispersed SBA-15 silica rods. *J. Am. Chem. Soc.*, **126**, 14348 (2004).
- [67] M. Grün, I. Lauer, K.K. Unger. The synthesis of micrometer- and submicrometer-size spheres of ordered mesoporous oxide MCM-41. *Adv. Mater.*, **9**(3), 254 (1997).

- [68] W. Stöber, A. Funk, E. Bohn. Controlled growth of monodisperse silica spheres in the micron size range. *J. Colloid Interf. Sci.*, **26**(1), 62 (1968).
- [69] M. Kruk, M. Jaroniec. Accurate method for calculating mesopore size distributions from argon adsorption data at 87 K developed using model MCM-41 Materials. *Chem. Mater.*, **12**, 222 (2000).
- [70] C.-Y. Mou, H.-P. Lin. Control of morphology in synthesizing mesoporous silica. *Pure Appl. Chem.*, **72**, 137 (2000).
- [71] H. Yang, G. Vovk, N. Coombs, I. Sokolov, G.A. Ozin. Synthesis of mesoporous silica spheres under quiescent aqueous acidic conditions. *J. Mater. Chem.*, **8**(3), 743 (1998).
- [72] K.W. Gallis, J.T. Araujo, K.J. Duff, J.G. Moore, C.C. Landry. The use of mesoporous silica in liquid chromatography. *Adv. Mater.*, **11**(17), 1452 (1999).
- [73] K.K. Unger, D. Kumar, M. Grün, G. Büchel, S. Lüdtkke, T. Adam, K. Schumacher, S.J. Renker. Synthesis of spherical porous silicas in the micron and submicron size range: challenges and opportunities for miniaturized high-resolution chromatographic and electrokinetic separations. *J. Chromat. A.*, **892**(1–2), 47 (2000).
- [74] R.I. Nooney, D. Thirunavukkarasu, Y. Chen, R. Josephs, A.E. Ostafin. Synthesis of nanoscale mesoporous silica spheres with controlled particle size. *Chem. Mater.*, **14**, 4721 (2002).
- [75] Y. Ma, L. Qi, J. Ma, Y. Wu, O. Liu, H. Cheng. Large-pore mesoporous silica spheres: synthesis and application in HPLC. *Colloids Surf. A.*, **229**(1–3), 1 (2003).
- [76] K. Yano, Y.J. Fukushima. Particle size control of mono-dispersed super-microporous silica spheres. *J. Mater. Chem.*, **13**(10), 2577 (2003).
- [77] B. Alonso, C. Clinard, D. Durand, E. Vérona, D. Massiot. New routes to mesoporous silica-based spheres with functionalised surfaces. *Chem. Commun.*, **13**, 1746 (2005).
- [78] Q. Huo, J. Feng, F. Schüth, G.D. Stucky. Preparation of hard mesoporous silica spheres. *Chem. Mater.*, **9**, 14 (1997).
- [79] Y. Miyake, T. Kato. The formation process of spherical mesoporous silica with reverse nanostructure of MCM-41 in a two-phase system. *J. Chem. Eng. Japan.*, **38**(1), 60 (2005).
- [80] S. Liu, P. Cool, O. Collart, P. Van Der Voort, E.F. Vansant, O.I. Lebedev, G. Van Tendeloo, M. Jiang. The influence of the alcohol concentration on the structural ordering of mesoporous silica: cosurfactant versus cosolvent. *J. Phys. Chem. B.*, **107**, 10405 (2003).
- [81] G. Van Tendeloo, O.I. Lebedev, O. Collart, P. Cool, E.F. Vansant. Structure of nanoscale mesoporous silica spheres?. *J. Phys. Condens. Matter.*, **15**, S3037 (2003).
- [82] O.I. Lebedev, G. Van Tendeloo, O. Collart, P. Cool, E.F. Vansant. Structure and microstructure of nanoscale mesoporous silica spheres. *Solid State Sci.*, **6**, 489 (2004).
- [83] N. Israelachvili, D.J. Mitchell, B.W. Niham. Theory of self-assembly of hydrocarbon amphiphiles into micelles and bilayers. *J. Chem. Soc., Faraday Trans.*, **72**(2), 1525 (1976).
- [84] Q. Huo, D.I. Margolese, G.D. Stucky. Surfactant control of phases in the synthesis of mesoporous silica-based materials. *Chem. Mater.*, **8**, 1147 (1996).
- [85] Y. Lu, H. Fan, A. Stump, T.L. Ward, T. Rieker, C.J. Brinker. Aerosol-assisted self-assembly of mesostructured spherical nanoparticles. *Nature*, **398**, 223 (1999).
- [86] Y. Lu, R. Ganguli, C.A. Drewien, M.T. Anderson, C.J. Brinker, W. Gong, Y. Guo, H. Soyey, B. Dunn, M.H. Huang, J.I. Zink. Continuous formation of supported cubic and hexagonal mesoporous films by sol-gel dip-coating. *Nature*, **389**, 364 (1997).
