Award Accounts

The Chemical Society of Japan Award for Creative Work for 2004

Highly Ordered Mesoporous Organosilica Hybrid Materials

Mahendra P. Kapoor[1] **and Shinji Inagaki***[2]

[1]Taiyo Kagaku Co., Ltd., Nano-Function Division, Yokkaichi, Mie 510-0844

[2]Toyota Central R & D Laboratories Inc., Nagakute, Aichi 480-1192

Received February 2, 2006; E-mail: inagaki@mosk.tytlabs.co.jp

The latest developments in periodic mesoporous organosilicas (PMO) have been compiled. The discovery of mesoporous hybrid organosilicas with molecular scale periodicity resulting from alternating hydrophilic and hydrophobic layers, and a cost effective solution showing the use of allyl derivatives of the bis-silyl precursors are discussed. Relevant uses of the periodic mesoporous materials in diverse applications are summarized. For example, the metal-incorporated periodic mesoporous organic frameworks are likely to offer an advantage in catalytic transformations, while the functionalized PMOs show promise in fascinating catalytic applications via enhancing the physical properties of guest molecules and clusters. In general, the advancement in PMOs have showed great promise and are expected to deliver exciting achievable future findings.

Introduction

Porous materials created by nature or by defined synthetic routes have emerged as being particularly important and have found great utility in diverse aspects of human activity. Vast amounts of research and considerable progress have been made in the field of porous materials and to date, a new family of periodic mesoporous materials has been created.[1–3] Since the first discovery of ordered mesoporous silicas M41S[2] and FSM-16,[1,3] a variety of ordered mesoporous materials have been synthesized by a template method, using the supramolecular assembly of surfactants.[4–6] These materials have a range of framework compositions, external morphologies, and pore arrangement structures. The framework composition has been studied extensively since that governs the surface and bulk properties of mesoporous materials such as catalysis and adsorption. Mesoporous materials now include a variety of inorganic materials, e.g., non-Si transition-metal oxides, metals, and carbons. The integration of organic functional groups into an inorganic network has led to the discovery of organic-functionalized mesoporous silicas with well-defined pore-structures and unique properties, which have been recognized as useful materials suitable for versatile applications such as catalysts for a variety of organic chemical transformations, as adsorbents for the separation of organic molecules, as trapping agents for metal cation contaminants, chromatography, and chemical sensing, because the materials may possess unique optical, electrical, magnetic, and mechanical properties.[7–9] Suitable organosilane precursors have at least one hydrolysable group attached to the silicon center. Early organic-functionalized mesoporous materials were synthesized by direct synthesis through co-condensation of the organosilane precursor attached with one alkoxide group [$R–Si(OR')_3$] and tetraalkoxysilane [$Si(OR')_4$] in the presence of a surfactant (Fig. 1a) or by post-synthesis treatment of pre-formed mesoporous silica with an organosilane coupling reagent.[10–17] The mesoporous materials have a microscopically heterogeneous structure composed of an inorganic main framework with an organic layer grafted onto the framework. Generally, they exhibit poorer structural ordering and lower loading of organic content. There has been a need for mesoporous materials in which organic and inorganic moieties are homogeneously distributed in the framework with higher loading of organic content and a highly ordered mesostructure to advance the efficacy.[18]

Therefore, another positive approach was realized and periodic organofunctional mesophases were designed via hydroly-

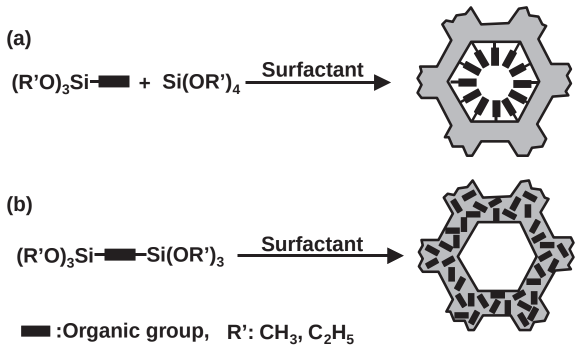


Fig. 1. Surfactant-directed synthesis of organic-functionalized mesoporous silicas from organosilane precursors attached with (a) one and (b) two Si–alkoxides.

Published on the web October 10, 2006; doi:10.1246/bcsj.79.1463

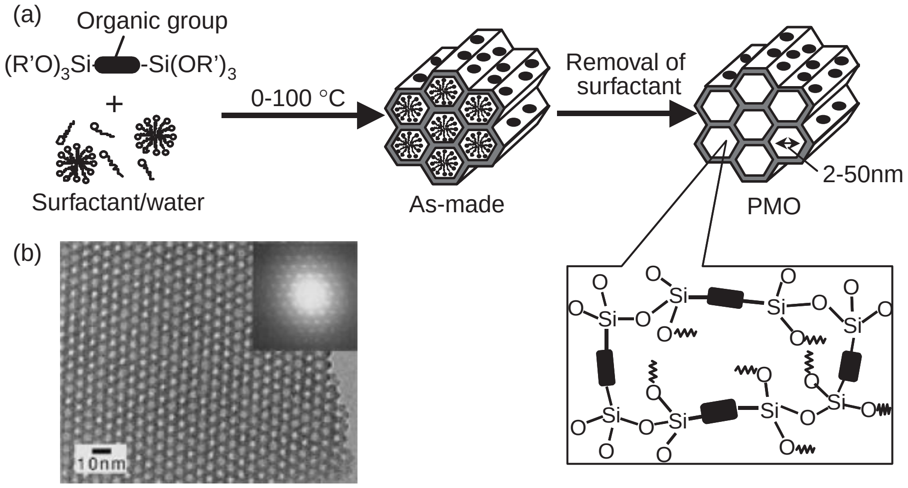


Fig. 2. (a) Synthesis of periodic mesoporous organosilica from organic-bridged silsesquioxane precursor. (b) TEM image of the periodic pore structure of mesoporous ethane–silica.

sis and condensation reactions of bridged organosilane precursors [$(R'O)_3Si–R–Si(OR')_3$] with two or more Si–alkoxide groups (Fig. 1b). More precisely, it was a surfactant directed self-assembly of so-called “bis-silyl” mesophases with a composition corresponding to [$_{1.5}OSi–R–SiO_{1.5}$] when written in dehydroxylated, surfactant-free, and anhydrous form,[19–21] the R group is an organic group that links directly two silicon atoms through silicon–carbon covalent bonds. Such mesophases were prepared through the hydrolysis/condensation of 100% of the $(R'O)_3Si–R–Si(OR')_3$ precursor, where the OR′ is the hydrolyzable group in the presence of a suitable surfactant. Thus, self-assembly of organosilane precursors in the presence of a surfactant led to another novel class of mesophases, wherein the organic functionalities are homogeneously distributed in the channel walls (Fig. 2). Mesoporous hybrids have uniform pores, higher stability, and control of the framework composition and morphologies. The benefits of such spontaneous organizations have been increasingly realized and are driven by their inherent potentials of fabricating sensors, optical, electronic, and electro-optical devices for communication, data storage, in diverse areas of nanotechnology, and overall in information technology. A diversity of organic spacers have since been incorporated in various successful syntheses of mesoporous organosilicas using a variety of surfactants in basic, acidic, or neutral media including various chemical, electrical, and optical functionalities integrated within the mesoporous network. Hexagonal, cubic, and wormhole framework structures have been reported.

Herein, we have summarized the systematic developments in the periodic mesoporous materials, including very recent developments from our laboratory and others with a special emphasis on the synthesis and functions of periodic mesoporous materials with a crystal-like pore walls structure.

