Chem. Mater. **2001,** *13,* 3151−3168

Periodic Mesoporous Silica-Based Organic−Inorganic Nanocomposite Materials

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Received February 8, 2001. Revised Manuscript Received July 10, 2001

The area of periodic mesoporous materials prepared by cooperative assembly in the presence of amphiphile molecules underwent dramatic growth. Among the silica-based materials, many types may be regarded as ordered organic−inorganic nanocomposites. These were divided into five categories: (i) noncalcined amphiphile/silica mesophases, (ii) mesoporous silicas with organically modified surfaces, (iii) expanded mesoporous silicas, (iv) mesoporous organosilicates, and (v) mesoporous silica with occluded organic materials such as polymers. The diversity of such nanocomposites created new potential opportunities in materials sciences, catalysis, separation, and environmental remediation. These applications involved the development of new chemistry not only within the confined pores and channels but also on functionalized surfaces as well as within the channels walls. The current review deals with recent progress in the synthesis, characterization, and applications of each of these types of periodic mesoporous silica-based hybrid materials.

1. Introduction

Since the publication of the first paper on the so-called M41S periodic mesoporous silica[1] in the early 1990s, this field has attracted so much interest that it has grown into a separate field that has been the subject of numerous reviews.[2−10] A number of driving forces were behind this spectacular progress. What began as the synthesis of three M41S mesophases, namely, MCM-41 (hexagonal, *p*6*mm*), MCM-48 (cubic, *Ia*3*d*), and MCM-50 (lamellar), under basic conditions in the presence of alkyltrimethylammonium surfactants as supramolecular templates grew into a large number of synthesis strategies. At present, periodic mesoporous silicas may be readily synthesized under a wide range of pHs from strongly acidic to highly basic conditions and from subambient temperatures to ≈150 °C using cationic, anionic, neutral, zwitterionic, bolaamphiphile, gemini, and divalent surfactants and a variety of commercially available polymers. Numerous new mesophases were also discovered. These included SBA-1 and SBA-6 (*Pm*3*n*),[12−14] SBA-2 and SBA-12 (*P*6$_3$/*mmc*),[14,15] SBA-11 (*Pm*3*m*),[15] SBA-16 (*Im*3*m*),[15] SBA-8 (*cmm*),[16] and disordered HMS,[17] MSU-n,[18] MSU-V,[19] and KIT-1.[20] In addition, several approaches were invented to control the pore size of such materials from the low end of mesopore dimensions, ≈2 nm, to well in the macropore regime.[21] Mesostructured materials with unique morphologies were also synthesized.[22−28]

This review will be limited to periodic mesoporous organic−inorganic silica-based nanocomposite materials. Alternatively, these materials will be referred to as hybrid. Before calcination, all silica-based mesophases may be regarded as organic−inorganic composite materials. However, except for few studies, little attention has been paid to the properties and applications of noncalcined periodic mesophases. As a general rule, such materials were either solvent-extracted or calcined before being investigated further. Sugi et al.[29] however, found that noncalcined MCM-41 silica exhibits high catalytic activity for the Knoevenagel condensation. On the basis of ^{29}Si NMR data, the authors came to the conclusion that the catalytic activity is attributable to basic $(SiO)_3SiO^-$ sites, which occur in large amounts in noncalcined silica mesophases. Tolbert and co-workers[30,31] discovered recently that an ordered silica/surfactant MCM-41 mesophase exhibits remarkable behavior under high pressure. It was found that the mesoscopic order can be retained up to 12 GPa and the distortions induced under high pressure are reversible, whereas bulk silica glass is known to undergo irreversible densification above 8 GPa. A MCM-41 surfactant/silica nanocomposite prepared in the presence of cetyltrimethylammonium bromide (CTMAB) at 100 °C under basic conditions exhibited a rigidity half that of solid silica glass, but more than 5 times higher than that of disordered silica aerogel containing the same inorganic fraction. Furthermore, the rigidity of the composite improved by a factor of 2 upon postsynthesis annealing in water at 100 °C, which is known to improve the ordering and enhance the silica condensation. These unique properties were attributed to the nanoscale nature of the materials.[30] Further studies dealt with luminescence measurements as a function of pressure for a Re complex that was incorporated into a CTMAB/silica composite during synthesis.[31] Variations of the luminescence peak position reflect changes in the local environment of the complex inside the mesophase. The obtained data indicated that the surfactant did not

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10.1021/cm011039l CCC: $20.00

Table 1. Postsynthesis Modification of Periodic Mesoporous Silicas

silica mesophase	modification agent	refs
MCM-41	disilazane: $HN(SiR^1R^2_2)_2$; $R^{1,2}$: H; Me; Ph; vinyl	44
MCM-41	TMCS	45
MCM-41; Ce−MCM-41	APTES; OTES; ODCS; MPTMS	46−48
MCM-41	$Nd(N(SiMe_3)_2)_3$; $Nd(N(SiHMe_2)_2)_3$	49
mesoporous silica via acid route	TMCS	50
	MPTMS	
	APTMS	
MCM-41	VTCS	51
MCM-41; Ti−MCM-41; MCM-48; Ti−MCM-48	TMCS	52
MCM-41	TMCS; BDMCS; ODMCS; APTES; hexanoyl chloride	53
MCM-41	Ph_2SiCl_2 and $(MeO)_3Si(CH_2)_3NH_2$	54
FSM-type	TMCS; ODMCS; ODMCS; APTES; APDMES	55
MCM-41; MCM-48	TMCS	56
SBA-15; MCM-41	ODMCS; TMCS	57
Ti−MCM-41; Ti−MCM48	TMCS	58
Ti−MCM-41	HMDS	59, 60
Ti−MCM-41	HADS	61
mesoporous silica−transition metal complexes	APTES	62
Ti−MCM-41	DCDPS	63
Ti−MCM-41	BSTFA	64
Ti−MCM-41	TMSI; BSTFA; MSTFA	65, 66
MCM-41; Ti−MCM-41	APTMS; CPTMS	67
MCM-41	VCp_2Cl_2; TMCS	68
HMS	chromium complex	69
MCM-41	TMSPEO	70
MCM-41	APTES; CPTES; HMDS	71
MCM-41	TMSPDA	72
MCM-41	APTES; CPTES	73, 74
MCM-41	CPMS; HMDS; TBD	75
MCM-41	MPTMS	76
MCM-41	MPEDA	77
HMS	APDMS	78

become completely rigid up to 10 GPa, well above the solidification point of most organics. This is again consistent with the high mechanical strength of the nanostructured silica shell, which protects the organic molecules located inside the channels.

In addition to the as-synthesized amphiphile/silica hybrids, the following materials fit a broad definition of periodic mesoporous silica based organic−inorganic nanocomposites: (1) mesoporous silicas with organically modified surfaces, (2) expanded mesoporous silicas, (3) mesoporous organosilicates, and (4) mesoporous silica with occluded organic materials such as polymers. The current review will be devoted to the synthesis, characterization, and applications of each one of these types of materials. It will, however, not address another important issue regarding periodic surfactant or polymer/silica nanocomposites, namely, the occurrence of numerous phase transitions depending on the synthesis conditions, particularly temperature and time as reported by several groups.[32−37]

2. Mesoporous Silicas with Organically Modified Surfaces

Chemical surface modification of periodic mesoporous silicas via covalent bonding of organic molecules has been achieved using two general strategies. The postsynthesis procedure was the first to be used as it was already described in the early work on Mobil M41S[38] and Toyota FSM-16[39] silicas. Subsequently, co-condensation procedures were introduced by Burkett et al.,[40] Macquarrie,[41] and others.[6,9] The following is an account on the different synthesis procedures, characterization, and the potential applications of mesoporous silica with organically modified surfaces.

2.1. Synthesis. 2.1.1. Postsynthesis Procedures. As reported by Maschmeyer[6] and others,[9,42] there have been three main approaches for postsynthesis surface modification or derivatization of mesoporous silica.

(i) Primary modification via direct grafting, which consists of reacting a suitable organosilane reagent with the silica surface using an appropriate solvent under reflux conditions.[42] Grafting with silane coupling agents such as chlorosilanes, alkoxysilanes, and silylamines under anhydrous conditions is more commonly referred to as silylation.[43] Silylation may also be achieved in the presence of disilazane reagents $[HN(SiR_3)_2]$ under mild conditions.[43,44] The grafting reactions use the silanol groups present on the silica surface. There are three different types of surface silanols, that is, single, hydrogen-bonded, and geminal hydroxyl groups.[8,9,45] Only free ($\equiv$SiOH) and geminal ($=$Si(OH)$_2$) silanol groups take part in silylation reactions, but hydrogen-bonded silanol groups are less accessible to modification because they form hydrophilic networks.[9] When the silylation procedure is performed under controlled wet conditions, because of the increased density of surface hydroxyl groups, the grafted organosilane species forms a continuous layer on the silica surface. This procedure is referred to as coating. Even though most primary surface modifications were carried out using calcined, and often rehydrated mesoporous silica, the simultaneous extraction of the surfactant and grafting of organic functionalities without prior calcination was also shown to be feasible.[39,46−48]

(ii) Secondary and higher order modifications that consist of further reactions of the previously grafted species to create new functionalities.

(iii) Transformation of the materials prepared under procedure (i) or (ii) by additional treatments.

As shown in Table 1, even though MCM-41 received the greatest attention, other types of ordered mesoporous silicas have also been used for surface modification by postsynthesis grafting.[46−80] In one of the earliest studies, Jaroniec et al.[53] modified 5-nm pore MCM-41 silica using monomeric ligands such as trimethylsilyl, butyldimethylsilyl, and octyldimethylsilyl and polymeric-type 3-aminopropylsilyl and octylsilyl ligands.[53] On the basis of extensive characterization of the obtained materials, the following conclusions were drawn: (i) the surface coverages were between 2.5 and 3 μmol/m^2; (ii) the pore diameters decreased as the size of the ligands increased; (iii) the chemical-bonding procedure did not alter the structural ordering of the starting material; (iv) the surface affinity to water was strongly dependent on the nature of the ligands. Using trimethylchlorosilane, Zhao and Lu[45] found that, under otherwise the same conditions, the surface coverage increases linearly from 30 to 85% as the pre-outgassing temperature of the parent material increased from 373 to 723 K. This was due to increased density of free SiOH groups as a result of gradual dehydroxylation of hydrogen-bonded OH groups. Lim and Stein[51] found that postsynthesis grafting of vinyl groups takes place mostly at the external surface and near the pore openings of the materials. In connection with this finding, Shephard et al.[54] proposed a two-step approach to selective functionalization of the internal surface. The authors proceeded first to the passivation of the external surface upon reaction with 0.01 equiv of Ph_2SiCl_2 based on the assumption that the external Si−OH would be the most kinetically favored for silylation. Subsequently, they functionalized the internal surface with $(CH_3O)_3Si(CH_2)_3NH_2$ followed by protonation with HBF_4 and then anchored a coordination complex onto the ammonium tethers. The degree of silylation of MCM-41 using various disilazane agents of the general formula $(HN(SiR^1R^2{}_2)_2$ was found to depend on the steric bulk/shape of the R groups.[43,44] The highest surface coverage was obtained with the sterically less demanding silyl groups such as $SiH(CH_3)_2$. Adsorption of *tert*-butanol on such modified materials used to probe the remaining free hydroxyl groups indicated that the amount and accessibility of the silanol groups were in the following order: MCM-41 $\gg$ MCM-41SiMePh$_2$ > MCM-41SiMe$_3$ $\approx$ MCM-41SiMe$_2$Ph.