- [87] C.J. Brinker, Y. Lu, A. Sellinger, H. Fan. Evaporation-induced self-assembly: nanostructures made easy. *Adv. Mater.*, **11**, 579 (1999).
- [88] N. Baccile, D. Grosso, C. Sanchez. Aerosol generated mesoporous silica particles. *J. Mater. Chem.*, **13**, 3011 (2003).
- [89] M.T. Bore, S.B. Rathod, T.L. Ward, A.K. Datye. Hexagonal mesostructure in powders produced by evaporation-induced self-assembly of aerosols from aqueous tetraethoxysilane solutions. *Langmuir*, **19**, 256 (2003).
- [90] B. Alonso, A. Douy, E. Véron, J. Perez, M.-N. Rager, D. Massiot. Morphological and textural control of spray-dried mesoporous silica-based spheres. *J. Mater. Chem.*, **14**, 1 (2004).
- [91] D. Zhao, P. Yang, Q. Huo, B.F. Chmelka, G.D. Stucky. Topological construction of mesoporous materials. *Current Opin. Solid State Mater. Sci.*, **3**, 111 (1998).
- [92] X. Pang, F. Tang. Morphological control of mesoporous materials using inexpensive silica sources. *Microp. Mesop. Mater.*, **85**, 1 (2005).
- [93] X. Pang, J. Gao, F. Tang. Controlled preparation of rod- and top-like MCM-41 mesoporous silica through one-step route. *J. Non-Cryst. Solids*, **351**, 1705 (2005).
- [94] Q. Cai, Z.-S. Sheng, W.-Q. Pang, Y.-W. Fan, X.-H. Chen, F.-Z. Cui. Dilute solutions routes to various controllable morphologies of MCM-41 silica with a basic medium. *Chem. Mater.*, **13**, 258 (2001).
- [95] M. Ogawa. Formation of novel oriented transparent films of layered silica-surfactant nanocomposites. *J. Am. Chem. Soc.*, **116**, 7941 (1994).

- [96] M. Ogawa. A simple sol-gel route for the preparation of silica-surfactant mesostructured materials. *Chem. Comm.*, **10**, 1149 (1996).
- [97] Y. Lu, R. Ganguli, C.A. Drewien, M.T. Anderson, C.J. Brinker, W. Gong, Y. Guo, H. Soyey, B. Dunn, M.H. Huang, J.I. Zink. Continuous formation of supported cubic and hexagonal mesoporous films by sol-gel dip-coating. *Nature*, **389**, 364 (1997).
- [98] H. Fang, W.-H. Shi, C.-Y. Ma. Ordered large-pore mesoporous silica films with *Im3m* symmetry synthesized in ternary copolymer-butanol-water system. *Mater. Lett.*, **60**, 581 (2006).
- [99] S.-B. Jung, H.H. Park. Concentration-dependent mesostructure of surfactant-templated mesoporous silica thin films. *Thin Solid Films*, **494**, 320 (2006).
- [100] C.J. Brinker, G.C. Frye, A.J. Hurd, C.S. Ashley. Fundamentals of sol-gel dip coating. *Thin Solid Films*, **201**, 97 (1991).
- [101] L. Huang, S. Kawi, K. Hidajat, S.C. Ng. Preparation of M41S family mesoporous silica thin films on porous oxides. *Microp. Mesop. Mater.*, **82**, 87 (2005).
- [102] S.P. Naik, M. Ogura, H. Sasakura, Y. Yamaguchi, Y. Sasaki, T. Okubo. Phase and orientation control of mesoporous silica thin film via phase transformation. *Thin Solid Films*, **495**, 11 (2006).
- [103] R.E. Williford, X.S. Li, R.S. Addleman, G.E. Fryxell, S. Baskaran, J.C. Birnbaum, C. Coyle, T.S. Zemanian, C. Wang, A.R. Courtney. Mechanical stability of templated mesoporous silica thin films. *Microp. Mesop. Mater.*, **85**, 260 (2005).
- [104] D. Grosso, F. Cagnol, G.J. de, A.A. Soler-Illia, E.L. Crepaldi, H. Amenitsch, A. Brunet-Bruneau, A. Bourgeois, C. Sanchez. Fundamentals of mesostructuring through evaporation-induced self assembly. *Adv. Funct. Mater.*, **14**(4), 309 (2004).
- [105] N.A. Melosh, P. Davidson, B.F. Chmelka. Monolithic mesophase silica with large ordering domains. *J. Am. Chem. Soc.*, **122**, 823 (2000).
- [106] H. Yang, Q. Shi, B. Tian, S. Xie, F. Zhang, Y. Yan, B. Tu, D. Zhao. A fast way for preparing crack-free mesostructured silica monolith. *Chem. Mater.*, **15**, 536 (2003).
- [107] X.-F. Zhou, C.-Z. Yu, J.-W. Tang, X.-X. Yan, D.-Y. Zhao. The effect of water content on the preparation of mesoporous monoliths and films. *Microp. Mesop. Mater.*, **79**, 283 (2005).