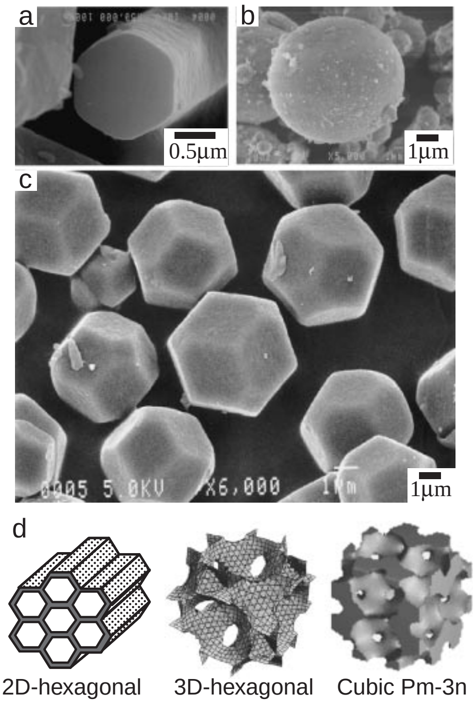


Fig. 3. SEM images of mesoporous ethane–silica hybrid materials with (a) 2D-hexagonal, (b) 3D-hexagonal, and (c) cubic *Pm*$\bar{3}$*n* mesophases. (d) Schematic models of pore structures.

Organic-Bridged Periodic Mesoporous Organosilicas

Actually, three independently working groups were the first to report the synthesis of hybrid mesoporous organosilicas in 1999.[19–21] The most commonly used structure directors are trimethylhexadecylammonium bromide/chloride, trimethyloctadecylammonium bromide/chloride, and hexadecylpyridinium bromide/chloride for the self-assembly of hybrid mesoporous materials. Removal of the structure directing surfactant by solvent extraction produces an open framework structure of a hybrid material with accessible uniform sized pores. In fact, Inagaki et al. first reported the synthesizing of a novel organic–inorganic hybrid material by using 1,2-bis(trimethoxysilyl)-ethane (BTME) in the presence of trimethyloctadecylammonium chloride as a surfactant under basic conditions, wherein the mesophase symmetry (e.g., 2-dimensional hexagonal or 3-dimensional hexagonal) was largely dependent on the synthesis temperature and alkyl-chain length of the surfactant (Fig. 3).[19]

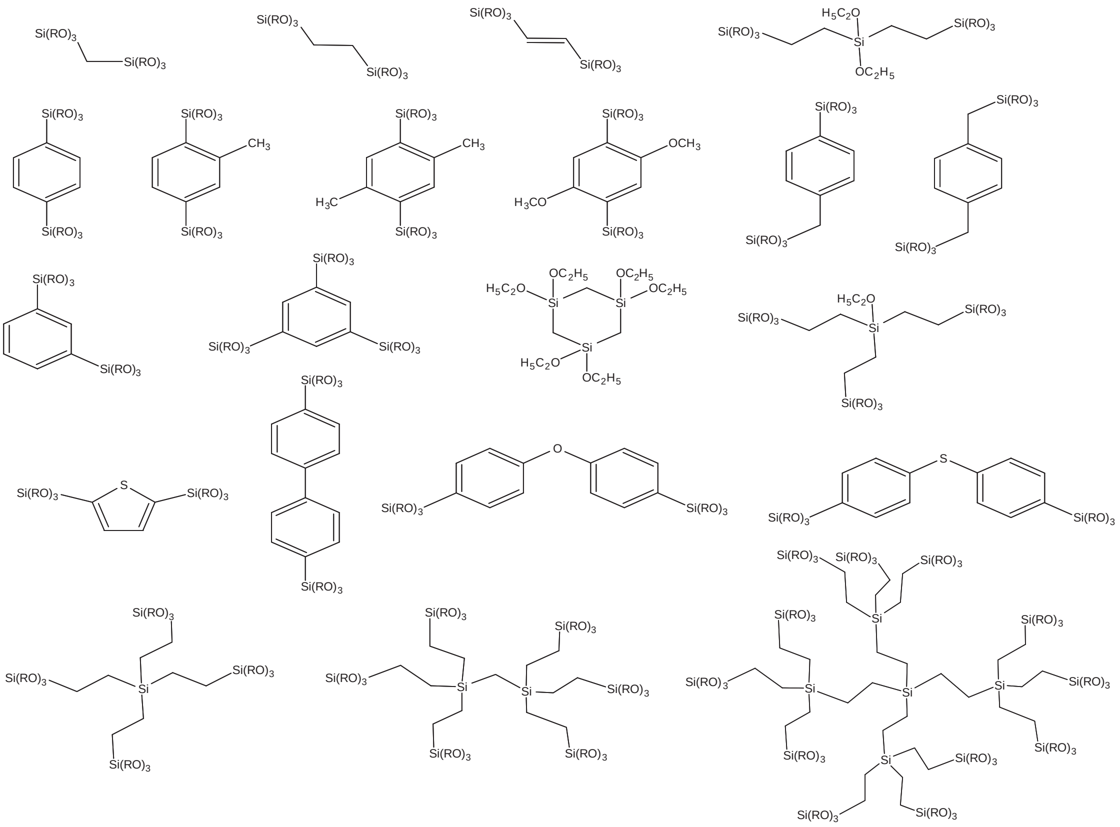
Later, Stein's group disclosed the synthesis of similar materials using 1,2-bis(triethoxysilyl)ethane (BTEE) or 1,2-bis(triethoxysilyl)ethylene in the presence of trimethylhexadecylammonium bromide surfactant; however, the material contained wormhole-like rather than straight parallel pores.[20] Simultaneously, Ozin's group also reported the syntheses of PMOs with an ethenylene linker using 1,2-bis(triethoxysilyl)ethylene as the precursor in the presence of trimethylhexadecylammonium bromide as a structure-directing surfactant in basic media.[21] Further, hybrid mesoporous materials with an ethane linker having cubic symmetry ($Pm\bar{3}n$), which is akin to the SBA-1 pure silica, were synthesized by Guan et al.,[22] Sayari et al.,[23] and Kapoor and Inagaki.[24] The crystal-like external morphology of these hybrid materials analyzed by scanning electron microscopy (SEM) was described as an decaoctahedron comprising of six squares and twelve hexagons (Fig. 3c). Kruk et al. detailed the surface properties of mesoporous ethane–silicas of different symmetries.[25] Later, several follow up syntheses were reported, well documented, and reviewed in the literature.[26,27] Very recently, Liang et al. have presented the synthesis of highly ordered three-dimensional periodic ethane–silica with cubic $Fm\bar{3}m$ symmetry under basic conditions using a divalent structure directing agent.[28] Lee et al. showed the systematic phase control of ethane-bridged periodic mesoporous silicas using Gemini surfactants. Highly ordered structures were synthesized with various mesostructures including lamellar, bicontinuous cubic ($Ia\bar{3}d$), 2d-hexagonal ($p6mm$), 3d-hexagonal ($P6_3/mmc$), and cubic ($Pm\bar{3}n$) by controlling the nature of the Gemini surfactant such as alkyl-chain length, spacer length, synthetic conditions (temperature, molar composition, etc.).[29]