Instead of grafting organic functions through Si−O−Si bridges using silicon-bearing species, Yamamoto and Tatsumi[79] developed an interesting strategy leading to methyl groups covalently bonded to surface silicon atoms. The first step of this procedure was the esterification of surface hydroxyl species with butanol to form Si−OBut, followed by reaction with the Grignard reagent CH_3MgI, leading to Si−CH$_3$.

Other types of mesoporous silicas such as SBA-15 and FSM-16 were also surface-modified using different silylating agents. Kimura et al.[55] derivatized calcined and acid-treated FSM-16 material. The maximum surface coverage for calcined materials was 73%, whereas for acid-treated materials, it reached 100% because of the presence of larger amounts of silanol groups on the surface. Organosilane modification of SBA-15 silica using bulky and small silyl groups (ODMS and TMS) allowed Ryoo et al.[57] to detect via selective pore blocking the occurrence of microporosity.

Simultaneous surfactant removal and surface derivatization via the formation of strong siloxane bonds was achieved by Antochshuk and Jaroniec[46−48] on MCM-41 and Ce−MCM-41. The authors showed that this displacement reaction was possible as long as the organosilane exhibits at least one reactive group such as Cl−Si≡, EtO−Si≡, or MeO−Si≡. Typical surface coverages were 2.2−2.8 mmol/g; however, the aminopropylsilyl ligand gave rise to lower coverages compared to other ligands of similar size. This was attributed by the authors to the specificity of interactions between the silica surface and amino species. According to Lin et al.,[50] the surfactant-silyl exchange process is greatly favored when applied to mesoporous silica prepared under acidic conditions because of the weaker interactions between the silica walls and the surfactant compared to materials prepared under basic conditions in the presence of alkyltrimethylammonium cations. Using alkyl and alkoxysilanes, namely, TMCS, MPTMS, and APTMS, higher surface coverages (3.5−4.5 mmol/g) were obtained in ethanol under milder conditions (50−70 °C; 1−3 h).

Postsynthesis surface modification of mesoporous silicas with basic functional groups was achieved via primary or secondary modification. As described by Cauvel et al.[71] and Jaenicke and co-workers,[73,74] direct grafting of 3-aminopropyltriethoxysilane into MCM-41 affords NH_2 bearing mesoporous silica. Likewise, Choudary et al.[72] grafted trimethoxysilylpropylenediamine. To synthesize mesoporous silica with a piperidine-modified surface, Cauvel et al.[71] proceeded in two steps, first grafting chloropropyltriethoxysilane and then refluxing in the presence of piperidine in toluene. Neutralization of the residual OH groups was achieved by reaction with hexamethyldisilazane either before[75] or after[71] contacting with the secondary amine. Subba Rao et al.[70] reported another two-step procedure where the inner surface of a MCM-41 was contacted with 3-trimethoxysilylpropoxymethyloxyrane and then the epoxide group was reacted with 1,5,7-triazabicyclo[4,4,0]-dec-5-ene under mild conditions.

In contrast with mesoporous silicas bearing basic functionalities, only few investigations were devoted to the preparation of similar hybrid materials with acidic functions. The most relevant investigations dealt with the grafting of Bronsted propylsulfonic acid groups on MCM-41 silica surface.[76,80] The modification was performed by surface coating using 3-mercaptopropyltriethoxysilane followed by oxidation in the presence of hydrogen peroxide and acidification with dilute sulfuric acid solution.

Modification of MCM-48 via grafting of VO_x species on the surface using DMDCS as a coupling agent was reported by Van Der Voort and co-workers.[81,82] They first silylated the material with DMDCS and then hydrolyzed it to create Si−O−Si(CH$_3$)$_2$OH surface species, which were used to anchor VO(acac)$_2$. Calcination of the obtained material at 450 °C led to surface VO_x supported mesoporous silica. The grafting or tethering of metal complexes to the internal surface of mesoporous silicas was also reported by several authors.[49,56,83−87] The covalent attachment of the organometallic or coordination complexes occurred either by direct grafting,[49,85,86] or via a spacer ligand (tethering).[83,84,88]

Surface postsynthesis derivatization of MCM-41 silica with appropriate ligands to be used as chiral catalysts[89−93] or as the stationary phase in chiral HPLC[94] attracted much interest. The modification procedure consisted generally of deactivating the external surface of the silica and then reacting the support first with a chiral catalytic precursor, followed by an organometallic complex.

Using a multistep approach inspired from molecular imprinting techniques, Liu and co-workers[95,96] created on the internal surface of a 10-nm pore ordered silica a soft structure with micropores of different shapes. This procedure required the synthesis of tripod and dipod molecules, which were treated with APTMS and grafted on the internal silica surface. Long-chain alkyltrimethoxysilanes were then used to cover the free surface via reaction with the remaining SiOH groups. The last step was the removal of the tripod and dipod molecules by acid hydrolysis, thus generating cavities with designed shapes.

2.1.2. One-Pot Synthesis of Mesoporous Silicas with Organically Modified Surfaces. Co-condensation of siloxane and organosiloxane precursors via the sol−gel technique to produce functionalized amorphous xerogels silica has been extensively investigated.[97] In these materials, an organic moiety is covalently linked via a nonhydrolyzable Si−C bond to a siloxane species, which hydrolyzes to form a silica network. Burkett et al.[40] and Macquarrie[41] were the first to combine this approach with the supramolecular templating technique to generate, in a single step, ordered mesoporous silica-based nanocoposites with covalently linked organic functionalities protruding from the inorganic walls into the pores. The former authors prepared phenyl bearing MCM-41, while the latter synthesized a hexagonal mesoporous silica (HMS) via the nonionic amine route modified with cyanoethyl ligands. The structural ordering of the hybrid material was preserved in the presence of up to 20 mol % of organosiloxane, while the upper limit of its incorporation into the mesoporous hybrid material was ≈40%. One-step synthesis of MCM-41-type hybrid materials containing vinyl functional groups was reported by Stein and co-workers.[51,98] They used the bromination reaction to prove the occurrence and accessibility of the vinyl groups. In addition, the authors compared the vinyl-containing materials prepared via the postsynthesis treatment vs the one-pot synthesis procedure and concluded that in the latter case the functional groups were homogeneously distributed throughout the material, while in the first case, the vinyl ligands occurred mostly near the openings of the channels. Hall et al.[99] attempted to synthesize cubic (MCM-48) hybrid mesoporous silica containing phenyl, allyl, aminopropyl, and mercaptopropyl functional groups. However, the cubic mesophase was obtained only in the presence of phenyltriethoxysilane (PTES) with a molar content of 10%, while other groups afforded materials with no apparent structural ordering. In the case of the MCM-41 hexagonal phase, the authors demonstrated the possibility of incorporating two organic functionalities up to 20 mol % into the ordered silica framework without disruption of the long-range mesoscopic order.

As shown in Table 2, the one-step preparation of surface-functionalized mesoporous silicas was extended to materials prepared via nonionic surfactant (e.g., alkylamines) or polymer−silica self-assembly such as the so-called HMS and MSU type of mesoporous silicas.[102,103,106−108] In the case of HMS materials, Mercier and Pinnavaia[103] adopted two different approaches for the formation of hybrid organic−inorganic nanocomposites using different organotriethoxysilanes, that is, (i) template substitution involving the partial replacement of equal numbers, *x*, of moles of TEOS and alkylamine surfactant with *x* moles of organosilane, and (ii) direct addition of organosilane, while maintaining the same ratio of alkylamine surfactant to TEOS used to synthesize unfunctionalized HMS silica. The former approach was found to be suitable for incorporating organic moieties whose size is comparable to the amine surfactant, while the latter was found to be convenient for the incorporation of organic groups smaller than the amine surfactant. This work showed that successful incorporation of organosilanes into the pore walls of the mesostructure requires a chain length of at least three methylene units to ensure interaction with the hydrophobic core of the surfactant micelle.

Table 2. One-Pot Synthesis of Surface-Modified Periodic Mesoporous Silicas

silica mesophase	modification agent	refs
MCM-41	PTES; OTES	40
HMS	APTMS; CES	41
MCM-41	VTES	98
MCM-41; MCM-48	PTES + ATMS: APTES; MPTES	99
MCM-41	$(RO)_3Si{-}R'$: R = Me; R′ = $(CH_2)_3SH$, $(CH_2)_3NH_2$; $(CH_2)_3OCH_2CH(O)CH_2$; $(CH_2)_3NCHNCH_2CH_2$; CH_2CHCH_2	100
MCM-41	DEDMS	101
MSU-1; MSU-2	MPTMS	102
HMS−C8; HMS−C12	OTES; MPTMS; PTES; BTMS; PTMS; ETES	103
SBA-15	MPTMS	104
SBA-15	ETES; EDAPTMS CES-triol;	105

The one-pot synthesis of different mesoporous silicas functionalized with sulfonic acid groups was reported by several authors.[76,106,109−111] In most cases, a thiol-bearing hybrid mesoporous molecular sieve was first synthesized via co-condensation of TEOS or TMOS and MPTES. The mercaptopropyl groups were then oxidized by nitric acid[112] or hydrogen peroxide,[76,80,109,110,113] leading to sulfonic acid groups. Very detailed investigations on the direct synthesis of MCM-41 silica containing methyl or propyl groups in addition to mercaptopropyl ligands under a wide range of synthesis conditions was reported recently by Diaz et al.[110,111] The average density of the functional groups and the average distance between the organic groups on the surface were estimated to be 3−4 organic moieties/100 Å^2 and 5−6 Å, respectively. To represent the surface of the hybrid MCM-41, the authors proposed the model shown schematically in Figure 1. In another variation of the one-pot synthesis procedure, Stucky and co-workers[104] used MPTMS in the presence of hydrogen peroxide to prepare sulfonic acid bearing SBA-15 silica. This approach was found to apply also for simultaneous incorporation of multiple surface functionalities. Mixtures of MPTMS and BTES and of MPTMS and MTES were used in the presence of TEOS, P123, and H_2O_2 to prepare SBA-15 with two functional groups. In situ oxidation of the thiol

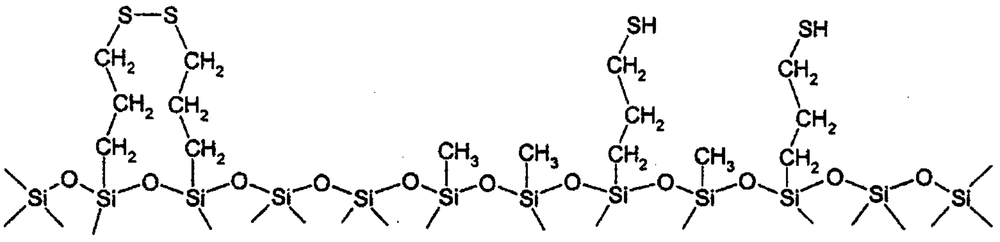

Figure 1. Schematic representation of the surface of the [Me/SH]−MCM-41 materials. Adapted from ref 110.