- [108] S.A. El-Safty, T. Hanaoka, F. Mizukami. Stability of highly ordered nanostructures with uniformly cylindrical mesochannels. *Acta Materialia*, **54**, 899 (2006).
- [109] A. Corma. From microporous to mesoporous molecular sieve materials and their use in catalysis. *Chem. Rev.*, **97**(6), 2373 (1997).
- [110] Y. Liu, T.J. Pinnavaia. Aluminosilicate mesostructures with improved acidity and hydrothermal stability. *J. Mater. Chem.*, **12**(11), 3179 (2002).
- [111] A.P. Wight, M.E. Davis. Design and preparation of organic-inorganic hybrid catalysts. *Chem. Rev.*, **102**, 3589 (2002).
- [112] D.E. De Vos, M. Dams, B.F. Sels, P.A. Jacobs. Ordered mesoporous and microporous molecular sieves functionalized with transition metal complexes as catalysts for selective organic transformations. *Chem. Rev.*, **102**(10), 3615 (2002).
- [113] G.J.D. Soler-Illia, C. Sanchez, B. Leveau, J. Patarin. Chemical strategies to design textured materials: from microporous and mesoporous oxides to nanonetworks and hierarchical structures. *Chem. Rev.*, **102**(11), 4093 (2002).
- [114] D.T. On, D. Desplandier-Giscard, C. Danumah, S. Kaliaguine. Perspectives in catalytic applications of mesostructured materials. *Appl. Catal. A: Gen.*, **253**(2), 545 (2003).
- [115] A. Wingen, F. Kleitz, F. Schüth, M. Baerns (Eds), 'Ordered Mesoporous Materials: Their Preparation and Application in Catalysts'. In *Basic Principles in Applied Catalysis*, p. 281, Springer, Berlin (2003).
- [116] A. Taguchi, F. Schüth. Ordered mesoporous materials in catalysis. *Microp. Mesop. Mater.*, **77**, 1 (2005).
- [117] F.A. Twaiq, A.R. Mohamed, S. Bhatia. Liquid hydrocarbon fuels from palm oil by catalytic cracking over aluminosilicate mesoporous catalysts with various Si/Al ratios. *Microp. Mesop. Mater.*, **64**, 95 (2003).
- [118] E. Byambajav, Y. Ohtuska. Cracking behavior of asphaltene in the presence of iron catalysts supported on mesoporous molecular sieve with different pore diameters. *Fuel*, **82**(13), 1571 (2003).
- [119] Y. Sun, L. Zhu, H. Lu, R. Wang, S. Lin, D. Jiang, F.-S. Xiao. Sulfated zirconia supported in mesoporous materials. *Appl. Catal. A: Gen.*, **237**(1-2), 21 (2002).
- [120] Q.-H. Xia, K. Hidajat, S. Kawi. Structure, acidity, and catalytic activity of mesoporous acid catalysts for the gas-phase synthesis of MTBE from MeOH and (BuOH)-O-t. *J. Catal.*, **209**, 433 (2002).
- [121] B. Chiche, E. Sauvage, F. Di Renzo, I.I. Ivanova, F. Fajula. Butene oligomerization over mesoporous MTS-type aluminosilicates. *J. Mol. Catal. A: Chem.*, **134**, 145 (1998).
- [122] A. Corma, M.T. Navarro, J. Pérez Pariente. Synthesis of an ultralarge pore titanium silicate isomorphous to MCM-41 and its application as a catalysts for selective oxidation of hydrocarbons. *J. Chem. Soc. Chem. Commun.*, **2**, 147 (1994).

- [123] O. Franke, J. Rathousky, G. Schulz-Eklo, J. Starek, A. Zukal. In *Zeolites and Related Microporous Materials: state of the Art. Studies in Surface Science Catalysis*, J. Weitkamp, H.G. Karge, H. Pfeifer, W. Hölderich (Eds), p. 77, Elsevier, Amsterdam (1994).
- [124] I.W.C.E. Arends, R.A. Sheldon. Activities and stabilities of heterogeneous catalysts in selective liquid phase oxidations: recent developments. *Appl. Catal. A: Gen.*, **212**, 175 (2001).
- [125] L.J. Davies, P. McMorn, D. Bethell, P.C.B. Page, F. King, F.E. Hancock, G.J. Hutchings. Oxidation of crotyl alcohol using Ti-beta and Ti-MCM-41 catalysts. *Mol. Catal. A: Chem.*, **165**(1–2), 243 (2001).
- [126] A. Bhaumik, T. Tatsumi. Organically modified titanium-rich Ti-MCM-41, efficient catalysts for epoxidation reactions. *J. Catal.*, **189**(1), 31 (2000).
- [127] M.L. Peña, V. Dellarocca, F. Rey, A. Corma, S. Coluccia, L. Marchese. Elucidating the local environment of Ti(IV) active sites in Ti-MCM-48: a comparison between silylated and calcined catalys. *Microp. Mesop. Mater.*, **44–45**, 345 (2001).