In addition, the synthesis of bridged mesoporous organosilicas could also be realized under acidic conditions using an ethane-bridged organosilane precursor. A particular difference in the synthesis was the reaction pathway. The "$S^+X^-I^+$"-route was adopted in acidic conditions in contrast to the usual "S^+I^-"-route under basic conditions. However, the acid synthesis approach produced less ordered mesoporous materials showing only one broad peak in the XRD pattern; however, the products with wormhole-like channels and relatively high specific surface areas could be formed. Ren et al. used BTEE as the precursor in the presence of hexadecylpyridinium bromide as the structure director.[30] In another development, the detailed synthesis of ethane-linked mesoporous organosilicas under acidic conditions were reported in the presence of biodegradable Brij-56 [$(EO)_{10}C_{16}H_{33}$] and Brij-76 [$(EO)_{10}C_{18}H_{37}$] oligomers as a structure director.[31,32] Fröba et al. used neutral Pluronic P123 triblock copolymer as the structure directing agent and BTME as the organosilica source under acidic conditions.[33] Their materials exhibited hexagonal symmetry akin to SBA-15 silica with large pores (6.5 nm). Likewise, Burleigh et al. were able to enlarge the pore sizes ranging from 6 to 20 nm using the same triblock copolymer surfactant along with a trimethylbenzene micelle-swelling agent under acidic conditions.[34] Using B50-6600 ($EO_{39}BO_{47}EO_{39}$) triblock copolymer surfactant and the BTEE precursor under acidic conditions, the well-ordered periodic mesoporous organosilica with large cage-like pores, whose diameter was ca. 12 nm, were obtained.[35] The structure was similar to that of FDU-1 silica[36] derived using TEOS under similar synthetic conditions. Guo et al. found that the addition of a salt such as NaCl improves the degree of ordering of the materials.[37] More recently, they also reported that the addition of a large amount of K_2SO_4 to a synthesis mixture containing BTME and pluronic F127 ($EO_{106}PO_{70}EO_{106}$) under acidic conditions affords a high quality cubic ($Im\bar{3}m$) ethane–silica mesophase with large cavities 9.8 nm in diameter.[38]

Therefore, the most commonly studied typical organic linker group is the ethane group ($-CH_2-CH_2-$) because 1,2-bis(trialkoxysilyl)ethane is a widely available bridged organosilane precursor. Although the ethane linker group has limited chemical functionality, the mesophases containing ethane–silica have a lower surface polarity in comparison to pure silica mesophases and are expected to be useful in adsorption applications and molecular separations. Other linker groups that have been used to form bis-silyl hybrid mesophases are the methylene ($-CH_2-$), ethenylene ($-CH{=}CH-$), ethynylene ($-C{\equiv}C-$), butylylene ($-CH_2CH_2CH_2CH_2-$), phenylene ($-C_6H_4-$), ferrocenylene ($-C_5H_4C_5H_4-$), thiophenylene ($-C_4H_2S-$), biphenylylene ($-C_6H_4-C_6H_4-$), bithiophenylene ($-C_4H_2S-C_4H_2S-$), tolyl, xylyl, dimethoxyphenyl, and vinyl groups. An overview of the structures of the organosilsesquioxane precursors, which were successfully used to create the periodic mesoporous organosilicas, is presented in Scheme 1.

The synthesis of ethenylene ($-CH{=}CH-$)-bridged mesoporous organosilica was also presented showing a wide range of opportunities for further surface modifications based on olefin chemistry. Melde et al. synthesized mesoporous ethenylene–silica with 2.4 nm wormhole-like channels and the pure ethenylene–silica mesoporous solids with 4 nm pores with hexagonal symmetry were synthesized in basic conditions.[20] Later, Nakajima et al. showed the synthesis of mesoporous ethenylene–silicas with a long-range order of the mesopores.[39] Wang et al. prepared high quality ethenylene–silicas mesophases under acidic conditions with varied pore sizes using oligomeric (4–5 nm) and triblock copolymer (8–9 nm) surfactant templates,[40] while Nakajima et al. detailed the synthesis ethenylene-bridged mesoporous silicas with large pores.[41]

The number of reports on the corresponding phenylene-bridged mesoporous silicas is very limited. Ozin et al. described the synthesis of phenylene-bridged mesophases using hexadecylpyridinium chloride as a structure director and 1,4-bis(triethoxysilyl)benzene precursor.[21b] Temtsin et al. also reported the mesophases from 2-methylbenzene-1,4-bis(triethoxysilyl), 2,5-dimethylbenzene-1,4-bis(triethoxysilyl), and 2,5-dimethoxybenzene-1,4-bis(triethoxysilyl) precursors using hexadecylpyridinium chloride as the surfactant under acidic conditions and also by adding ammonium fluoride as the catalyst after neutralization.[42] Goto and Inagaki have summarized the synthesis of mesoporous phenylene–silica with large pores ranging from 6.0 to 7.4 nm in diameter using pluronic P123, a triblock copolymer surfactant.[43] In another very recent development, Kapoor et al. have reported the detailed synthesis of average-pore phenylene-bridged mesoporous materials in the presence of oligomeric Brij-56 and Brij-76 surfactant templates under acidic conditions.[44] Kuroki et al. presented the successful synthesis of periodic mesoporous materials made of three-point attachments for the 1,3,5-tris(triethoxysilyl)benzene precursor.[45] The materials showed relatively small pore diameters



Scheme 1. Representative polysilsesquioxane precursors used for the periodic mesoporous materials.

(≈2.2 nm). Later, Landskron et al. summarized PMO synthesis from the cyclic precursor [1,3,5-tris(diethoxysilyl)cyclohexene], which leads to interconnected $[Si(CH_2)]_3$ rings.[46] They have also presented the synthesis of oriented thin-films of such precursors showing very low dielectric constants. Recently, Ozin's group presented the dendritic mesoporous organosilicas compositions from the self-assembly of various dendrimer building blocks under ionic and non-ionic surfactant routes using trimethyloctadecylammonium chloride or triblock copolymer surfactant templates.[47] In an other development, Hunks et al. also synthesized 4-phenylsulfide-bridged periodic mesoporous silicas using the bis-4-(triethoxysilyl)phenylsulfide precursor and Brij-76 surfactant.[48] However, the material has a less ordered preassembly due to the lack of efficient packing of the organic units in the channel walls. Similarly, periodic mesoporous structures could be obtained having aryl-methylene bridging groups from the corresponding 1,4-bis(triethoxysilyl)$(CH_2)_nC_6H_4(CH_2)_n$, where $n = 1$ or 2, precursors in the presence of Brij-56 surfactant under acid conditions.[49]

In addition to the above-mentioned phenylene and its derivative silsesquioxane precursors, the synthesis of thiophenylene-bridged periodic mesoporous silicas have also been reported. Yoshina-Ishii et al.[21b] disclosed synthesis using the 2,5-bis(triethoxysilyl)thiophene precursor in the presence of trimethylhexadecylammonium bromide as the surfactant template. The Si–C bonding was found to cleave in basic conditions, while mild acidic conditions were proved to be stable in such a case. Recently, Morell et al. presented the synthesis of very high order thiophene-bridged periodic mesoporous materials using the 2,5-bis(triethoxysilyl)thiophene precursor in the presence of the pluronic P123 triblock copolymer surfactant.[50] The pore size ranged from 5 to 6 nm with a specific surface area up to 550 $m^2\,g^{-1}$. They have also confirmed using ^{29}Si NMR and Raman spectroscopy that under the conditions applied (although it was a highly acidic medium) only less than 4% of the Si–C bonds were cleaved. It is worth mentioning that the thiophenylene group is a single heterocyclic compound incorporated into the periodic mesoporous organosilicas.

Periodic Mesoporous Organosilicas with Crystal-Like Pore Walls

Although well-defined ordered mesophases could be formed, the chemical functionality of the pore walls surface was rather poor and limited in the above described hybrid mesoporous materials due to the amorphous (atomically disordered) nature of the pore walls, which usually limits their applications. In spite of various efforts made for the crystallization of pore walls, very limited success was achieved and the crystallization was confined to only a fraction of the pore walls. A plausible explanation of the lack of crystallinity may lie in the correlation between framework density (the number of atoms per nm^3) and the structural features of porous materials.[51]

In a further effort to crystallize the pore walls of mesoporous materials, Inagaki et al. have reported the first surfactant-mediated synthesis of ordered phenylene-bridged hybrid mesoporous organosilicas from the assembly of $[(EtO)_3Si–C_6H_4–Si(OEt)_3]$ and trimethylalkylammonium chloride surfactants (Fig. 4a).[52] The precise control of the nano-architecture