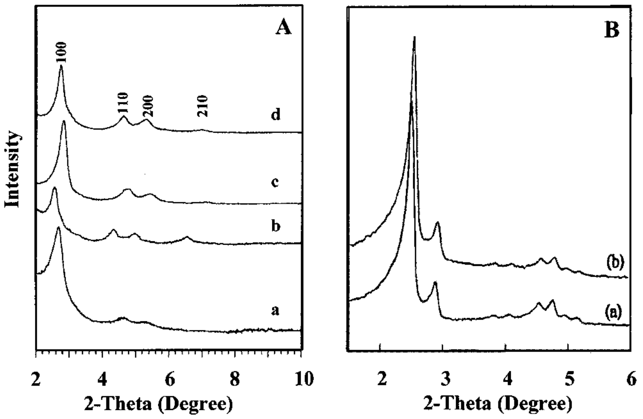

Figure 2. (A) XRD patterns for (a) template-free Na−MCM-41, (b) as-synthesized Si−MCM-41, (c) template-extracted Si−MCM-41, and (d) fully silylated Si−MCM-41. Co Kα (λ = 0.179 nm). Adapted from ref 45. (B) XRD patterns for (a) Si−MCM-48 (nonsilylated) and (b) Si−MCM-48 (silylated). Adapted from ref 52.

group by H_2O_2 was found to be more efficient than postsynthesis oxidation (100% vs 25−77%). The obtained material exhibited an acid-exchange capacity of 1−2 mequiv of H^+/g of silica.

Direct synthesis of basic MCM-41- and HMS-type silicas in the presence of APTMS was also reported by several researchers.[41,115] Furthermore, Macquarrie et al.[113] described a large number of one-step single and dual functionalizations of HMS silica.

Titanosilicate molecular sieves are known as good catalysts for selective oxidation of organic substrates in the presence of dilute hydrogen peroxide. However, it is believed that their catalytic activity depends on the surface hydrophobicity. To achieve high hydrophobicity, several workers carried out one-step syntheses of organically modified Ti−MCM-41, Ti−MCM-48, and Ti−HMS via co-condensation in the presence of different functional groups such as methyl,[116−119] phenyl,[116,117,119] and chloropropyl.[117,120]

2.2. Characterization. Hybrid mesoporous silicate molecular sieves were characterized by a battery of techniques including XRD, TEM, adsorption measurements, ^{29}Si and ^{13}C NMR, IR, UV−visible, TGA, and elemental analysis. Similar to their pure silica counterparts, surface-functionalized mesoporous materials exhibit XRD patterns dominated by low-angle peaks. Representative X-ray diffractograms for MCM-41, MCM-48, HMS-n, and SBA-15 hybrid materials prepared via postsynthesis and one-pot synthesis procedures are shown in Figures 2 and 3, respectively. Generally, postsynthesis surface functionalization does not drastically affect their structural ordering.[46,51,52,56,62,73,120] In the case of MCM-41, for example, Lim and Stein[51] showed that the overall intensity of the XRD peaks decreased, while the d_{220} and d_{310} diffractions disappeared upon grafting with vinyl groups. However, Antochshuk and Jaroniec[48] found that the simultaneous surfactant removal and grafting of amino- and mercaptopropyl ligands actually improves the structural ordering of MCM-41.

In the case of hybrid mesoporous materials synthesized in a single step via co-condensation, the structural ordering was strongly dependent on the relative amount of the organic precursor present in the synthesis mixture. Several research groups observed a progressive decrease in the mesoscopic order as the relative amount of organosilane in the synthesis mixture increased.[40,99,100,105] The upper limit for the organosiloxane to TEOS ratio in the synthesis gel, above which no structural ordering occurred, was determined in many cases.[40,99,103,105,110] This limit was found to be dependent on the nature of the organosiloxane as well as on the mesophase structure. For instance, Mann and co-authors[40,99] found that the hexagonal ordering of a hybrid MCM-41 vanished completely when more than 20% mol (silica basis) of organotrialkoxysilane was used in the synthesis mixture. As for SBA-15, this limit was also estimated to be around 10% (wt/wt total silica) for MPTMS[104] or 20% for ETES, EDAPTMS, and CES-triol.[105] In addition to the overall decrease in the structural ordering of the material upon addition of organosilanes as demonstrated by the decline of the intensity of the main XRD peaks and the disappearance of high-order diffraction peaks, several authors reported a gradual decrease in the d_{100} spacing of surface-functionalized mesophases such as MCM-41,[40,51,99,100] SBA-15,[104,105] HMS,[103] and MSU.[102] In the case of MCM-48, Hall et al.[99] showed that functionalization with phenyl groups (10%) afforded ordered cubic material whose structure collapsed upon surfactant extraction, while amino, thiol, or allyl groups did not lead to MCM-48 mesophases.

Another important effect of silylation is the increased stability of the hybrid materials against moisture and compression compared to their pure silica counterparts. For instance, Tatsumi and co-workers[52,56] found that trimethylsilylation improved the stability toward moisture and compression of both Ti-containing and Ti-free MCM-41 and MCM-48. Similar observations were made in the case of other mesophases and other ligands.[40−48,51,79,104,121]

Nitrogen adsorption measurements revealed a systematic decrease in the BET surface area and the pore volume for hybrid materials prepared by postsynthesis procedures.[7,49,46−50,53,55,57,122] Generally, the type IV adsorption isotherm characteristic of mesoporous materials was preserved upon postsynthesis modification,

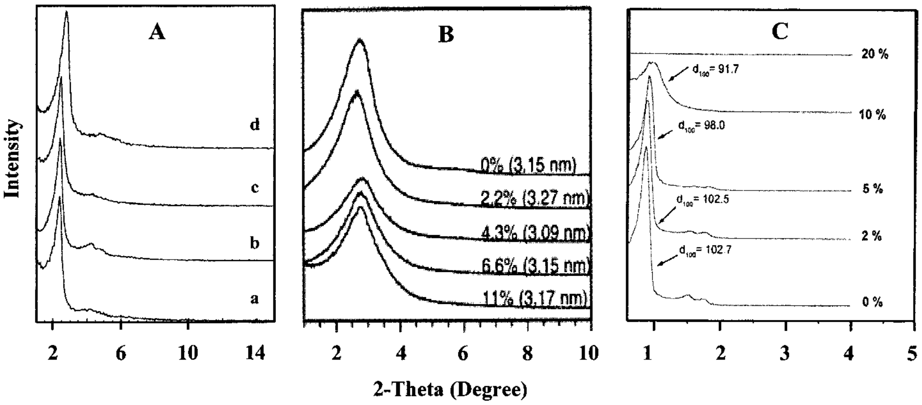

Figure 3. (A) Powder XRD patterns for (a) as-synthesized -MCM-41 (1:4 VTES/TEOS), (b) MCM-41 after surfactant extraction, (c) sample [b] after bromination for 6 days, (d) sample [a] calcined in air at 550 °C for 10 h. Adapted from ref 98. (B) Powder XRD patterns for octylamine-assembled HMS−C8 silicas functionalized with octyltriethoxysilane. Adapted from ref 103. (C) XRD patterns for extracted functionalized SBA-15 with different molar ratios of MPTMS/(MPTMS + TEOS) in the initial mixture. Adapted from ref 104.

but the capillary nitrogen condensation step shifted gradually to lower relative pressures indicative of decreasing pore sizes. This decrease was dependent on the size of the grafted ligand[43,46−48,53,55] and the surface coverage.[53,55] In contrast, Anwander and Roesky[49] observed that the characteristic type IV isotherm for pure MCM-41 silica was replaced by the type I isotherm after anchoring silylamide species on the internal surface. As for functionalized periodic mesoporous silicas prepared by co-condensation procedures, they often exhibit high surface areas[40,41,98−102] and pore sizes of 1.8−3.5 nm for modified MCM-41 and 6 nm for functionalized SBA-15.[40,99,102,104,112,117,123] Moreover, it appears that the hybrid mesoporous silicas prepared via co-condensation exhibit thicker pore walls compared to their corresponding pure silica derivatives.[51,100−102,104,106,120]

Solid-state ^{29}Si, ^{13}C, and to a lesser extent ^{1}H MAS NMR measurements were used to gain insights into the silicon,[40,45,50,52,55,56,79,102,104,107,114,123−125] carbon,[40,51,79,99,101,104,110,124,125] and hydrogen[43,44] environments and to assess the degree of surface functionalization of mesoporous silicas. For instance, ^{1}H MAS NMR showed that, upon surface modification, the resonance at 1.8 ppm attributable to isolated SiOH groups in dehydrated MCM-41 disappear, while new signals whose chemical shifts depend on the nature of the ligand appear (Figure 4). ^{29}Si MAS NMR data showed that postsynthesis modification results often in a decrease in the amount of Q^3 [$HOSi(OSi)_3$] in favor of Q^4 [$Si(OSi)_4$] species, and the appearance of T^n [$C-Si(OSi)_n(OH)_{3-n}$; $n = 1-3$] sites. In a comparative investigation of vinyl−MCM-41 samples prepared by postsynthesis grafting or by direct synthesis, Lim and Stein[51] found that one-pot synthesis leads to more tightly incorporated vinyl groups in the silica wall surface as only T^3 and T^2 resonances were observed. Identification of grafted moieties was performed mainly by ^{13}C MAS NMR on the basis of well-known chemical shifts corresponding to specific functional groups and sometimes in combination with FTIR data.[75,99]

Infrared spectroscopy was used to monitor the consumption of silanol groups that exhibit a sharp and strong absorption band at 3695 cm^{-1} [43−45] and the functionalization of the silica surface through the development of characteristic vibrations.[40,44,45,50,75,101,104,110,126]

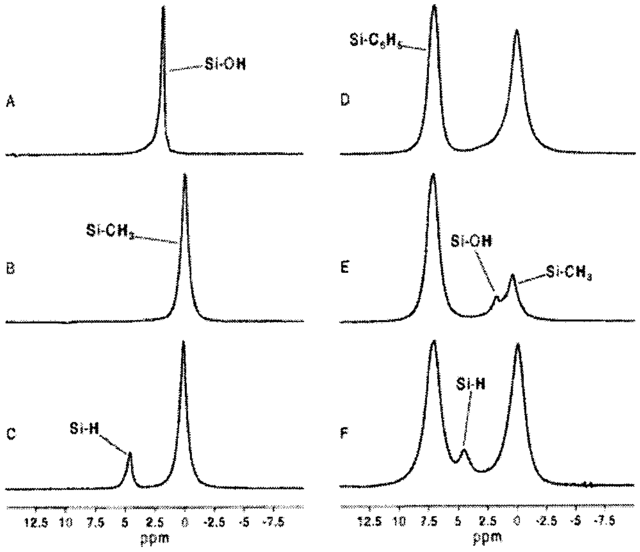

Figure 4. ^{1}H MAS NMR spectra for nonmodified and silylated samples: (A) MCM-41 dehydrated at 280 °C/10^{-5} Torr, (B) [MCM-41]SiMe$_3$, (C) [MCM-41]SiHMe$_2$, (D) [MCM-41]SiMe$_2$-Ph, (E) [MCM-41]SiMePh$_2$, and (F) [MCM-41](SiMePh$_2$)-(SiHMe2). For silylated samples, all measurements were made after pretreatment at 250 °C/10^{-3} Torr. Adapted from ref 43.