- [128] P. Wu, T. Tatsumi, T. Komatsu, T. Yashima. Postsynthesis, characterization, and catalytic properties in alkene epoxidation of hydrothermally stable mesoporous Ti-SBA-15. *Chem. Mater.*, **14**, 1657 (2002).
- [129] R. Garro, M.T. Navarro, J. Primo, A. Corma. Lewis acid-containing mesoporous molecular sieves as solid efficient catalysts for solvent-free Mukaiyama-type aldol condensation. *J. Catal.*, **233**, 342 (2005).
- [130] M. Yonemitsu, Y. Tanaka, M. Iwamoto. Metal ion-planted MCM-41 – 2. Catalytic epoxidation of stilbene and its derivatives with tert-butyl hydroperoxide on Mn-MCM-41. *J. Catal.*, **178**(1), 207 (1998).
- [131] V. Caps, S.C. Tsang. Structural and oxidative properties of Mn-MCM-41 catalysts synthesized by MOCVD method. *Catal. Today*, **61**(1–4), 19 (2000).
- [132] W.A. Carvalho, M. Wallau, U. Schuchardt. Iron and copper immobilized on mesoporous MCM-41 molecular sieves as catalysts for the oxidation of cyclohexane. *J. Mol. Catal. A: Chem.*, **144**(1), 91 (1999).
- [133] A. Sakthivel, P. Selvam. Mesoporous (Cr)MCM-41: a mild and efficient heterogeneous catalysts for selective oxidation of cyclohexane. *J. Catal.*, **211**(1), 134 (2002).
- [134] E. Armengol, A. Corma, V. Fornés, H. Garcia, J. Primo. Cu²⁺-phthalocyanine and Co²⁺-perfluorophthalocyanine incorporated inside Y faujasite and mesoporous MCM-41 as heterogeneous catalysts for the oxidation of cyclohexane. *Appl. Catal. A: Gen.*, **181**, 305 (1999).
- [135] R.K. Rana, B. Viswanathan. Mo incorporation in MCM-41 type zeolite. *Catal. Lett.*, **52**(1–2), 25 (1998).
- [136] K. Moller, T. Bein. Inclusion chemistry in periodic mesoporous hosts. *Chem. Mater.*, **10**, 2950 (1998).
- [137] G.A. Ozin. Nanochemistry: synthesis in diminishing dimensions. *Adv. Mater.*, **10**, 612 (1992).
- [138] P.L. Llewellyn, U. Ciesla, H. Decher, R. Stadler, F. Schüth, K.K. Unger. MCM-41 and related materials as media for controlled polymerization processes. *Stud. Surf. Sci. Catal.*, **84**, 2013 (1994).
- [139] C.G. Wu, T. Bein. Conducting carbon wires in ordered, nanometer-sized channels. *Science*, **266**, 1013 (1994).
- [140] C.G. Wu, T. Bein. Conducting Polyaniline filaments in a mesoporous channel host. *Science*, **264**, 1757 (1994).
- [141] J. Wu, A.F. Gross, S.H. Tolbert. Host–guest chemistry using an oriented mesoporous host: alignment and isolation of a semiconducting polymer in the nanopores of ordered silica matrix. *J. Phys. Chem. B*, **103**, 2374 (1999).
- [142] J.F. Diaz, K.J. Balkus Jr. Enzyme immobilization in MCM-41 molecular sieve. *J. Mol. Catal. B: Enzym.*, **2**, 115 (1996).
- [143] T. Abe, Y. Tachibana, T. Uematsu, M. Iwamoto. Preparation and characterisation of Fe₂O₃ nanoparticles in mesoporous silicate. *Chem. Commun.*, **16**, 1617 (1995).
- [144] P. Selvam, D. Singh, R. Tyagi, S.K. Badamali, V. Raghi, A.Q. Contractor. Conducting polyaniline (PANI) filaments in mesoporous MCM-41. In *Recent Trends in Catalysis*, V. Murugesan, B. Arabindo, M. Palanichamy (Eds), p. 550, Narosa, New Delhi (1999).
- [145] R. Leon, D. Margolese, G. Stucky, P. M. Petroff. Nanocrystalline Ge filaments in the pores of a mesosilicate. *Phys. Rev. B*, **52**, 2285 (1995).
- [146] J.M. Baker, J.C. Dore, P. Behrens. Nucleation of ice in confined geometry. *J. Phys. Chem. B*, **101**, 6226 (1997).
- [147] K. Moller, T. Bein. Inclusion chemistry in periodic mesoporous hosts. *Chem. Mater.*, **10**, 2950 (1998).
- [148] C.-M. Yang, H.-S. Sheu, K.-J. Chao. Templated synthesis and structural study of densely packed metal nanostructures in MCM-41 and MCM-48. *Adv. Funct. Mater.*, **12**(2), 1438 (2002).