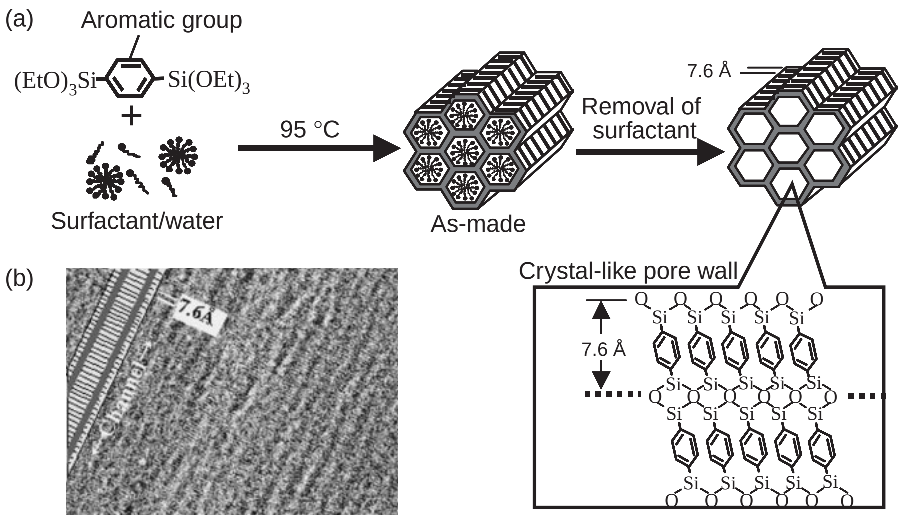


Fig. 4. Synthesis of mesoporous organosilica with a crystal-like pore wall structure. (b) TEM image of molecular-scale periodicity in the pore walls.

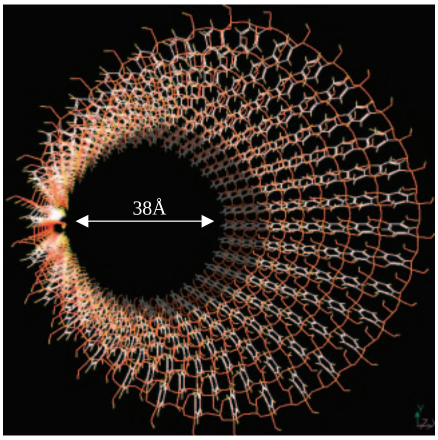


Fig. 5. Simulated image of the crystal-like pore walls structure of surfactant-free mesoporous phenylene–silica with crystal-like pore walls.

displayed a hexagonal array of mesopores and crystal-like pore walls expressed as molecular periodicity in the walls along the channel directions due to the hydrophobic–hydrophilic interaction between hydrolyzed precursors [$(HO)_3Si–C_6H_4–Si(OH)_3$]. In fact, the addition of crystallinity to the pore walls of mesoporous materials has long been sought after, and has been the most important discovery in the field of porous materials. The material has a hexagonal array of mesopores with a lattice constant of 52.5 Å and exhibits atomic scale periodicity with a spacing of 7.6 Å along the channel direction in the whole region of pore walls. In addition to three peaks in the small-angle scattering regime ($2\theta < 10°$), with d-spacings of 45.5, 26.0, and 22.9 Å, the material also displayed four sharp diffraction peaks at spacings $d = 7.6$, 3.8, 2.5, and 1.9 Å in the medium scattering angles region ($2\theta = 10–50°$). The TEM images of staked lattice fringes with a uniform basal spacing of 7.6 Å along with the corresponding electron diffraction spot confirmed the molecular-scale periodic structure in the pore walls (Fig. 4b). Figure 5 shows the pore surface structure of mesoporous phenylene–silica with crystal-like pore walls. Benzene rings are aligned in a circle around the pore, fixed at both sides by silicate chains. The silicate is terminated by silanol (Si–OH) at the surface. Hydrophobic benzene layers and hydrophilic silicate layers array alternatively at an interval of 7.6 Å along the channel direction. The periodically arranged hydrophobic–hydrophilic surface has a great advantage in using this material as a catalyst and host material for inclusion chemistry because it can enable structural orientation of guest molecules or clusters enclosed in the pores. Later, Bion et al. reported the synthesis of phenylene-bridged hybrid mesoporous solids having crystal-like pore walls with varied pore diameter by using C_{14} to C_{18} trimethylammonium halides surfactants under basic conditions.[53] The pore diameters were varied in the range of 2.3 to 2.9 nm depending on the alkyl-chain length of the respective surfactant.

Recently, Onida et al. presented an infrared and ab initio molecular modeling study to deduce the surface properties of the mesoporous phenylene–silica hybrid materials with crystal-like pore walls.[54,55] Morell and co-workers reported the in situ synchrotron SAXS/XRD study to give further insight on the formation of ordered mesoscopic hybrid phenylene–silicas with crystal-like pore walls.[56] Recently, Okamoto et al. showed the self-organization of non-porous phenylene–silica hybrid solids with a crystal-like long range-ordered structure.[57]

However, prepared under acidic conditions using the triblock copolymer Pluronic P123 surfactant, the phenylene-bridged mesoporous organosilicas showed little evidence of molecular order within the pore walls.[43] Recently, Goto et al. reported the post-synthesis treatment for the formation of molecular scale periodicity within the pore walls of mesoporous organosilica derived using the triblock copolymer Pluronic P123 surfactant.[58] Periodic mesoporous organosilicas with aryl groups such as tolyl, xylyl, and dimethoxyphenyl derived under acidic conditions in the presence of cetylpyridinium chloride showed an indication of aryl-silica ordering in the channel walls.[42] The other material that showed little atomic-scale periodicity is ethenylene (–CH=CH–) bridging organosilica.[21b] X-ray diffraction studies measured the periodicity of 5.6 Å. Very recently, Mokaya and co-workers have reported the synthesis and characterization of crystal-like structurally well-ordered ethenylene containing bifunctional hybrid mesoporous organoaluminosilicates materials, which exhibit molecular-level periodicity in the pore walls and enhanced hydrothermal stability.[59] Later, Wang et al. tried to define the pore wall ordering by TEM measurements in the phenylene-bridged mesoporous organosilica derived using oligomeric (Brij-56 and Brij-76) surfactant templates.[60]

Since the discovery of the first phenylene-bridged mesoporous hybrid material with crystal-like pore walls, the numbers of mesoporous hybrid materials exhibiting molecular scale periodicity have been increasing. Further, we have also revealed that the synthesis of phenylene-bridged mesoporous solids with a crystal-like organization of the pore walls is not restricted to symmetrically substituted precursors such as 1,4-bis(triethoxysilyl)benzene.[61] We have demonstrated a similar arrangement using 1,3-bis(triethoxysilyl)benzene as the precursor, a nonlinear symmetric bridged organosilica precursor, in a similar synthesis route as described for 1,4-bis(triethoxysilyl)benzene.[52] The material also showed somewhat similar atomic-scale periodicity at 7.6 Å as well as its higher order diffractions. Figure 6 displays a structural model of the pore wall region of 1,3-phenylene–silica and 1,4-phenylene–silica mesoporous materials supporting the lamellar pore walls structure. Interestingly, both experimental and simulation results demonstrate that there are very little differences in the molecular scale periodicities of mesoporous materials derived from 1,4-bis(triethoxysilyl)benzene and 1,3-bis(triethoxysilyl)benzene precursors, although they have quite different molecular geometry. Recently, Sayari and Wang presented synthesis from a precursor containing an aromatic ring and two ethylene groups [bis(triethoxysilylethane-2-yl)benzene], showing the occurrence of molecular order within the pore walls of mesoporous materials with or without a surfactant.[62]

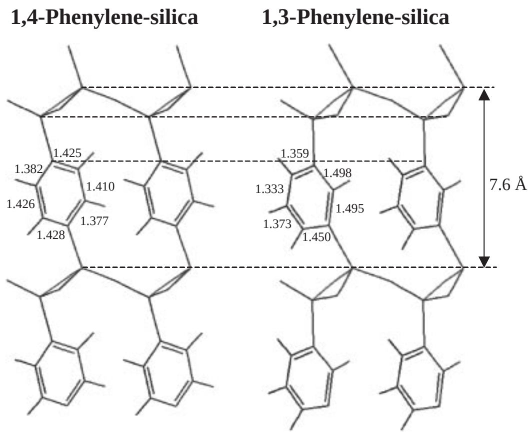


Fig. 6. Simulated image of the crystal-like pore walls structures derived from 1,4-bis(triethoxysilyl)benzene and 1,3-bis(triethoxysilyl)benzene precursors.