For instance, the presence of methyl groups bonded to Si may be unambiguously demonstrated by the appearance of a strong infrared band at 1276 cm^{-1},[64−66,101,110] while the bands around 2575 and 2890−2930 cm^{-1}, which correspond to the stretching vibrations of CH$_2$ and S−H species, respectively indicate the occurrence of alkylthiol groups.[104,110]

Thermogravimetric analysis was used often to probe the thermal stability as well as the hydrophobic or hydrophilic character of the hybrid materials. For instance, Jaroniec et al.[53] showed that the weight loss profile of MCM-41 silica was drastically altered upon silylation with different functional groups (Figure 5). The hydrophobic character of the silylated MCM-41 was evidenced by the moderate weight loss around 373 K. At higher temperatures (650−1000 K), the otherwise flat weight loss profile of MCM-41 silica changed into a rapidly declining profile corresponding to the decomposition of the organosilane moieties. Similar findings

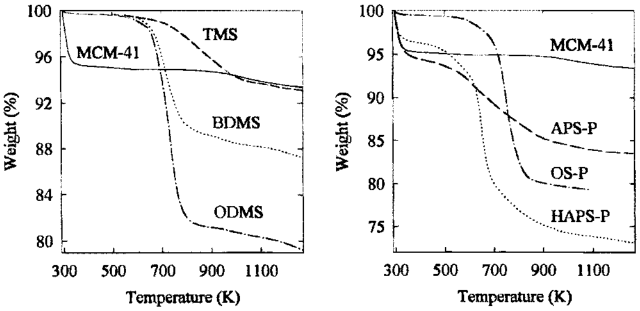

Figure 5. (A) Weight loss curves for unmodified MCM-41 and for samples with bonded trimethylsilyl, butyldimethylsilyl, and octyldimethylsilyl groups. (B) Weight loss curves for unmodified MCM-41 and for the aminopropyl, hexanoyl-3-aminopropyl, and octyl polymeric bonded phases. Adapted from ref 53.

were reported by others workers.[41,47,51,52,74,77,104,110,127] Furthermore, thermogravimetric measurements showed that materials prepared via postsynthesis surface modification or via direct co-condensation procedures exhibit similar thermal stability.[47]

The TEM technique in combination with electron diffraction was used to elucidate the structure of the hybrid materials, especially for co-condensed nanocomposites.[40,51,96,98−101,104,110,128] Interestingly, in one instance,[54] TEM provided direct evidence of the location of tethers bearing functional groups. The strong contrast observed for a MCM-41 derivatized via a three-step process: (i) APTMS grafting, (ii) acidification of the amine groups by HBF_4, and (iii) anchoring a bulky cluster, $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4C_{10}H_{20}O_6]$, revealed that, in this case, the Ru-containing cluster was located predominantly on the outer surface of the material. In another experiment, the MCM-41 silica underwent a treatment in the presence of Ph_2SiCl_2 before the three-step modification mentioned above. In this case TEM provided evidence that the Ru-containing clusters were uniformly distributed within the pore channels. This was attributed to the complete poisoning of the external silanol sites with Ph_2SiCl_2, thus forcing the ammonium tethers to bind to the internal surface.

2.3. Applications of Functionalized Mesoporous Silica. The most important applications of functionalized mesoporous silica reported in the literature were in the field of catalysis and environmental remediation. These will be summarized hereafter.

2.3.1. Catalysis. 2.3.1.1. Oxidation Catalysis. Since the advent of titanosilicates[129] with their remarkable catalytic properties in selective oxidation of organic substrates in the presence of dilute H_2O_2, it was recognized that the intrinsic activity of Ti is strongly dependent on the nature of the siliceous matrix. Among the reasons put forward to explain this dependence was the hydrophobicity of the matrix as the more hydophobic the surface, the higher the reaction rate because of increased concentration of the organic substrate at the Ti active site. On the basis of this contention, many research groups enhanced the hydrophobicity of mesoporous titanosilicates such as Ti−MCM-41 and Ti−MCM-48 via postsynthesis silylation by alkylsilanes,[58,117] alkyldisilazane,[59−61] or chloroalkylsilanes.[63,67] As expected, silylation gave rise to materials with enhanced activity and selectivity to the desired products in the catalytic oxidation of several substrates including alkenes,[58−61,63−66,118] ketones,[70] aromatic or aliphatic hydrocarbons,[58,67,130] and fatty esters[131] by hydrogen peroxide or *tert*-butylhydroperoxide (Table 3). In the case of epoxidation of cyclohexene, Corma et al.[59] found that the increased activity upon sylilation was not due to an increase in the intrinsic activity of Ti, but rather to reduced hydrolysis of the epoxide, leading to diols that poison the catalyst. In addition to postsynthesis silylated mesoporous materials, one-pot synthesized hydrophobic Ti-containing MCM-41, MCM-48, and HMS were also used as catalysts for selective oxidation reactions such as epoxidation and oxidative cyclization.[116−120] These materials also exhibited enhanced activity and selectivity. For instance, in the case of cyclohexene epoxidation over methyl-bearing Ti−MCM-41, a 94% selectivity toward epoxide was achieved at 98% conversion. In addition, the initial reaction rate was 21 $\text{mol}\cdot\text{min}^{-1}\cdot(\text{mol of Ti})^{-1}$, the highest ever.[118]

Various organometallic complexes were grafted or anchored to MCM-41 and Ti−MCM-41 previously modified with aminopropyl or chloropropyl functional groups. This approach also afforded efficient oxidation catalysts.[62,67,133,136,138,139]

2.3.1.2. Acid Catalysis. Sulfonic acid bearing MCM-41 silicas prepared via coating or silylation were tested as acid catalysts for glycerol esterification by lauric acid.[76] Both types of materials were almost equally active, displaying 47 and 53% monoglyceride yield in 24 h, respectively. Under otherwise the same conditions, a HMS−SO_3H prepared via co-condensation gave 52% yield within 10 h, presumably because of its more open structure (Table 4). Esterification of glycerol with lauric or oleic acids was also carried out by Diaz et al.[111] using one-pot synthesized MCM-41 silica containing both methyl and sulfonic acid ligands. Higher monoglyceride yields were obtained in the presence of lauric acid compared to oleic acid. Furthermore, as shown in Table 4, the catalytic activity was found to be dependent on the surface density of methyl groups. Hydroxylation-condensation[80,109] as well as alcohol dehydration[112] reactions were also shown to be catalyzed by MCM-41 or HMS functionalized with sulfonic acid groups via silylation, coating, or co-condensation.

2.3.1.3. Base Catalysis. Postsynthesis modifications of mesoporous silicas leading to base catalysts was achieved either by direct silylation with species containing amine functional groups[71−74,78] or via a two-step procedure consisting of silylation with chloroalkoxysilane followed by reaction with free secondary amines such as piperidine.[71,73,74] In both cases, the residual unreacted silanol groups were removed with hexamethyldisilazane.[71,75] The catalytic activity of the obtained materials was investigated in various esterifications and Knoevenagel condensations. For instance, Cauvel et al.[71] showed that the best yield (90%) in the base-catalyzed esterification of glycidol was obtained with MCM-41 modified by a piperidine-derived species followed by elimination of the residual hydroxyl groups by hexamethyldisilazane compared to a nonmodified material and to MCM-41 derivatized with APTES. Using similar synthesis procedures and the same test reaction, Jaenicke et al.[73] obtained the best yield (68%) in the presence of CPTES-functionalized MCM-41 reacted with TBD. As summarized in Table 5, in addition to Knoevenagel

Table 3. Oxidation Reactions over Surface-Modified Mesoporous Silicas

		reaction conditions and catalytic activity				
catalyst	substrate	oxidant	*T* (°C)	time (h)	yield	refs
Ti−MCM-41; Ti−MCM48	cyclohexene	H_2O_2	50	3	1.8−0.8	58
	hexane				3.6−9.3	
	pent-2-en-1-ol				2.7−5.5	
Ti−MCM-41	cyclohexene	TBHP	60	5	90[a]	59, 60
Ti−MCM-41	cyclohexene	TBHP	60	5	36.8−64.6	61
Ti−MCM-41	cyclooctene; norbornene; 1-octene	TBHP	50	2	55−77[a]	63
Ti−MCM-41	1-octene	H_2O_2	25	24	24	64
Ti−MCM-41	cyclohexene	H_2O_2	70	2	5−15	65, 66
MCM-41; Ti−MCM-41; metallophthalocyanines	methylnaphthalene		40	24	10−34	67
	trimethylphenol		30	2	16−80	
MCM-41/vanadium active centers	cyclohexane	TBHP	70	70	1.9	68
	cyclohexene		30	6	0.4−2.6	
HMS/chromium complex	tetralin	Air	100		1.2	69
MCM-41	methyl vinyl ketone	H_2O_2	0	1−2	63	70
	cyclopentenone				>95	
	cyclohexenone				89	
	trans-2-hexenal				31	
Ti−HMS	cyclooctene	H_2O_2	60	4	0.3−8.6	116
Ti−MCM-41	oxidative cyclization	TBHP	60	12	33	117
	4-penten-1-ol			12	92	
	cis-4-hexene-1-ol					
Ti−MCM-41	cyclohexene; 2-penten-1-ol; 3-methyl-2-buten-1-ol	H_2O_2	50	2	2.2−2.8	119
Ti−MCM-41	cyclododecene	TBHP	60	6	54[a]	120
Co-complex immobilized on HMS	ethylbenzene	air	130	22	70	130
	chlorotoluene		130	22	25	
	toluene		100	22	5	
FSM-16; MCM-41; SBA-15/ horseradish peroxidase	1,2-diaminobenzene	TBHP	37	7	20−80[a]	132
MCM-41-glycine functionalized through bromoalkyl tethers	cyclohexane	TBHP	70	4	3.6	133
MCM-41 (manganese triazacyclononane)	styrene	H_2O_2	0	1	24−87[b]	134
	cyclohexene				86[b]	
MCM-41 (Ru-*meso*-tetrakis(2,6-dichlorophenyl)porphyrin complex)	styrene; *cis*-stilbene; *cis*-β-methylstyrene; *cis*-β-deuteriostyrene; cyclohexene; norbornene; cyclooctene; 1-octene; (+)-limonene; 1,2-anhydrosugars; *trans*-stilbene	Cl_2pyNO	40	18−30	10−93	88, 135
MCM-41/organometallic complex	cyclohexene	TBHP	40	1	50[a]	136
	pinene					
MCM-41/perruthenate immobilized	various alcohols	O_2	80	3		137
MCM-41/chromium-binaphthyl	various alkenes		0−20	12−16	21−62	138

[a] Activity expressed in terms of conversion. [b] Selectivity to epoxide.