- [149] X.-J. Guo, C.-M. Yang, P.-H. Liu, M.-H. Cheng, K.-J. Chao. Formation and growth of platinum nanostructures in cubic mesoporous silica. *Crystal Growth Design*, **5**, 33 (2005).
- [150] P.V. Adhyapak, P. Karandikar, K. Vijayamohanab, A.A. Athawalec, A.J. Chandwadkar. Synthesis of silver nanowires inside mesoporous MCM-41 host. *Mater. Lett.*, **58**(7–8), 1168 (2004).
- [151] V. Hornebecq, M. Antonietti, T. Cardinal, M. Treguer-Delapierre. Stable silver nanoparticles immobilized in mesoporous silica. *Chem. Mater.*, **15**, 1993 (2003).
- [152] W. Cai, L. Zhang. Synthesis and structural and optical properties of mesoporous silica containing silver nanoparticles. *J. Phys.: Condens. Matter*, **9**, 7257 (1997).

- [153] W. Cai, Y. Zhang, J. Jia, L. Zhang. Semiconducting optical properties of silver/silica mesoporous composite. *Appl. Phys. Lett.*, **73**, 2709 (1998).
- [154] A.P. Alivisatos. Semiconductor clusters, nanocrystals, and quantum dots. *Science*, **271**, 933 (1996).
- [155] M.J. MacLachlan, P. Aroca, N. Coombs, I. Manners, G.A. Ozin. Ring-opening polymerization of a [1] silaferrocenophane within the channels of mesoporous silica: poly(ferrocenylsilane)-MCM-41 precursors to magnetic iron nanostructures. *Adv. Mater.*, **10**(2), 144 (1998).
- [156] K.S. Napol'skii, I.V. Kolesnick, A.A. Eliseev, A.V. Lukashin, A.A. Vertegel, Y.D. Tret'yakov. Synthesis of filamentary iron nanoparticles in a mesoporous silica matrix. *Doklady Chem.*, **386**, 242 (2002).
- [157] A.A. Eliseev, K.S. Napol'skii, A.V. Lukashin, Y.D. Tret'yakov. Ordered iron nanowires in the mesoporous silica matrix. *J. Magn. Magn. Mater.*, **272–276**, 1609 (2004).
- [158] M.S. Moreno, M. Weyland, P.A. Midgley, J.F. Bengoa, M.V. Cagnoli, N.G. Gallegos, A.M. Alvarez, S.G. Marchetti. Highly anisotropic distribution of iron nanoparticles within MCM-41 Mesoporous Silica. *Micron.*, **37**, 52 (2006).
- [159] N.A. Grigorieva, S.V. Grigoriev, A.I. Okorokov, H. Eckerlebe, A.A. Eliseev, A.V. Lukashin, K.S. Napol'skii. Iron nanowires embedded in mesoporous silica: polarized neutron scattering study. *Physica E*, **28**, 286 (2005).
- [160] M.V. Chernysheva, A.A. Eliseev, K.S. Napol'skii, A.V. Lukashin, Y.D. Tret'yakov, N.A. Grigoryeva, S.V. Grigoryev, M. Wolff. Ordered nanowire arrays in the mesoporous silica thin films. *Thin Solid Films*, **495**, 73 (2006).
- [161] S. Liu, Q. Wang, P. Van Der Voort, P. Cool, E.F. Vansant, M. Jiang. Magnetism of iron-containing MCM-41 spheres. *J. Magn. Magn. Mater.*, **280**, 31 (2004).
- [162] G. Ennas, M.F. Casula, A. Falqui, D. Gatteschi, G. Marongiu, G. Piccaluga, C. Sangregorio, G. Pinna. Nanocrystalline iron-cobalt alloys supported on a silica matrix prepared by the sol-gel method. *J. Non-Cryst. Solids*, **293–295**, 1 (2001).
- [163] S.E. Dapurkar, S.K. Badamali, P. Selvam. Nanosized metal oxides in the mesopores of MCM-41 and MCM-48 silicates. *Catalysis Today*, **68**, 63 (2001).
- [164] J.F. Bengoa, M.V. Cagnoli, N.G. Gallegos, A.M. Alvarez, L.V. Moggi, M.S. Moreno, S.G. Marchetti. Iron oxide nanoparticles inside the MCM-41 channels: study of the structural stability of the support. *Microp. Mesop. Mater.*, **84**, 153 (2005).
- [165] R. Köhn, D. Paneva, M. Dimitrov, T. Tsoncheva, I. Mitov, C. Minchev, M. Fröba. Studies on the state of iron nanoparticles in MCM-41 and MCM-48 silica materials. *Microp. Mesop. Mater.*, **63**, 125 (2003).
- [166] T.A. Crowley, K.J. Ziegler, D.M. Lyons, D. Erts, H. Olin, M.A. Morris, J.D. Holmes. Synthesis of metal and metal oxide nanowire and nanotube arrays within a mesoporous silica template. *Chem. Mater.*, **15**, 3518 (2003).