Another mesoporous hybrid system that showed periodically ordered mesopores as well as molecular-scale periodicity in the whole region of pore walls was also synthesized by us using 4,4′-bis(triethoxysilyl)biphenyl (BTEBP) as the organosilica precursor, wherein hydrophilic silicate layers and hydrophobic biphenylylene layers arrayed alternatively.[63] The results successfully demonstrated that such a unique arrangement in the pore walls can also be generalized for hierarchically ordered mesoporous solids by changing the nature of the organic linkers. The material showed molecular-scale pore surface periodicity along the channel direction with a basal spacing of 11.6 Å (Fig. 7). The five additional well-resolved diffraction peaks at *d*-spacings of 11.6, 5.9, 3.9, 2.9, and 2.4 Å were observed together with the lower angle diffraction peak (d_{100}) with a *d*-spacing of 41.8 Å. The periodicity of 11.6 Å, confirmed from the many lattice fringes on the TEM image, is larger than the periodicity of 7.6 Å observed for phenylene-bridged hybrid mesoporous solids. The difference between the molecular scale periodicity was obviously due to the longer length (molecular size) of the biphenylylene moieties compared to the benzene molecule. The pore diameter and BET surface areas were determined to be 3.5 nm and 869 $m^2\,g^{-1}$, respectively.

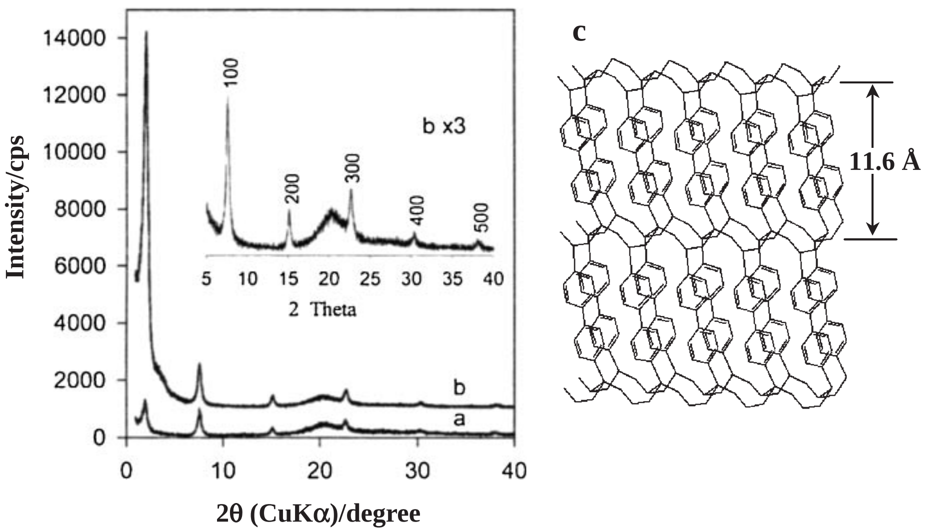


Fig. 7. X-ray diffraction patterns of mesoporous biphenylylene–silica materials. (a) As-made and (b) surfactant-extracted materials. (c) Simulated image of the crystal-like pore walls of mesoporous biphenylene–silica material.

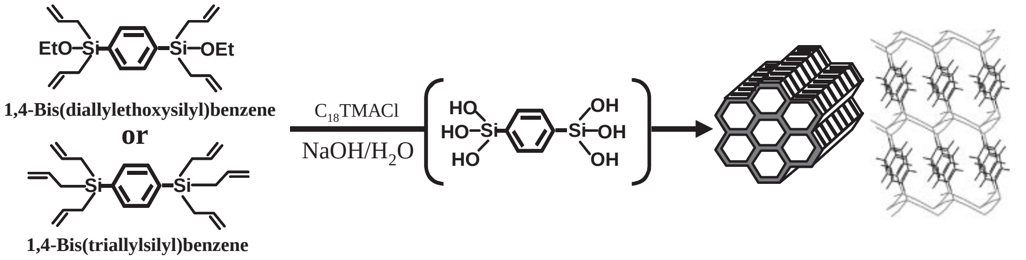


Fig. 8. Alternate route for the synthesis of mesoporous phenylene–silicas from allylorganosilane precursors.

Periodic Mesoporous Organosilicas from Allyl-Derivatives of Precursors

Until the mesoporous organosilica with molecular scale periodicity were reported, the most commonly used organosilane precursors contained a trialkoxy leaving group [$(OR')_3$], such as the trialkoxy derivatives of bridged organosilane molecules $(R'O)_3Si–R–Si(OR')_3$. However, the range of suitable alkoxysilane precursors is limited because alkoxysilane precursors containing relatively large organic groups are difficult to obtain in high purity due to the limitations of distillation and chromatographic separation for such nonvolatile compounds. It is therefore vital to discover alternative precursors for the synthesis of novel mesoporous organosilicas. Alkoxy, halide, acyloxy, and amino groups on silicon atoms have also been used for Si–O–Si bond formation.[64] However, these functional groups are highly reactive towards hydrolysis, rendering the silicon compounds difficult to handle under hydrolytic conditions and during purification by silica-gel chromatography. Shimada et al. have showed a new method for functionalizing the surface of mesoporous silica using allylorganosilanes at toluene reflux temperatures.[65,66] Recently, we have presented the preparation of a new family of bridged allylorganosilane precursors that upon surfactant-assisted assembly afford ordered mesoporous organosilica having pore walls with molecular-scale periodicity.[67] This approach provides important insight into the development of molecular-scale periodicity, spurring new debate on the formation of periodic mesostructures with crystal-like pore walls.

The XRD patterns of the as-synthesized phenylene–silica hybrid mesoporous material derived from 1,4-bis(diallylethoxysilyl)benzene display a d_{100} reflection peak at 41.6 Å and sharp peaks at $d = 7.6$, 3.8, and 2.5 Å at intermediate scattering angles ($2\theta = 10$–$40°$), indicating that the pore walls are formed of crystal-like domains with a spacing of 7.6 Å in the channel direction (Fig. 8). The surfactant-free material also exhibited a well-defined pattern with diffraction peaks in the low-angle region (d_{100} spacing of 45.7 Å). The XRD peak (d_{100}) for the surfactant-free material strengthened significantly upon solvent extraction due to enhancement of the contrast of density between the framework and pore channel. The as-synthesized material displayed a slightly smaller lattice constant of $a = 48.1$ Å. The molecular-scale periodicity was fully retained upon surfactant removal, indicating substantial framework ordering with crystalline pore walls. The final material was identical to the materials synthesized from the alkoxy derivative of the phenylene-bridged precursor [1,4-bis(triethoxysilyl)benzene],[52] which exhibited weaker peaks related to molecular-scale periodicity. The BJH pore diameter, BET surface area, and mesopore volume were 23.5 Å, 744 $m^2\,g^{-1}$, and 0.53 $cm^3\,g^{-1}$, respectively.

In another approach, we have also presented the synthesis of a stable 1,4-bis(triallylsilyl)benzene precursor without any alkoxy group, and the formation of mesostructures under basic conditions was attempted.[67] The XRD pattern of the surfactant-free material clearly shows the successful formation of a mesostructure with a d_{100} spacing of 35.5 Å. The other two broad reflections at $d = 9.5$ and 4.4 Å were due to the molecular-scale periodicity of the pore walls. However, the peaks are not as sharp as those observed for the phenylene–silica mesoporous materials prepared from 1,4-bis(triethoxysilyl)benzene and 1,4-bis(diallylethoxysilyl)benzene. This material exhibits structural ordering, with a BET surface area of 968 $m^2\,g^{-1}$ and a BJH pore diameter of 23.2 Å.