Table 4. Acid Catalysis over Surface-Modified Mesoporous Silicas

catalyst mesophase	reaction	temp (°C)	time (h)	catalyst composition	yield (%)	refs
MCM-41	esterification reactions:	112	10.2	HMS−SO_3H (20%)[a]	52	76
HMS	glycerol + lauric acid		24	MCM−SO_3H (coating)	47	
			24	MCM−SO_3H (silylation)	53	
MCM-41	hydroxylation-condensation:	50	24	MCM−SO_3H (coating)	81.6	80, 109
HMS	synthesis of 2,2-bis(5-methylfuryl)propane			HMS−SO_3H (10%)	57.3	
	(DMP) from 2-methylfuran (MF) and acetone			HMS−SO_3H (20%)	69.3	
				MCM−SO_3H (20%)	45.2	
				MCM−SO_3H (silylation)	52.4	
	esterification of D-sorbitol with lauric acid	112	24	MCM−SO_3H (20%)	>29.7	
MCM-41	esterification of glycerol with lauric acid	100	16	MCM−SO_3H (29%)	49.2	111
			7	MCM−SO_3H−Me(27.5/0.5%)	55.2	
			7	MCM-SO_3H−Me(26.1/2.9%)	57.0	
			7	MCM−SO_3H−Me(17.4/11.6%)	57.0	
			24	MCM−SO_3H−Me(11.6/17.4%)	49.2	
	or oleic acid		5	MCM−SO_3H (29%)	36.0	
			6	MCM−SO_3H−Me(27.5/0.5%)	43.2	
			8	MCM−SO_3H−Me(26.1/2.9%)	42.0	
			9	MCM−SO_3H−Me(17.4/11.6%)	46.8	
			24	MCM−SO_3H−Me(11.6/17.4%)	36.0	
MCM-41	alcohol dehydration: 3,4-dihydro-2H-pyran + ethanol	25	0.66	MCM−SO_3H (29%)	100[b]	112

[a] Percentage of ligand-bearing Si to total Si in the synthesis gel. [b] Activity expressed in terms of conversion.

condensation, Michael reactions were also used to evaluate the activity of base catalysts[70] and significant yields were obtained with aminopropyl-modified HMS.[78] As for base catalysts prepared via the one-step co-

Table 5. Base Catalysis over Surface-Modified Mesoporous Silicas

catalyst mesophase	reaction	temp (°C)	time (h)	catalyst or reactant		yield (%)	refs
MCM-41	Michael reactions: ethylcyanoacetate (ECA) or diethylmalonate (DEM) [Donnors] with # acceptors (ketones)	65	0.5	ECA/MVK		98	70
		65	0.5	DEM/MVK		34	
		40	0.5	ECA/acrolein		100	
		40	0.5	DEM/acrolein		100	
		80	0.5	ECA/cyclopentenone		52	
		80	2	ECA/cyclohexenone		65	
		65	1	ECA/acrylonitrile		84	
		65	1	ECA/ethylacrylate		75	
		65	5	DEM/ethylacrylate		49	
		80	60	DEM/cyclohexenone		15	
		65	0.5	DEM/MVK		7	
	Knoevenagel condensation: ethylcyano-acetate (ECA) or malononitrile (MN) with # aldehydes	70	1−2	ECA/PhCHO		54	
				ECA/PhCHO		41	
				ECA/p-NO_2−PhCHO		95	
				ECA/p-CH_3O−PhCHO		9	
				MN/PhCHO		95	
				MN/p-NO_2−PhCHO		98	
				MN/p-CH_3O−PhCHO		48	
MCM-41	glycidol + lauric acid	120	24	NH_2−MCM		16	71
				Pip−MCM		67	
				NH_2−HMDS−MCM		62	
				Pip−HMDS−MCM		90	
MCM-41	monoglyceride synthesis (glycydol + lauric acid); Jasminaldehyde synthesis (benzaldehyde + heptaldehyde)	110	2	NH_2−MCM		17.1	73
		120−170		CPTES−TAP−MCM		31.1	
				CPTES−Pyr−MCM		40.4	
				CPTES−Pip−MCM		42.5	
				CPTES−TBD−MCM		68.2	
MCM-41	glycidol + lauric acid	110	2	NH_2-MCM		17	74
				CPTES−Pip−MCM		42.5	
				CPTES−TBD−MCM		68.2	
				CPTES−Pyr−MCM		31.1	
MCM-41	transesterification: ethylpropionate + n-butanol	100	24	G−Cl−MTS		13	75
				G−AZA−Cl−MTS		43[b]	
MCM-41	synthesis of conjugated nitroalkenes: $R'CHO + R''CH_2NO_2$	50		**R′**:	**R″**:	100	77
			3	Ph	Me	97	
			3	Ph	H	80	
			3	Ph−NO_2	H	74	
			3	Ph−OH	H	99	
			3	Ph−Cl	H	100	
			3	Ph−Cl	Me	61.5	
			1	p-Ph−H_3CO	H	100	
			3	o-Ph−H_3CO	Me	100	
			1	o-Ph−H_3CO	H	94	
			3	Ph $(H_3CO)_3$	H	92	
			1	cyclodiene ox	H	92	
			2	CH_3CH_2	H	100	
			2	$(CH_3)_2CHCH_2$	H		
HMS	Michael additions: nitroalkanes + α,β-unsaturated carbonyl compounds (methyl vinyl ketone (MVK) and 2-cyclohexen--one (Cy-one)		3−4	$MeNO_2$	MVK	70	78
			2−1.2	Et−NO_2	MVK	80	
			2−1.5	Pr−NO_2	MVK	92	
			6−4	$MeNO_2$	Cy-one	94	
			4.5−1.5	Et-NO_2	Cy-one	90	
			5−2.5	Pr−NO_2	Cy-one	95	
HMS	Knoevenagel condensation of ketones with ethyl cyanoacetate	110	2	cyclohexanone		92	113
			4	3-pentanone		97	
			36	acetophenone		48	
			0.5	cyclohexanone[a]		98	
			2.5	3-pentanone[a]		96	
			24	acetophenone[a]		86	
MCM-41	Knoevenagel condensation of aldehydes and ketones (R−CO−R′) with cyanoacetate solvent: cyclohexane (82 °C) or toluene (110 °C)	82	4	R: C_5H_{10}; R′: H		96	115
		110	2			92	
		82	30	R: Et; R′: Et		89	
		110	18			95	

[a] Results obtained with aminopropyl/phenyl−HMS. [b] Conversion.

condensation, they consisted mainly of aminopropyl-containing MCM-41[41,115] and HMS.[113] They were also used to catalyze the Knoevenagel condensation of different aldehydes and ketones. The activity of such catalysts was promising as the obtained yields varied between 89 and 96% (Table 5).

2.3.1.4. Chiral Catalysis. Catalysts prepared via anchoring of appropriate chiral complexes onto the inner walls of mesoporous silicas proved to be active and stereoselective in several reactions (Table 6).[89−93] Bae et al.[91] reported interesting results in the asymmetric addition of diethylzinc to benzaldehyde over MCM-41 and SBA-15 modified with proline-derived ligands. The same reaction was carried out to probe the catalytic properties of (−)ephedrine anchored to MCM-41 through halogen substitution.[89] The production of highly isotactic

Table 6. Chiral Catalysis over Surface-Modified Mesoporous Silicas

catalyst or support mesophase	reaction	catalyst	enantioselectivity (%)	refs
MCM-41	enantioselective addition of diethylzinc to benzaldehyde	MCM−I−eph	33	89
		MCM−eph−HMDS	33	
		MCM−Cl−eph	28	
MCM-41	allylic amination between cinnamyl acetate and benzylamine	homogeneous	0	90
		Cabosil-supported	2	
		MCM-41-confined	50	
MCM-41; SBA-15	enantioselective addition of diethylzinc to benzaldehyde	MCM-41	79−96	91
		SBA-15	95−98	
MCM-41	propene polymerization cocatalyst: methylauminoxane (MAO)	MCM-41−MAO-*rac*-[$ZrCl_2$(EBI)]	1163[a]	92, 93
		rac-[$ZrCl_2$(EBI)]	4941[a]	

[a] Catalytic activity in kg·mol (Zr h)$^{-1}$.

propylene was shown to be favored by the use of a chiral metallocene (rac-ethylenebis(1-indenyl)zirconium dichloride) anchored on the surface of MCM-41.[93] Johnson et al.[90] used MCM-41 anchored with 1,1′-bis(diphenylphosphino)ferrocene ligands coordinated with Pd^{II} as a chiral catalyst in the allylic amination of cynnamyl acetate. Such a catalyst exhibited a high degree of regioselectivity and enantiomeric excess far superior to the homogeneous analogous catalyst.

2.3.2. Environmental Applications. Periodic mesoporous silicas were purposely modified to be used as adsorbents for pollutants in wastewaters. The most extensive work dealt with adsorption of heavy metals in water using mercaptopropyl-bearing materials. It was carried out by the group of Liu et al.[124,140] and the groups of Mercier and co-workers.[106,107,114,141] The latter used modified HMS and MSU silica samples synthesized via either postsynthesis grafting or co-condensation with 3-mercaptopropyltrialkoxysilane. They found that not only the adsorption capacity was proportional to the thiol-loading but also at saturation the Hg to S ratio was strongly dependent on the pore size of the material, thus on the accessibility of the binding sites. For example, in ≈2-nm pore HMS matrix, about one-half of the thiol groups were accessible to Hg^{2+} binding,[106] whereas larger pore HMS,[141] MSU,[114] and MCM-41[124] exhibited a ratio of 1, indicating that all thiol-containing ligands were accessible. Interestingly, there are indications that the HMS and MSU materials are very selective to Hg^{2+} removal when mixtures of cations are contacted with the adsorbent.[106,114] In the same vein, Liu and co-workers[124,140] reported a remarkable adsorption capacity of 600 mg of Hg/g for a thiol-functionalized large pore MCM-41. These materials were found to remove other metals such as actenides and the extremely toxic methylmercury. In a more recent work, Liu et al.[125] prepared thiol- and amino-functionalized SBA-15 samples and tested them for the removal of heavy-metal cations from wastewaters. The thiolated SBA-15 exhibited high complexation affinity to mercury cations, while the aminated SBA-15 showed a high binding ability to copper, zinc, chromium, and nickel cations. Dai et al.[142] improved the selectivity toward adsorption of specific cations through surface imprinting. This modification consisted of coating the surface not with the pure ligand as in mere grafting, but with the complex of the ligand and the target cation so that when the ion is freed by pH change, the binding site thus created reflects the size and stereochemical requirements of the selected cation, which enhances ion recognition and selective binding. This methodology was used for imprint coating of MCM-41 with [Cu(EDAPTMS)$_2$S$_2$]$^{2+}$ and [Cu(APTMS)$_x$S$_{n-x}$]$^{2+}$ complexes, S being H_2O or CH_3OH. These materials showed improved selectivity toward the adsorption of copper compared to nonimprinted analogues. One common problem of such materials is the limited regenerability. For example, Liu et al.[124] found that thiol-functionalized MCM-41 saturated with mercury can be freed completely from the mercury by treatment with 12 N HCl. However, not only concentrated acid was required but also the adsorption capacity was recovered to only 50% of its original value.

Many harmful metals occur as anions under a wide range of conditions. However, only limited work has been devoted to the modification of mesoporous silica with the purpose of anion sequestration. Liu and co-workers[143] first functionalized the MCM-41 surface with EDAPTMS and then incorporated Cu(II) ions, giving rise to positively charged octahedral complexes on the surface. This material was found to adsorb efficiently chromate and arsenate anions in the presence of sulfate. The adsorption mechanism is believed to consist first in electrostatic interaction followed by displacement of one ligand and direct binding with the copper center.