- [167] R. Thiruvengadathan, O. Regev. Hierarchically ordered cadmium sulfide nanowires dispersed in aqueous solution. *Chem. Mater.*, **17**, 3281 (2005).
- [168] J.-H. Park, S.-G. Oh, B.-W. Jo. Fabrication of silver nanotubes using functionalized silica rod as templates. *Mater. Chem. Phys.*, **87**, 301 (2004).
- [169] G. Kamalakar, Q.-Z. Zhai, D.W. Hwang, S.-H. Chien, Y.-H. Yang, J.-D. Lin, Y.-T. Chen, L.-P. Hwang. Optical properties of host(SBA-15)-guest(AgI) composite materials. *J. Chin. Chem. Soc.*, **50**, 59 (2003).
- [170] V. Leon, Y. Ren, M.-L. Saboungi. Private Communication (2006).
- [171] A. Fukuoka, H. Araki, Y. Sakamoto, N. Sugimoto, H. Tsukada, Y. Kumai, Y. Akimoto, M. Ichikawa. Template synthesis of nanoparticles arrays of gold and platinum in mesoporous silica films. *Nanolett.*, **2**(7), 793 (2002).
- [172] R.J. Martýn-Palma, M. Hernandez-Velez, I. Dýaz, H. Villavicencio-García, M.M. García-Poza, J.M. Martýnez-Duart, J. Perez-Pariente. Optical properties of semiconductors clusters grown into mordenite and MCM-41 matrices. *Mater. Sci. Engng. C*, **15**(1–2), 163 (2001).
- [173] Y. Shan, L. Gao, S. Zheng. A facile approach to load CdSe nanocrystallites into mesoporous SBA-15. *Mater. Chem. Phys.*, **88**(1), 192 (2004).
- [174] H. Parala, H. Winkler, M. Kolbe, A. Wohlfart, R.A. Fisher, R. Schmechel, H. von Seggern. Confinement of CdSe nanoparticles inside MCM-41. *Adv. Mater.*, **12**, 1050 (2000).
- [175] L. Chen, P.J. Klar, W. Heimbrodt, F. Brielerb, M. Froba, H.-A. Krug von Nidda, A. Loidl. Magneto-spectroscopy of ordered arrays of magnetic semiconductor quantum wires. *Physica E*, **10**(1–3), 368 (2001).
- [176] C.M. Kowalchuk, G. Schmid, W. Meyer-Zaika, Y. Huang, J.F. Corrigan. Preparation, characterization, and condensation of copper telluroate clusters in the pores of periodic silica MCM-41. *Inorg. Chem.*, **43**, 173 (2004).
- [177] X.-Y. Hao, Y.-Q. Zhang, J.-W. Wang, W. Zhou, C. Zhang, S. Liu. A novel approach to prepare MCM-41 supported CuO catalyst with high metal loading and dispersion. *Microp. Mesop. Mater.*, **88**, 38 (2006).

- [178] R. Leon, D. Margolese, G. Stucky, P.M. Petroff. Nanocrystalline Ge filaments in the pores of a mesosilicate. *Phys. Rev. B*, **52**, R2285 (1995).
- [179] C.A. Koh, R. Nooney, S. Tahir. Characterization and catalytic properties of MCM-41 and Pd/MCM-41 materials. *Catal. Lett.*, **47**, 199 (1997).
- [180] Z. Liu, Y. Sakamoto, T. Ohsuna, K. Hiraga, O. Terasaki, C.H. Ko, H.J. Shin, R. Ryoo. TEM studies of platinum nanowires fabricated in mesoporous silica MCM-41. *Angew. Chem.*, **112**, 3237 (2000).
- [181] C.-M. Yang, H.-S. Sheu, K.-J. Chao. Templated synthesis and structural study of densely packed metal nanostructures in MCM-41 and MCM-48. *Adv. Funct. Mater.*, **12**, 143 (2002).
- [182] B. Gates, Y. Yin, Y. Xia. A solution-phase approach to the synthesis of uniform nanowires of crystalline selenium with lateral dimensions in the range of 10–30 nm. *J. Am. Chem. Soc.*, **122**, 12582 (2000).
- [183] J.D. Holmes, D.M. Lyons, K.J. Ziegler. Supercritical fluid synthesis of metal and semiconductor nanomaterials. *Chem. Eur. J.*, **9**, 2144 (2003).
- [184] K. Zhu, H. He, S. Xie, X. Zhang, W. Zhou, S. Jin, B. Yue. Crystalline WO₃ nanowires synthesized by templating method. *Chem. Phys. Lett.*, **377**, 317 (2003).
- [185] F.J. Brieler, P. Grundmann, M. Fröba, L. Chen, P.J. Klar, W. Heimbrod, H.-A.K. von Nidda, T. Kurz, A. Loidl. Formation of Zn_{1-x}Mn_xS nanowires within mesoporous silica of different pore sizes. *J. Am. Chem. Soc.*, **126**, 797 (2004).