The 1,4-bis(diallylethoxysilyl)benzene precursor is preferable to 1,4-bis(triethoxysilyl)benzene in terms of the cost and the ease of handling and purification during synthesis. However, the final yield of the mesoporous phenylene–silica derived from the allylorganosilane precursor is slightly lower (ca. 34.1%) than that from the trialkoxyorganosilane precursor[52] (36.7%). The triethoxy derivative of the benzene precursor releases ethanol during the hydrolysis reaction, whereas propane is the main leaving species in the hydrolysis of 1,4-bis(diallylethoxysilyl)benzene or 1,4-bis(triallylsilyl)benzene.[65,66] Propane is unreactive toward silica and readily leaves from the reaction mixture. The reaction pathway for the deallylation of allylorganosilane precursors under acidic conditions has been reported for the protodesilylation of allylic silanes.[68–70] However, under basic conditions, it is likely that deallylation starts with a nucleophilic attack by hydroxide ions toward the silicon atoms of the precursors.

As a continuation, the synthesis of mesoporous hybrid organosilicas with a crystal-like framework walls structure was also reported via the co-condensation of equimolar ratios of 1,4-bis(diallylethoxysilyl)benzene and TEOS under basic conditions. The ordered mesoporous material obtained exhibited molecular-scale periodicity in the pore walls.

Lamellar Mesophases of Periodic Mesoporous Organosilicas

Recently, we disclosed the synthesis of lamellar mesophases of phenylene– and biphenylylene–silica composites with periodicity within the silicate layers from the mixtures of bridged organosilane precursors and surfactants at room temperature.[71] Interestingly, the phenylene–silica layers of the lamellar mesophase include 4.2 Å periodicity, which is different from the

7.6 Å periodicity observed in the pore walls of crystal-like mesoporous phenylene–silicas. The periodicity of 4.2 Å, which is very close to the phenylene–phenylene distance (4.4 Å), was also observed in the simulated model of the 2D-hexagonal mesophase of phenylene–silica. It was also shown that the lamellar mesophases with periodicity within the layers could also be obtained even upon refluxing the initial mixture at 55 and 75 °C, respectively, indicating that stable lamellar mesophases are likely to be formed under a wide range of condensation temperatures. In addition, the intercalation of a biphenylylene–silica mesophase with toluene also demonstrated the unique flexible features of these expandable interlayered structured materials. Similar molecular-scale periodicity has been observed for the lamellar silica–surfactant mesophase[72] and 2D-hexagonal mesoporous silica.[73]

Functionalized Periodic Mesoporous Organosilicas

Organofunctional mesoporous silica compositions have been recognized as useful materials, particularly molecular sieves, for use as catalysts for a variety of organic chemical transformations, as trapping agents for metal cation contamination, as adsorbents for the separation of organic molecules, and as film-forming compositions for electronic applications. In this context, several organo-functionalized mesostructures have been prepared through direct assembly pathways, as well as through grafting reactions of pre-assembled frameworks using different organosilane precursors.[10–18] The potential usefulness of these derivatives, as well as other organo-functional derivatives, depends critically on the loading of accessible functional groups in the framework.

The mercapto-functional mesoporous molecular sieve silicas have received considerable attention as heavy metal ion trapping agents.[74–77] The anchored thiol group can also be oxidized to provide sulfonic acid functionality for applications in solid acid catalysis. In all cases, open framework structures have been obtained for compositions in which fewer than 25% of the silicon centers have been functionalized.[10,15,78,79] Ozin and co-workers reported the bifunctionalized periodic mesoporous organosilicas having bridging ethenylene groups in the walls and vinyl groups protruding into the channels.[80] Later, a series of organic functionalities such as amine, thiol, diamine, imidazole, pyridine, and phenyl were incorporated into the channel of mesoporous silica with bridging ethylene groups in the framework using cationic surfactants.[81] Recently, Voss et al. showed the synthesis and characterization of highly amine functionalized mesoporous organosilicas by an "all-in-one" approach using boron-containing silsesquioxane surfactant precursors for the functionalization of the channel walls with primary amine groups.[82] Additionally, the hierarchically ordered mesophases with crystal-like pore walls could also be grafted with an interactive bridging organic spacer inside the pore walls, and also offered an opportunity to modify the organic functional groups via further chemical transformations for versatile applications.[83] Indeed, it was very interesting to synthesize a sulfuric acid-functionalized mesoporous hybrid having both hydrophobic and acidic functionalities because it could facilitate the diffusion of reactants and products during acid-functionalized catalytic reactions. In addition, by simply varying the nature of the bridging organic group in the framework, the surface properties can be modified and tuned for the catalysis.[84]

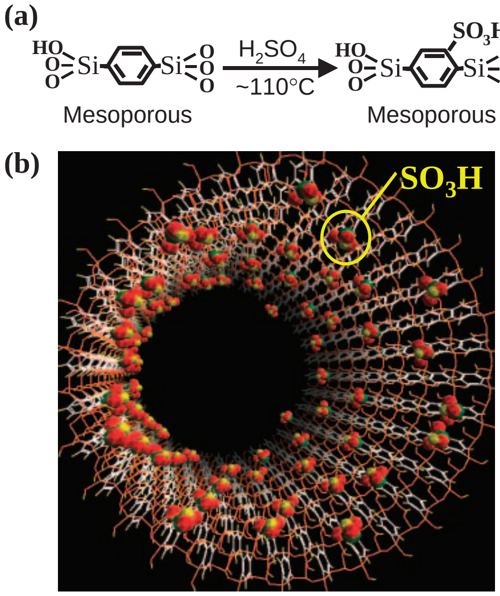


Fig. 9. (a) Post-synthesis treatment for the sulfonation of phenylene groups in the pore walls of mesoporous phenylene–silica with sulfuric acid and (b) CG image of the pore surface functionalized with sulfonic acid groups.

In attempts to design a highly functionalized acid catalyst by introducing the sulfonic acid groups (–SO_3H) onto the periodic crystal-like pore walls surface of phenylene-bridged hybrids the two different routes were adopted. In the first approach to develop the sulfuric acid-functionalized hybrids,[52] the sulfonic groups were directly attached to the phenylene groups in the wall of phenylene-bridged hybrid solids by sulfonation using a fuming sulfuric acid at ≈110 °C (Fig. 9). Under any severe conditions adopted for the sulfonation process, the mesoscopic ordered structure and atomic scale periodicity in the wall were retained. The concentration of the sulfonic acid group, determined by acid–base titration with a sodium hydroxide solution, was 0.4 meq./g; i.e, approximately 10% of the phenylene groups in the walls were functionalized with sulfonic acid groups and stable enough for high-temperature applications (<500 °C). Whereas, in another approach, we developed the mesoporous sulfuric acid-functionalized phenylene–silica by co-condensation of 1,4-bis(triethoxysilyl)benzene and 3-mercaptopropyltrimethoxysilane using a cationic surfactant template in a basic medium followed by oxidative transformation of thiol (–SH) to (–SO_3H) groups using HNO_3 (Fig. 10).[83] The materials showed similar molecular scale periodicity (7.6 Å) to that previously observed for phenylene-bridged mesoporous materials. Characterization results revealed that the mercaptopropyl group (C_3H_6–SH) or its oxidized derivatives (C_3H_6–SO_3H) are linked to silicate layers of the hybrid mesoporous solids. The degree of oxidation of –SH to –SO_3H was 41.7% and the sulfonic acid group concentration was 0.70 meq./g.