In addition to metallic cations and anions, modified mesoporous materials were tested for the adsorption of some organic pollutants. Octylsilane-grafted HMS was found to be hydrophobic enough to selectively adsorb low concentrations of nonylphenol, an endocrine disrupter, in water but without adsorbing phenol.[144] Table 7 summarizes the main findings in the applications of surface-modified mesoporous silicas for adsorption of heavy metals and organic pollutants.

3. Expanded Mesoporous Silica

As mentioned in the Introduction, noncalcined silica based mesophases may be regarded as organic−inorganic hybrid materials. In this context, silica mesophases prepared in the presence of expander molecules such as trimethylbenzene,[38] alkanes,[145,146] or alkylamines[21,147,148] may also be included in this type of composite materials. The idea of using aromatic or aliphatic hydrocarbon auxiliary molecules for the purpose of controlling the pore size of mesoporous silica was inspired from the behavior of surfactant solutions in the presence of such molecules. However, the use of amines stemmed from the following two observations: (i) me-

Table 7. Adsorption of Heavy Metals and Organic Pollutants

adsorbent mesophase	pollutant	$[c]_0$ (ppm)	$[c]_f$ (ppm)		S content (mmol/g)	capacity (mmol/g)	refs
HMS	Hg				0	0	106
					0.35	0.19	
					0.68	0.28	
					1.0	0.46	
					1.3	0.59	
C12−HMS	Hg				1.5 (1)	1.5	107
C8−HMS					0.90 (2)	0.55	
MCM-41					0.59 (3)	0.59	
MCM-41	Hg				4.7	2.1	112
MSU	Hg				0.9	0.9	114
					2.3	2.3	
MCM-41	Hg	6.2	0.0008		3.2	2.5	124
	Ag	1.8	<0.005				
	Cr	1.8	1.7				
	Pb	7.2	2.7				
SBA-15	Hg	10.1	0	2.15			125
	Cu	5.21	3.18	0.01			
	Zn	10.1	9.91	0			
	Cr	5.21	4.72	0			
	Ni	10.2	5.10	0			
MCM-41	Hg	10	<0.001				140
		0.5	$<5 \times 10^{-5}$				
MCM-41[a]	Cu	63				0.1	142
MCM-41[b]	CrO_4^{2-}	1	<0.01				143
		100	<0.01				
		500	12.1				
		1000	13.3				
		2000	1041				
		5858	4529				
	AsO_4^{3-}	1	0.03				
		100	1.4				
		500	11.6				
		1000	108				
		2000	584				
		5858	2875				
HMS[c]	nonylphenol	0.62				0.65	144

[a] Imprint-coated MCM-41 using Cu−EDAPTMS complex. [b] Cu complex bearing MCM-41. [c] Octyltrimethylammonium-modified HMS.

soporous silicas made via direct synthesis[21,149] or postsynthesis hydrothermal restructuring[150,151] at high temperature, ≈150 °C, often exhibit large pore sizes, typically 5−7 nm; (ii) ^{13}C CP MAS NMR data showed that such materials contain *N*,*N*-dimethylalkylamine originating from partial decomposition of the alkyltrimethylammonium surfactant.[151] To account for these findings, it was proposed that the neutral amine formed in situ migrates to the center of the alkyltrimethylammonium cylindrical micelle and plays the role of a swelling agent. To substantiate this contention, two synthetic strategies were designed as described hereafter.

3.1. Synthesis. The objective of the first approach was to demonstrate the swelling ability of alkylamines. This was achieved by adding different amines to the gel and carrying out the synthesis at low temperature, that is, 70 °C.[21,147] The gel composition was as follows: 1.0:0.33:0.17:*x*:0.17:17 SiO_2:TMAOH:CTMAB:amine:NH_4OH:H_2O. Different amounts of the following amines were used: DMHA, DMDA, DMAO, TOA, TDDA, TMA, and TEA.

The second strategy aimed at proving that even preformed (noncalcined) mesoporous silica can be expanded by postsynthesis treatment in the presence of amines under mild conditions. A silica sample was prepared as described above at 70 °C for 3 days and used as the starting material. When calcined, this material exhibited a narrow pore size distribution with a maximum at ≈3.5 nm. The noncalcined form was treated in water emulsions containing different amines including DMHA, DMDA, DMOA, TOA, TDDA, TMA, and TEA for different contact times (2−3 days) in the temperature range of 80−150 °C.[21]

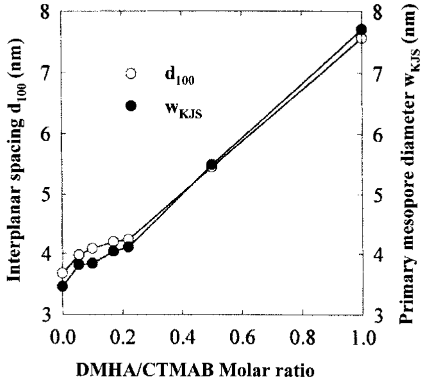

Figure 6. Influence of the DMHA:CTMAB molar ratio in the gel used for direct synthesis of large-pore MCM-41 on the (100) interplanar spacing and the primary mesopore size calculated using the KJS method. Adapted from ref 21.

3.2. Characterization. On the basis of XRD and nitrogen adsorption data, both methods led to materials with amine-dependent pore sizes. In the case of materials prepared using gels containing different amounts of DMHA, Figure 6 shows that the interplanar d_{100} distance and the average pore size w_{KJS}[152] varied linearly as a function of the DMHA/CTMAB ratio. The swelling took place in the presence of *N*,*N*-dimethylal-

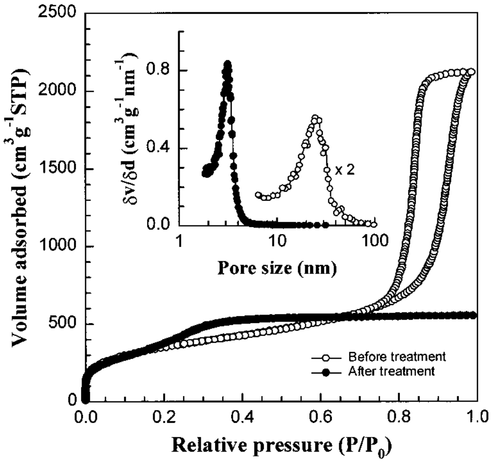

Figure 7. Nitrogen adsorption−desorption isotherms for MCM-41 before and after treatment with DMDA. Inset: Corresponding pore size distributions. Adapted from ref 153.

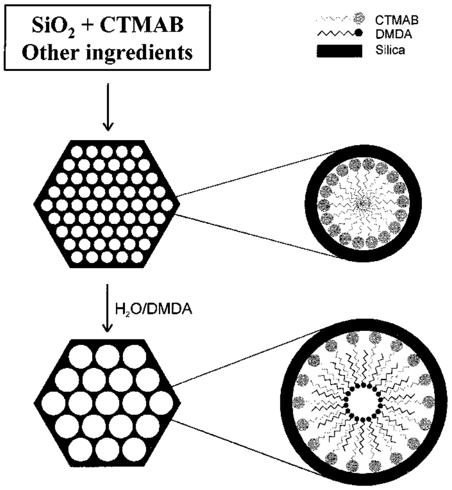

Figure 8. Schematic representation of the pore size expansion process via postsynthesis treatment in the presence of DMDA. Adapted from ref 153.

kylamines with 8−16 carbon atom chains. However, small amine molecules such as TEA and TMA had hardly any effect on the pore structure.

Surprisingly, postsynthesis treatment with DMDA was proven to be very effective as pore sizes as high as 25 nm were obtained using 3.5-nm pore silica as the starting material without any loss of surface area (Figure 7).[153] The pore volume also grew tremendously, from 0.8 to unprecedented 3.3 cm^3/g. A comparison of the swelling action of the different amines revealed that DMDA was the most efficient.[21,147] XRD analysis indicated that the pore size expansion was often accompanied by a gradual decrease in the hexagonal ordering of the pore system.[147] As schematically shown in Figure 8, it is believed that the amine self-assembles into an inverted cylindrical micelle inside the alkyltrimethylammonium micelle and is held via attractive hydrophobic forces. This unique organization allows a number of potential applications in environmental remediation and stabilization of metallic and semiconductor nanoparticles to be envisaged.

With ^{29}Si MAS NMR,[151] the degree of condensation of the silica framework for long-chain alkylamine-treated MCM-41 was found to be higher than that of untreated samples. The proportion of Q^4 silicon atoms increased from 40% for the as-synthesized sample to 60−65% for postsynthesis treated samples. Thermogravimetric analysis revealed that amine modification leads to composite materials with characteristic thermal behavior depending on the synthesis procedure and the type of amine used.[147] For instance, samples that underwent postsynthesis amine treatment featured sharply defined temperature ranges for template desorption/decomposition. In contrast, samples prepared via direct synthesis exhibited weight change events over broader temperature intervals. This behavior was related to the higher extent of penetration of the expander in the surfactant layer of the silicate for the one-step prepared samples.

4. Periodic Mesoporous Organosilicates

Periodic mesoporous organosilicates (PMOs) where the organic component is built in the walls of the channels[22,154−161] instead of protruding into them are the latest innovation in this area. This exciting new development is the result of combining the self-assembly approach for making ordered mesoporous silica and the use of bridged silsesquioxanes $(RO)_3Si-R'-Si(OR)_3$ as precursors, which have been known in sol−gel chemistry for some time.[162−164] In contrast to the previously described hybrid mesophases in which the organic moieties are located on the pore surface, in this class of materials, the organic constituents are fully incorporated in the pore walls as molecularly dispersed bridging ligands.[165] Hence, the organic groups constitute an integral part of the mesoporous framework. Furthermore, the use of bridged silsesquioxanes as silica precursors allowed the complete incorporation of organic functionalities into the final hybrid material, whereas incorporation of organotrialkoxysilanes leveled off at around 25% because additional silica, usually in the form of TEOS, is required for condensation into rigid walls. In addition, highly ordered surface-modified mesoporous silica is difficult to obtain using organotrialkoxysilanes because the surfactant micelle structure is perturbed by the organic groups that share the same confined channels.