- [186] J. Zhang, B. Han, Z. Hou, Z. Liu, J. He, T. Jiang. Novel method to load nanoparticles into mesoporous materials: impregnation of MCM-41 with ZnS by compressed CO₂. *Langmuir*, **19**(18), 7616 (2003).
- [187] W.-S. Chae, J.-H. Yoon, H. Yu, D.-J. Jang, Y.-R. Kim. Ultraviolet emission of ZnS nanoparticles confined within a functionalized mesoporous host. *J. Phys. Chem. B*, **108**(31), 11509 (2004).
- [188] Y. Xiong, L.Z. Zhang, G.-Q. Tang, G.-L. Zhang, W.-J. Chen. ZnO nanoparticles included within all-silica MCM-41: preparation and spectroscopic studies. *J. Lumin.*, **110**, 17 (2004).
- [189] J.M.F.B. Aquino, A.S. Araujo, D.M.A. Melo, J.E.C. Silva, M.J.B. Souza, A.O.S. Silva. Synthesis, characterization, and luminescence properties of MCM-41 and Al-MCM-41 mesoporous materials containing Eu(III) ions. *J. Alloys Comp.*, **374**, 101 (2004).
- [190] M. Kargol, J. Zajac, D.J. Jones, J. Rozière, Th. Steriotis, A. Jimenez-Lopez, E. Rodriguez-Castellon. Copper- and silver-containing monolithic silica-supported preparations for selective propene-propane adsorption from the gas phase. *Chem. Mater.*, **17**, 6117 (2005).
- [191] S. Lim, D. Ciuparu, C. Pak, F. Dobek, Y. Chen, D. Harding, L. Pfefferle, G. Haller. Synthesis and characterization of highly ordered Co-MCM-41 for production of aligned single walled carbon nanotubes (SWNT). *J. Phys. Chem. B*, **107**, 11048 (2003).
- [192] Y. Yang, S. Lim, Y. Chen, D. Ciuparu, G.L. Haller. Synthesis and characterization of highly ordered Ni-MCM-41 mesoporous molecular sieves. *J. Phys. Chem. B*, **109**, 13237 (2005).
- [193] D. Ciuparu, Y. Chen, S. Lim, G.L. Haller, L. Pfefferle. Uniform-diameter single-walled carbon nanotubes catalytically grown in cobalt-incorporated MCM-41. *J. Phys. Chem. B*, **108**, 503 (2004).
- [194] Y. Chen, D. Ciuparu, S. Lim, G.L. Haller, L.D. Pfefferle. The effect of the cobalt loading on the growth of single wall carbon nanotubes by CO disproportionation on Co-MCM-41 catalysts. *Carbon*, in press (2006).
- [195] Y. Yang, Z. Hu, Y.N. Lü, Y. Chen. Growth of carbon nanotubes with metal-loading mesoporous molecular sieves catalysts. *Mater. Chem. Phys.*, **82**, 440 (2003).
- [196] Y. Yang, S. Lim, C. Wang, G. Du, G.L. Haller. Statistical analysis of synthesis of Co-MCM-41 catalysts for production of aligned single walled carbon nanotubes (SWNT). *Microp. Mesop. Mater.*, **74**, 133 (2004).
- [197] M. Urban, D. Mehn, Z. Konya, J. Zhu, I. Kiricsi. Production of multiwall carbon nanotubes in the modified pore system of mesoporous silicates. *Diamond Related Mater.*, **13**, 1322 (2004).
- [198] M. Urban, D. Mehn, Z. Konya, J. Zhu, I. Kiricsi. Production of carbon nanotubes inside the pores of mesoporous silicates. *Chem. Phys. Lett.*, **359**, 95 (2002).
- [199] D. Ciuparu, R.F. Klie, Y. Zhu, L. Pfefferle. Synthesis of pure boron single-wall nanotubes. *J. Phys. Chem. B*, **108**, 3967 (2004).
- [200] J. Kim, J.W. Grate, P. Wang. Nanostructures for enzyme stabilization. *Chem. Engng. Sci.*, **61**, 1017 (2006).
- [201] M. Hartmann. Ordered mesoporous materials for bioadsorption and biocatalysis. *Chem. Mater.*, **17**, 4577 (2005).
- [202] H.H.P. Yiu, P.A. Wright. Enzymes supported on ordered mesoporous solids: a special case of an inorganic-organic hybrid. *J. Mater. Chem.*, **15**, 3690 (2005).
- [203] P. Wang, S. Dai, S.D. Waezsada, A.Y. Tsao, B.H. Davison. Enzyme stabilization by covalent binding in nanoporous sol-gel glass for non-aqueous biocatalysis. *Biotechnol. Bioeng.*, **74**, 249 (2001).
- [204] P.H. Pandya, R.V. Jasra, B.L. Newalkar, P.N. Bhatt. Studies on the activity and stability of immobilized α -amylase in ordered mesoporous silica. *Microp. Mesop. Mater.*, **77**, 67 (2005).