Further, the synthesis of sulfuric acid-functionalized biphenylylene-bridged mesoporous materials with similar characteristics is also interesting because it has an equimolar ratio of

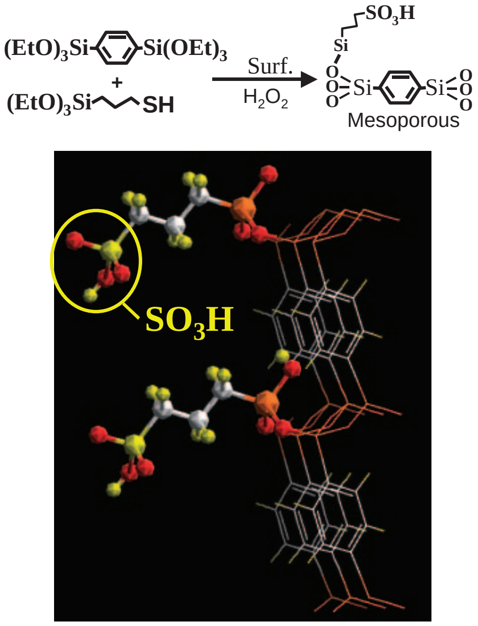


Fig. 10. (a) Direct synthesis of sulfonic acid-functionalized phenylene–silica by co-condensation of 1,4-bis(triethoxysilyl)benzene and 3-mercaptopropyltrimethoxysilane and the successive oxidation of thiol groups to sulfonic acid groups and (b) CG image of the surface functionalized with propyl sulfonic groups.

phenylene to silica, which provides the possibility of enhanced hydrophobicity in catalytic applications. The materials were synthesized by co-condensation of the 4,4′-bis(triethoxysilyl)-biphenylylene precursor and 3-mercaptopropyltrimethoxysilane in a basic medium and a cationic surfactant, followed by oxidation treatment as described for phenylene-bridged functionalized materials. The presence of –SO$_3$H groups were confirmed by the acid–base titration method. The sulfonic acid group concentration was quite higher (0.99 meq./g) than those obtained for phenylene-bridged mesoporous materials (0.70 meq./g).[84] The method provides highly hydrophobic biphenylylene-bridged bifunctional hybrid mesoporous solids with sulfonic acid functionalities and crystalline pore walls, which may be useful for potential applications.

Kamegawa et al. presented the preparation and characterization of unique inorganic–organic hybrid mesoporous materials incorporating arenetricarbonyl complexes [–C$_6$H$_4$M(CO)$_3$–] of Cr and Mo within the organosilica framework of phenylene-bridged mesoporous hybrid materials by a simple chemical vapor deposition (CVD) method.[85] Such functionalized materials could be useful in the effective catalysis of the hydrogenation of polyunsaturates into cis-unsaturated products.

In a recent development, Nakajima et al. have showed the first example of the synthesis of stable and catalytically active sulfonic acid-functionalized hybrid mesoporous material.[86] The ethenylene sites (–CH=CH–) on the surface of periodic mesoporous materials were successfully coverted to phenylene sulfonic acid groups (Ph–SO$_3$H) by a two step chemical modification. The procedure involves the Diels–Alder reaction with benzocyclobutene followed by sulfonation in concentrated H$_2$SO$_4$.

Morphological Controls in Periodic Mesoporous Organosilicas

In addition to structural symmetry, the control of the particle morphologies of the periodic mesoporous organosilicas has also been attempted. Beginning from the cubic morphologies of ethane-linked organosilicas, the influence of the synthetic conditions on the morphology of ethylene-bridged periodic mesoporous materials has been summarized.[87–89] Several morphologies such as rope-type aggregates, small rods, spiral, gyroid, spheres, etc., were observed. Lee et al. showed morphology control in ethane-bridged periodic mesoporous silicas using Gemini surfactants.[29] We were able to synthesize phenylene-bridged periodic mesoporous materials (pore diameters ≈2.0 nm) with spherical morphology, having diameters between 0.6 and 1.0 μm (average size 0.8 μm) by applying very mild basic conditions with the use of an ethanolic dilute ammonia solution instead of an aqueous NaOH solution with surfactants.[90] The pore walls consist of rather poor molecular scale periodicity, in contrast to conventionally produced phenylene-bridged mesoporous organosilicas. While observing the morphological details of the particles by SEM at various stages of the condensation reaction, they have concluded that mild acidity and very slow reaction rates were required, where the fundamental aspects of the formation of monodispersed spherical particles is the simultaneous generation, followed by propagation and subsequent termination of each and every particle under a constant rate of condensation. Also, Rebbin et al. have presented the synthesis of spherical particles (0.4–0.5 μm) of ethane-bridged mesoporous organosilicas using a similar approach.[91] Later, Kim et al. fabricated the spheres of ethane-bridged mesoporous organosilica with diameters between 1.4 and 2.5 μm, which are necessary for the minimum desired size of HPLC applications.[92] In a very recent report, Bao and Zhao investigated the morphologies of large pore periodic mesoporous ethane–silicas derived from a triblock copolymer (P123) surfactant.[93] Controlling the synthetic parameters such as stirring, acidity, reaction time, reactants ratio, etc., they were able to prepare different morphologies such as spindle-, pearl-, diamonds-. rods-, plate-like particles, etc.

Functions of Periodic Mesoporous Organosilicas

Although the potential of hybrid mesoporous solids has been widely recognized, progress on their practical use has been very slow. Many of the mentioned applications require materials with stereo-chemical configuration, specific binding sites, charge density, and acidic behavior. Mesoporous hybrid inorganic–organic composites structures are an emerging class of new materials that also hold significant promise in catalysis. Indeed the hydrophobicity of the framework plays an important role in catalysis, especially in processes where water is generated during the reaction. In fact, the periodic mesoporous organosilicas have opened a wide range of new and exciting opportunities for designing materials with controlled surface properties at the molecular level. Likewise, in mesoporous ethenylene–silica about 29% of the C=C double bonds were found to be accessible to a bromination reaction, in other cases in the presence of gaseous bromine. While upon treatment with bromine in CH$_2$Cl$_2$ reflux only 10% of the C=C bonds were brominated, the reminder was hydrogenated.[20,21]

In the series of recent reports, we showed the benefits of periodic pores structural surfaces wherein the ethylene linker was involved for enhanced selectivity and activity in esterification.[94] The catalytic applications of sulfonic acid-functionalized mesoporous phenylene–silica with a crystal-like pore walls structure have also been disclosed, wherein the catalytic sites are dimensionally designed on the mesoporous hybrid solids surface along with the hydrophobic phenylene sites, which provide a better catalytic environment. The materials were found to be very reactive in the esterification of acetic acid with ethanol and the catalytic results showed higher conversion compared to commercially available Nafion-H.[95] Materials prepared by co-condensation of 1,4-bis(triethoxysilyl)benzene and 3-mercaptopropyltrimethoxysilane precursors were compared to the materials derived by post synthesis grafting of the 3-mercaptopropyltrimethoxysilane precursor onto the periodic mesoporous phenylene–silica, and an active role of crystal-like pore walls in esterification was proposed. Logically, the crystal-like lamellar pore wall structure of the mesoporous phenylene–silica along with both easily accessible hydrophobic and acidic species on the surface of the material are preferentially participated in the reaction, and thus, result in the predominately higher yield of ethyl acetate. Similarly, in other recent work they have evaluated the catalytic properties of the oligomeric Brij-76 surfactant derived sulfonic acid-functionalized ethane- and phenylene-bridged mesoporous organosilicas synthesized by co-condensation and the subsequent grafting procedure in the condensation of phenol with acetone to form Bisphenol A,[96] wherein they have also presented the comparative results of mesoporous phenylene–silica materials with or without crystal-like pore walls structure. The higher catalytic activity of mesoporous phenylene–silica materials functionalized via grafting was also explained due to the fact that sulfonic acid sites on the surface or near the pore mouth are easily accessible for the reactants in the catalytic reaction. Additionally, in a very recent article, the structural relation properties of hydrothermally stable sulfonic acid functionalized ethane-bridged mesoporous organosilicas derived from the triblock copolymer Pluronic P123 surfactant template were presented, wherein the positive influence of the ethane bridging group on the catalytic behavior of the materials was described.[97] In another report, the hydrolysis of sugars on ethane- and phenylene-bridged mesoporous hybrid materials were described.[98] In addition, Nakajima et al. showed the esterification and pinacol–pinacolone rearrangement reactions using their recently developed hybrid mesoporous solid acid catalyst, wherein the surface ethenlyene sites on the surface were modified to phenylene sulfonic acid via the Diels–Alder reaction.[86]