Changes in the nature of the organic spacer R′ offer synthesis chemists a wide range of opportunities to control the surface properties while maintaining a periodic pore system. A number of bridged silsesquioxanes have already been successfully used as precursors. These included bis-silylated methylene,[155,160,166] ethane,[22,156−159,161,165−167] ethylene,[158,161,166] acetylene,[166,168] saturated alkyl chains with 3−10 carbon atoms,[165] butene,[165] benzene,[165,166−168] thiophene,[166,168] bithiophene,[168] and ferrocene.[166,168]

4.1. Synthesis. As summarized in Table 8, periodic mesoporous organosilicates were prepared mostly under basic conditions, using procedures similar to those of their pure silica counterparts. The most common surfactants used were CTMAB,[155,158,161,168] CTMAC,[22,156] and ODTMAC.[22,156,167] Syntheses under acidic conditions were also used occasionally with silica precursors such as BTEB and BTET.[168] Inagaki and co-workers[156] described two different synthesis routes involving either one or two aging steps (Table 8). Both methods made use of ODTMAC as a surfactant and BTME as a silica

Table 8. Mesoporous Organosilicates

mesophase	precursors	synthesis mixture	synthesis conditions	refs
hexagonal and cubic	BTME BTEE	method I: BTME or BTEE, 1.0 ODTMAC or CTMAC, 0.12; NaOH, 1.0; H_2O, 231 method II: BTME or BTEE, 1.0; ODTMAC or CTMAC, 0.57; NaOH, 2.36; H_2O, 353	25 °C, 1 days; 25 °C, 14 h + 95 °C, 21 h	22
hexagonal	BTEM	BTEM, x; TEOS, y; CTMAB, 0.12; NH_4OH, 15.0; H_2O, 114 $x/y = 1/0$; 0.50/0.50; 0.25/0.75	80 °C, 4 days	155
cubic	BTME	BTME, 1.0; CTMAC, 0.91; NaOH, 2.28; H_2O, 363	25 °C, 19 h + 95 °C, 21 h	157
2D-hexagonal 3D-hexagonal	BTME BTME	method I: BTME, 1.0; ODTMAC, 0.12 NaOH, 1.0; H_2O, 231 method II: BTME, 1.0; ODTMAC, 0.57; NaOH, 2.36; H_2O, 353	25 °C; 24 h 25 °C, 14 h + 95 °C, 21 h	156, 167, 169
hexagonal	BTEEY	BTEEY, x; TEOS, y; CTMAB, 0.12; NH_4OH, 8.0; H_2O,114 $x/y = 1/0$; 0.75/0.25; 0.50/0.50; 0.25/0.75; 0/1	80 °C, 4 days	158
cubic	BTEE	BTEE, 1.0; C_2H_5OH, 22; HCl, 0.004; surfactant, 0.054−0.18; H_2O, 5 surfactant; CTMAB; Brij; SDS or P123	25 °C, several seconds	159, 165
hexagonal	BTEE BTEEY	BTEE, 3.38; CTMAB, 1.0; H_2SO_4, 1.32; NaOH, 6.42; H_2O, 1215−1620 BTEEY, 3.38; CTMAB, 1.0; H_2SO_4, 0.82; NaOH, 1.41; H_2O, 1215−1620	25 °C, 2 days	161
hexagonal	BTEB BTET BTEF BTEBT BTEA	Si, 1.0; CTMAB, 0.12; NH_4OH, 15.0; H_2O, 114 BTEB, 1.0; CPCI, 0.12; HCl, 3.38; H_2O, 648 → neutralization with $NaHCO_3$ + NH_4F	80 °C, 2 days 25 °C, 2 days	168

precursor[156,167] and gave rise to two- and three-dimensional hexagonal phases. Using CTMAC as a surfactant, Inagaki and co-workers[157] and Sayari et al.[22] made independent discoveries of a cubic ($Pm3n$) ethane−silica mesophase. Stein and co-workers developed a synthesis procedure requiring close control of the pH.[161] The hydrolysis of the bridged silsesquioxane (BTEE or BTEY) was performed under acidic conditions (pH = 2), while the precipitation step was performed under basic conditions (pH = 11) using either sulfuric acid or sodium hydroxide accordingly. Ozin and co-workers[158] synthesized a series of MCM-41-type hybrid materials using BTEY silica precursor alone or mixed in different ratios with TEOS in the presence of CTMAB surfactant. Further, they explored several bridged silsesquioxanes[155,160,166] under basic as well as acidic conditions. Brinker and co-workers[159,165] used an evaporation-induced self-assembly procedure to prepare poly(bridged silsesquioxane) films and spherical nanoparticles under acidic conditions in the presence of ethanol. They used four different surfactants, that is, cationic (CTMAB), nonionic (Brij-56), anionic (SDS), and block copolymer (P123). The removal of the templating surfactants was generally performed by acid solvent extraction.

4.2. Characterization. All techniques mentioned in section 2 were also used for the characterization of periodic mesoporous organosilicas. The great majority of these materials displayed more or less resolved X-ray diffraction patterns akin to those of the pure silica MCM-41 phase.[22,155,156,158,160,161,167,168] Cubic ($Pm3n$) as well as three-dimensional hexagonal oragnosilica mesophases were also reported.[22,156,157,167,169] Likewise, the nitrogen adsorption isotherms exhibited the characteristic features for periodic mesoporous materials and the BET surface areas were of the same order of magnitude as those of MCM-41-type materials. Table 9 summarizes the structural properties of different mesoporous organosilicas. The TEM technique was used to support the XRD data regarding the mesophase symmetry and the pore sizes. The SEM technique was used by Inagaki and co-workers[156,157,167] to illustrate the morphological features exhibited by the hybrid materials with cubic and two- and three-dimensional hexagonal symmetries. Using ODTMAC and CTMAC surfactants and both BTME and BTEE silica precursors, Sayari et al.[22] obtained organosilica mesophases with cubic ($Pm3n$) and hexagonal structures. New insights into the morphology and growth of the particles were gained from SEM measurements. Depending on the synthesis conditions, the cubic mesophase consisted of truncated rhombic dodecahedral particles (Figure 9a), or spheres with small flat areas (Figure 9b), the relative positions of which were related to each other via the same symmetry operations as the hexagonal faces of the particles shown

Table 9. Structural Properties for Mesoporous Organosilicates

mesophase	d (nm)[a]	lattice parameter (nm)	BET surface area (m^2/g)	pore size (nm)	refs
hexagonal	4.85		1150	2.9	22
			1202	3.3	
cubic		11.2	656	4.4	
2D-hexagonal	4.94	5.70	750	3.1 (4.1)[b]	156, 167, 169
3D-hexagonal	4.73	$a = 8.86$; $c = 5.54$	1170	2.7 (3.5)[b]	
cubic			770	2.90	157
hexagonal		4.70	637	3.94	158
hexagonal	3.4			1.8 (CTMAB)	159, 165
cubic		9.2	430	2.5 (Brij)	
hexagonal	4.20		1234	2.2	161
	4.10		1210	2.4	

[a] Interplanar distance of the strongest low-angle peak. [b] Pore size determined using the KJS approach.

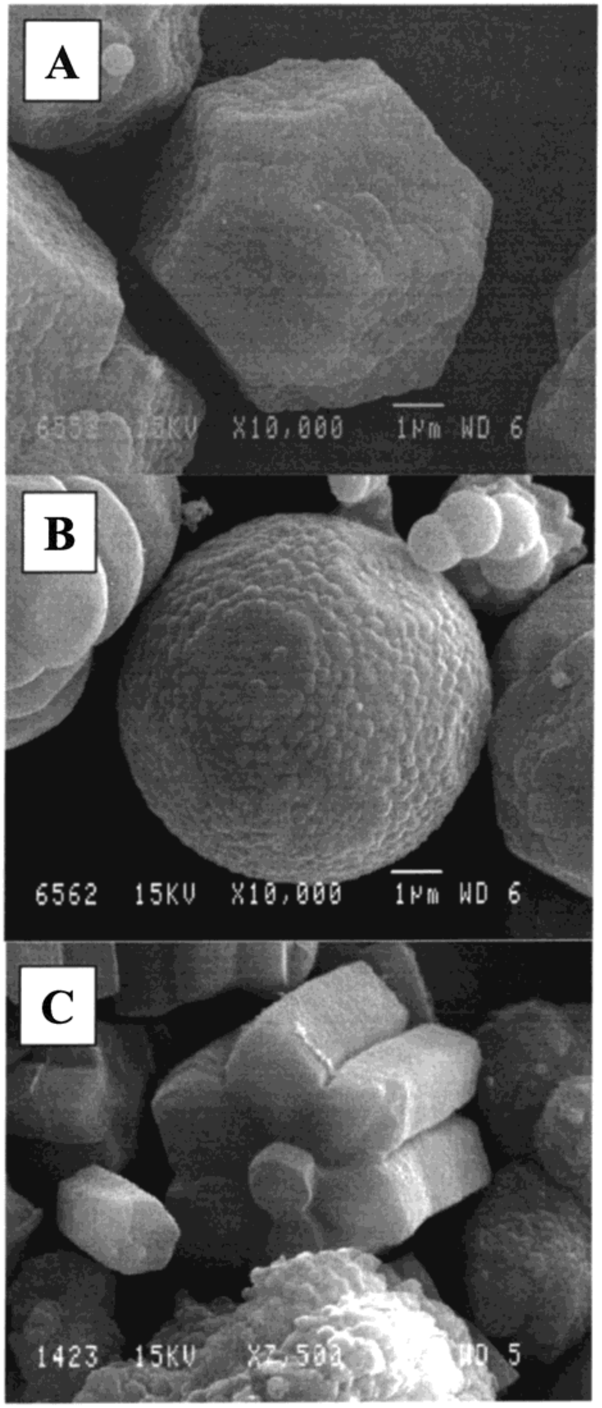

Figure 9. SEM images for CTMAC-derived sample prepared in the presence of BTME at (A) 85 °C, (B) 100 °C, and (C) ODTMAC-derived sample prepared at 100 °C in the presence of BTME. Adapted from ref 22.

in Figure 9a. This indicated that the truncated rhombic dodecahedral particles grew into spherical particles. Another interesting sample with two-dimensional hexagonal symmetry was comprised of $\approx$10-μm facetted rods concentrically self-assembled in sets of 6 rods (Figure 9c). Sometimes, a second layer of rods may self-assemble around the first one. The outermost facets of the tubules were at a lower than 120° angle to each other, which seems to be noncompatible with the hexagonal symmetry of the material. Actually, this was a result of the faster outward growth compared to very slow, or most likely the absence of, growth for the inner facet.[22] Ultimately, as shown in Figure 9c, only five faces persisted, the inner one being the smallest.

NMR spectroscopy is a key technique that confirmed that the integrity of the Si$-$R$'-$Si unit was preserved during the precipitation process and that the organic$-$inorganic moiety constituted the building block of the mesoporous channel walls. For example, regardless of the material's structure, ^{29}Si MAS NMR for ethane-silica mesophases showed mainly two peaks with chemical shifts at approximately -57.0 and -66.0 ppm attributable to T^2 [C*Si*(OSi)$_2$(OH)] and T^3 [C*Si*(OSi)$_3$] Si species covalently bonded to carbon atoms.[22,156,157,162,167] Similar chemical shifts were obtained for the methylene$-$silica material,[155] while the ethylene$-$silica showed T^2 and T^3 resonances at -75 and -83 ppm, respectively.[158,161] For the phenylene$-$silica mesophase, T^2 and T^3 resonances were observed at -71.0 and -78.2 ppm, respectively. Likewise, ^{13}C CP MAS NMR for surfactant-free materials was also used to confirm the preservation of the Si$-$R$'-$Si units in the framework. For the ethane$-$silica mesophase, the spectra exhibited a peak with chemical shift at $\approx$5$-$6 ppm assigned to methylene convalently bound to Si as in Si$-$CH$_2$CH$_2-$Si.[22,156,157,161,167] The ethylene$-$silica materials exhibited a strong resonance at $\approx$145 ppm,[158,161] while the phenylene-bridged system gave rise to a ^{13}C resonance at 133.4 ppm. The methylene-containing material generated a single peak at $\approx$0 ppm.[155] Ozin and co-workers[155,160,166] used^{13}C and ^{29}Si CP MAS NMR to monitor the fate of the methylene group during the thermal treatment of the methylene$-$silica mesoporous nanocomposite in air in the temperature range 400$-$700 °C. Interestingly, they found that as the calcination temperature increased, the quantity of Si Q sites increased at the expense of the T sites. Furthermore, the ^{13}C CP MAS NMR spectra exhibited a peak at $\delta \approx 3$ at calcination temperature up to 600 °C. This peak could be assigned to either the methylene or the methyl group. To discriminate between these two possibilities, the authors applied a nonquaternary suppression (NQS) pulse sequence to the ^{13}C CP MAS NMR spectrum for the selective observation of methyl groups. Using this experiment, a calcined sample showed a peak at $\delta = -6$, whereas the as-synthesized sample did not show any peak at $\delta \approx 0$. Therefore, it was concluded that, at high temperature, the bridging methylene groups transform via participation of neighboring OH groups into methyl covalently bound to Si.[155] The thermal behavior of ethane$-$silica mesophases with two- and three-dimensional hexagonal structures[156,167] was also investigated by high-resolution TGA.[169] These mesophases were found to be thermally stable up to 280 °C in air and up to 540 °C under a nitrogen atmosphere. In addition to conventional characterization techniques, Brinker and co-workers[165] measured the dielectric constants, Young's modulus, and hardness for ethane$-$silica mesoporous thin films prepared in the presence of different mixtures of TEOS and BTEE using Brij-56 as the supramolecular templating agent. With increasing amounts of silsesquioxane relative to TEOS in the synthesis mixture, the authors denoted an increase of the modulus and hardness and a decrease in the dielectric constant.