- [205] J.F. Diaz, K.F. Balkus Jr. Enzyme immobilization in MCM-41 molecular sieve. *J. Mol. Catal. B*, **2**(2–3), 115 (1996).
- [206] J.M. Kisler, A. Dähler, G.W. Stevens, A.J. O'Connor. Separation of biological molecules using mesoporous molecular sieves. *Microp. Mesop. Mater.*, **44–45**, 769 (2001).
- [207] F. Farzaneh, J. Taghavi, R. Malakooti, M. Ghandi. Immobilized vitamin B12 within nanoreactors of MCM-41 as selective catalyst for oxidation of organic substrates. *J. Mol. Catal. A: Chem.*, **244**, 252 (2006).
- [208] A.J. O'Connor, A. Hokura, J.M. Kisler, S. Shimazu, G.W. Stevens, Y. Komatsu. Amino acid adsorption onto mesoporous silica molecular sieves. *Separ. Purif. Technol.*, **48**, 197 (2006).
- [209] M. Vallet-Regi, A. Ramila, R.P. Del Real, J. Perez-Pariente. A new property of MCM-41: drug delivery system. *Chem. Mater.*, **13**, 308 (2001).
- [210] B. Muñoz, A. Rámila, J. Pérez-Pariente, I. Dýáz, M. Vallet-Regy. MCM-41 organic modification as drug delivery rate regulator. *Chem. Mater.*, **15**, 500 (2003).
- [211] M.E. Gimón-Kinsel, V.L. Jimenez, L. Washmon. Mesoporous molecular sieve immobilized enzymes. *Stud. Surf. Sci. Catal.*, **117**, 373 (1998).
- [212] L. Washmon-Kriel, V.L. Jimenez, K.J. Balkus Jr.. Cytochrome C immobilization into mesoporous molecular sieves. *J. Mol. Catal. B. Enzymatic*, **10**(5), 453 (2000).
- [213] J. Deere, E. Magner, J.G. Wall, B.K. Hodnett. Adsorption and activity of cytochrome C on mesoporous silicates. *Chem. Commun.*, **5**, 465 (2001).
- [214] J. Deere, E. Magner, J.G. Wall, B.K. Hodnett. Mechanistic and structural features of protein adsorption onto mesoporous silicates. *J. Phys. Chem. B*, **106**, 7340 (2002).
- [215] J. Deere, E. Magner, J.G. Wall, B.K. Hodnett. Adsorption and activity of proteins onto mesoporous silica. *Catal. Lett.*, **85**, 19 (2003).
- [216] A. Vinu, V. Murugesan, O. Tangermann, M. Hartmann. Adsorption of cytochrome C on mesoporous molecular sieves: influence of pH, pore diameter, and aluminum incorporation. *Chem. Mater.*, **16**, 3056 (2004).
- [217] A. Vinu, V. Murugesan, M. Hartmann. Adsorption of lysozyme over mesoporous molecular sieves MCM-41 and SBA-15: influence of pH and aluminum incorporation. *J. Phys. Chem. B*, **108**, 7323 (2004).
- [218] S. Adams, A.M. Higgins, R.A.L. Jones. Surface-mediated folding and misfolding of proteins at lipid/water interfaces. *Langmuir*, **18**, 4854 (2002).
- [219] F.-M. Fu, D.B. DeOliveira, W.R. Trumble, H.K. Sarkar, B.R. Singh. Secondary structure estimation of proteins using the amide-III region of Fourier-transform infrared-spectroscopy – Application to analyze calcium binding-induced structural changes in casequestrin. *Appl. Spectrosc.*, **48**(11), 1432 (1994).
- [220] J.M. Kisler, G.W. Stevens, A. O'Connor. Adsorption of proteins on mesoporous molecular sieves. *J. Mater. Phys. Mech.*, **4**, 89 (2001).
- [221] J. Yang, A. Daehler, G.W. Stevens, A.J. O'Connor. Adsorption of lysozyme and trypsin onto mesoporous silica materials. *Stud. Surf. Sci. Catal.*, **146**, 775 (2003).
- [222] H.H.P. Yiu, P.A. Wright, N.P. Botting. Enzyme immobilization using SBA-15 mesoporous molecular sieves with fictionalized surfaces. *J. Mol. Catal. B*, **15**, 81 (2001).
- [223] A.M. Tope, N. Srivinas, S.J. Kulkarni, K. Jamil. Mesoporous molecular sieve (MCM-41) as support material for microbial cell immobilization and transformation of 2,4,6-trinitrotoluene (TNT): a novel system for whole cell immobilization. *J. Mol. Catal. B*, **16**, 17 (2001).
- [224] Y.-S. Lin, C.-P. Tsai, H.-Y. Huang, C.-T. Kuo, Y. Hung, D.-M. Huang, Y.-C. Chen, C.-Y. Mou. Well-ordered mesoporous silica nanoparticles as cell markers. *Chem. Mater.*, **17**, 4570 (2005).