5. Other Organic−Inorganic Periodic Nanocomposites

Materials grown within the constrained space of periodic mesoporous silica may exhibit unusual mechanical, electronic, magnetic, and optical properties suitable for a large number of emerging applications. The spatial control of the growth process being limited by the channel network of the host allows the fabrication of materials with designed shapes, particularly nanofibers,[170] wires,[171−173] and porous particles.[174−177] In this context, nanofabrication of polymer fibers within the silica channels have attracted much attention. For instance, MCM-41 was used as a container for polymerization of ethylene,[170] aniline,[178,179] acrylonitrile,[180] methyl methacrylate,[181,182] and phenol-formaldehyde.[183] The monomers were first adsorbed from the gas phase into the inorganic host and then polymerized inside the channel network using initiators such as benzoyl peroxide or anhydrous HCl vapor. In addition to its role as a mold for the polymer fibers, periodic mesoporous silica was used as a support for polymerization catalysts such as titanocene.[170,184] A highly ordered molecular polymer−silica composite was also prepared by Moller et al.[185] by incorporating methacrylate groups into the walls of highly ordered MCM-41 materials through co-condensation of TMOS and 3-(trimethoxysilyl)propyl methacrylate. MCM-48 silica was also used as a host for the entrapment of strands of poly(methyl methacrylate).[182] Interestingly, the polymer fibers thus obtained did not exhibit the same properties as bulk polymers. For example, polystyrene fibers constrained inside the channels of MCM-41 silica did not exhibit glass transition.[186] Using a contactless microwave absorption technique, Wu and Bein[178] found that the microwave conductivity of oxidized polyaniline filaments entrapped inside the channels of MCM-41 was one-fourth that of bulk polyaniline, that is, 0.00014 S/cm compared to 0.0057 S/cm.

Conducting carbon wires were also synthesized by pyrolysis of polyacrylonitrile fibers grown within the channels of MCM-41.[180] The microwave conductivity of the carbon wires was 10 times that of bulk carbonized polyacrylonitrile, reaching 0.1 S/cm.

MacLachlan et al.[187,188] synthesized mesoporous silica/ferrocenylsilane composite materials via vapor deposition of silaferrocenophane monomers into the channels of a MCM-41 followed by thermal polymerization. Upon pyrolysis of the hybrid materials at 900 °C under flowing nitrogen, superparamagnetic iron nanoparticles were generated in the channels of MCM-41.

Photosensitive molecules such as chlorophyll and dyes were also incorporated into mesostructured silica materials via either postsynthesis grafting[189] or by co-condensation.[128,190,191] For instance, Zhou and Honma[128,191] developed two synthesis strategies for the preparation of photosensitive MCM-41-type material. The first approach consisted of using 11-ferrocenylundecyltrimethylammonium bromide, a dye-bound surfactant containing a ferrocenyl dye at the end of its tail. The other method was addition of phthalocyanine blue to CTMAB micelles. Microwave-assisted co-condensation in the presence of photochromic azo or fluorescent laser dyes was also reported to occur.[190]

6. Concluding Remarks

Progress in the area of periodic mesoporous materials has taken place at a breathtaking pace. From a materials science point of view, periodic mesoporous materials may be divided into five categories, each one of which created new opportunities for potential applications in catalysis, adsorption, separation, and advanced materials. These are listed hereafter with some final comments. The first three types of materials fall within the scope of the current review, while the two other will be mentioned for completeness.

(i) Mesoporous Silicas with Different Pore Networks, Sizes, and Volumes. As mentioned in the Introduction, there are many silica mesophase structures. The discovery of these materials allowed the development of chemistry within the confined void volumes, in particular, the nanofabrication of materials with designed morphology such as polymer fibers, metallic wires, and porous carbon and metals. Polymer fibers encapsulated within the constrained space of the silica tunnels exhibited different properties compared to bulk polymers. Because the silica walls are thin enough (≈1 nm), it would be possible to synthesize highly dispersed silica−polymer nanocomposites akin to polymer-delaminated clays, which exhibit highly improved properties such as modulus, resistance to distortion, and strength.[192−194]

(ii) Mesoporous Silicas with Organically Modified Surfaces. These organic−inorganic nanocomposites may be prepared via appropriate postsynthesis surface chemistry[38,39,70,195] or via direct funtionalization through co-condensation procedures. The one-pot synthesis affords periodic mesoporous silicas with functional groups covalently attached to Si in the inorganic wall. In addition to being more homogeneous in terms of ligand distribution, these materials are chemically more stable than their counterparts prepared by postsynthesis procedures where the functional groups are attached to the inorganic matrix via surface Si−O−Si bridges, which may be severed by hydrolysis. In many cases, additional transformations of the first function were required. Depending on the nature of their functionality, such materials were found to exhibit promising properties in areas such catalysis, chiral separation, and adsorption of heavy metals from wastewaters. The surface modifier may also consist of a hydrocarbon chain, thus creating a hydrophobic surface suitable for adsorption of organic pollutants.

(iii) Mesoporous Silicas with Organically Modified Frameworks. Synthesis of this newly discovered class of materials was made possible through a combination of the supramolecular templating technique for making periodic mesoporous materials and the use of bridged silsesquioxanes $(RO)_3Si{-}R'{-}Si(OR)_3$ as precursors. Depending on the nature of R′, researchers will be able to synthesize large surface area, mesoporous organosilicas with unique surface properties. New chemistry using the channel walls as a reactant will also be developed.

Tolbert and co-workers' work[30,31] showed that ordered surfactant/silica nanocomposites exhibit remarkably high rigidity. Similar experiments using mesoporous organosilicates with short saturated methylene chains will likely lead to new discoveries regarding their mechanical properties. Another area worth investigating is the combined use of transition metals and bridged silsesquioxanes to synthesize hydrophobic liquid-phase oxidation catalysts. One important possibility would be the use of bis-triethoxysilyl methane, TEOS, and Ti$(OC_2H_5)_4$ in the presence of a surfactant to synthesize Ti-containing methylene-bridged periodic mesoporous organosilica. Calcination of this material would lead to methyl terminally bonded mesoporous titanosilicate,[155] which would have three advantages: (i) it is hydrophobic, (ii) it would be stable against H_2O_2 because primary carbons are not oxidized under mild conditions, and (iii) it can be heat regenerated because it is stable to at least 500 °C.

(iv) Mesoporous Silicas with Metal-Modified Frameworks. A large number of base and transition metal cations were incorporated into the framework of silica mesophases, mostly to generate materials with acid or redox sites for catalysis. Of particular interest, one should mention the combined modification of the framework by a transition metal cation, and the surface by an organic ligand, to generate hydrophobic selective oxidation catalysts.

(v) Non-Silica Inorganic Mesoporous Materials. Several recent reviews were devoted to this important type of material.[3,5,196]

Notation

APDMES = 3-aminopropyldimethylethoxysilane
APDMS = 3-aminopropyldimethylsilane
APTES = 3-aminopropyltriethoxysilane
APTMS = 3-aminopropyltrimethoxysilane
ATMS = alkyltrimethoxysilane
BDMCS = *n*-butyldimethylchlorosilane
BSTFA = *N*,*O*-bis(trimethylsilyl)trifluoroacetamide
BTEA = bis(triethoxysilyl)acethylene
BTEB = 1,4-bis(triethoxysilyl)benzene
BTEBT = bis(triethoxysilyl)bithiophene
BTEE = 1,2-bis(triethoxysilyl)ethane
BTEEY = 1,2-bis(triethoxysilyl)ethylene
BTEF = 1,1′-bis(triethoxysilyl)ferrocene
BTEM = 1,2-bis(triethoxysilyl)methane
BTES = benzyltriethoxysilane
BTET = 2,5-bis(triethoxysilyl)thiophene
BTME = 1,2-bis-(trimethoxysilyl)ethane
BTMS = butyltrimethoxysilane
CES = cyanoethylsilane
CES-triol = carboxyethylsilanetriol
Cl_2PyNO = 2,6-dichloropyridine *N*-oxide
CPCl = cetylpyridinium chloride
CPTES = 3-chloropropyltriethoxysilane
CPTMS = 3-chloropropyltrimethoxysilane
CTMAB = cetyltrimethylammonium bromide
CTMAC = cetyltrimethylammonium chloride
DCDPS = dichlorodiphenylsilane
DEDMS = diethoxydimethylsilane
DMDA = *N*,*N*-dimethyldecylamine
DMDCS = dimethyldichlorosilane
DMHA = *N*,*N*-dimethylhexadecylamine
DMOA = *N*,*N*-dimethyloctylamine
EDAPTMS = 3-trimethoxysilylpropylethylenediamine
ETES = ethyltriethoxysilane
HADS = hexaalkyldisilazane
HMDS = hexamethyldisilazane
MPTMS = mercaptopropyltrimethoxysilane
MPTMS = mercaptopropyltrimethylsilane
MSTFA = *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide
MTES = methyltriethoxysilane
ODMCS = *n*-octyldimethylchlorosilane
ODTMAC = octadecyltrimethylammonium chloride
OTES = *n*-octyltriethoxysilane
P123 = pluronic acid block copolymer
PTES = phenyltriethoxysilane
PTMS = propyltrimethoxysilane
SDS = sodium dodecyl sulfate
TBD = triazabicyclo[4,4,0]dec-5-ene
TBHP = *tert*-butylhydroperoxide
TDDA = tridodecylamine
TEA = triethylamine
TMA = trimethylamine
TMCS = trimethylchlorosilane
TMSI = *N*-trimethylsilylimidazole
TMSPDA = 3-trimethoxysilylpropylenediamine
TMSPEO = 3-trimethoxysilylpropoxymethyloxyrane
TOA = trioctylamine
VTCS = vinyltrichlorosilane

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CM011039L