Further, the incorporation of the active metal species into the channel wall of the periodic mesoporous organosilicas was also described for useful modifications of their catalytic properties. We also explored the catalytic properties of periodic mesoporous nanocomposite materials and presented the advantage of their use in a number of oxidation reactions.[99–101] They synthesized a new class of titanium-containing hybrid silsesquioxane mesophases with integral ethane organic functionality from a single organosilane source, wherein the titanium necessarily incorporates along with the ethylene constituents into the framework (channel wall) as molecularly dispersed bridging ligands, while maintaining the structural integrity and order of the mesoporous organosilica material intact. Different possible routes for the synthesis were adopted to incorporate the titanium (with varied loadings) in the framework of the ethane-bridged mesoporous organosilica. The materials synthesized were highly hydrophobic and showed improved catalytic hydrophobic surface properties in three different probe reactions. As a first example, the epoxidation of the bulky aromatic alkenes using dilute H_2O_2 as an oxidation agent were described.[99] Second, the hydrophobicity induced vapor-phase oxidation of propene for improved of propene oxide selectivity was demonstrated.[100] And finally, the outstanding catalytic activity in the ammoximation of ketones under liquid-phase conditions using dilute aqueous hydrogen peroxide and ammonia was evaluated that had never been catalyzed by either titanium silicates (TS-1) or Ti-MCM-41 materials.[101]

Further, Hughes et al. recently presented the synthesis of ethane-bridged mesoporous silicas with incorporated aluminium, which could offer new prospects for the application of such hybrid silica in acid catalysis.[102] However, Yang and co-workers presented the synthesis of aluminium-containing mesoporous phenylene–silicas with crystal-like pore walls and demonstrated their application in the alkylation of 2,4-di-*t*-butylphenol with cinnamyl alcohol.[103]

The functionalized periodic mesoporous organosilicas also find uses as absorbents. Zhang et al. prepared a tetrasulfide-bridging mesoporous silica, which showed a high affinity for Hg^{2+} cations along with some affinity for other cations such as Cd^{2+}, Zn^{2+}, Pb^{2+}, and Cu^{2+},[104] while Jaroniec and Olkhovyk integrated the isocyanurate group to periodic mesoporous organosilicas for a high affinity to Hg^{2+} (1.8 g Hg^{2+}/g adsorbent).[105]

In addition, Fukuoka et al. disclosed a successful synthesis of pure Pt and Rh or mixed (Pt/Rh, Pt/Pd) necklace-shaped nanowires inside the ethane-bridged periodic mesoporous organosilica and confirmed them by HRTEM and EDX results.[106] It was concluded that the mixed metallic nanowires consist of uniform Pt/Rh alloy phases and the monometallic Pt and Rh are of mean lengths of about 120 and 48 nm, respectively. They also presented the synthesis of Pt nano-wires and their isolation by removing the mesoporous silica framework with a dilute aqueous HF solution.[107] In another development, Fukuoka et al. showed the improved catalysis of PMO embedded Pd nanowires for measuring the reaction rate of CO oxidation in the presence of excess O_2.[108]

Further, the thin-film morphology of the periodic mesoporous organosilicas is important for the patterned lithography, sensors technology, and microelectronic applications. In an attempt to generate low-*k* materials, Lu, Brinker, and co-workers first demonstrated the applicability of the evaporation induced self-assembly approach for PMO thin films.[109] Later, Dag et al. showed a significant modification to this approach and fabricated thin-films with different structures and symmetries from several bis-silylated precursors.[110] Ha and Park synthesized high quality free standing and oriented ethylene-bridged thin films with a uniform thickness between 180 and 800 nm.[111] In a very recent report, Ozin and co-workers[112] have demonstrated the preparation of periodic mesoporous thin films via a spin-coating method and studied their low-dielectric constant properties, including some of the mechanical and hydrophobic properties for microelectronic applications.

Hamoudi et al. synthesized an arene acid-functionalized ethane-bridged periodic mesoporous organosilica (surface area $= 1040\,m^2\,g^{-1}$ and pore diameter $= 4.5\,nm$), which showed high acidity ($H^+ = 1.38\,mmol\,g^{-1}$) and reasonable proton conductivity ($1.6 \times 10^{-2}\,S\,cm^{-1}$) suitable for fuel cell applications.[113]

Inagaki and co-workers[114,115] have recently showed a synthetic method of self-standing organosilica films that expands the application window of such structures to new application fields. The phenylene–silica–polyimide hybrid films showed enough flexibility and high thermal stability, up to 450 °C.

In another recent development, hierarchical mesoporous carbon/silica nanocomposites were derived from phenylene-bridged organosilicas for hydrogen storage, catalysis, fuel cells, and other applications.[116]

Summary

In this feature article, we have reviewed the latest developments in periodic mesoporous organosilicas with particular focus on the discovery of mesoporous hybrid organosilicas with molecular scale periodicity in the structure framework. The periodic pore surface structure results from alternating hydrophilic and hydrophobic layers, composed of silica and organic moieties respectively. The alternately arranged organic moieties and silica layer show fascinating catalytic applications by enhancing the physical properties of the guest molecules and clusters.

The use of ally derivatives of the bis-silyl precursors is very important because the costly alkoxy derivativer could limit the commercial viability of the resultant periodic mesoporous organosilicas. It is also noteworthy to point out the particular relevance of the periodic mesoporous materials and that such materials are certain to continue to find new uses in diverse applications. Metal-periodic mesoporous organic frameworks are the least studied and would likely offer an advantage in catalysis, especially in chiral catalytic transformations, which require mild temperatures.

Additionally, new types of organic molecules that can be self-assembled and act as a structure director are certainly needed for the fabrication of smart materials. Further, pure organic mesoporous polymers would be a promising development in the preparation of self-healing materials for biomedical applications.

In summary, various challenges still remain; however, the advancements in periodic mesoporous organosilicas have showed promise and are expected to deliver exciting outcomes and find great utility in diverse aspects of human activity.

We would like to express our sincere gratitude to Professors Osamu Terasaki, Kazuyuki Kuroda, Kazunari Domen, and Toyoshi Shimada for their guidance and discussions. The authors express their sincere thanks to Drs. Shiyou Guan, Yoshiaki Fukushima, Tetsu Ohsuna, Qihua Yang, Yasutomo Goto, Kentaro Okamoto, Osamu Ohtani, Atsushi Fukuoka, Junko N. Kondo, Asim Bhaumik, Barbara Onida, and Kiyotaka Nakajima. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan (No. 16310094) and by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology (JST) Agency.

References

1 T. Yanagisawa, T. Shimizu, K. Kuroda, C. Kato, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 988.

2 a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710. b) J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, *J. Am. Chem. Soc.* **1992**, *114*, 10834.

3 S. Inagaki, Y. Fukushima, K. Kuroda, *J. Chem. Soc., Chem. Commun.* **1993**, 680.

4 A. Corma, *Chem. Rev.* **1997**, *97*, 2373.

5 A. Sayari, P. Liu, *Microporous Mesoporous Mater.* **1997**, *12*, 149.

6 J. Y. Ying, C. P. Mehner, M. S. Wong, *Angew. Chem., Int. Ed.* **1999**, *38*, 56.

7 A. Stein, B. J. Melde, R. C. Schroden, *Adv. Mater.* **2000**, *12*, 1403.

8 A. Sayari, S. Hamoudi, *Chem. Mater.* **2001**, *13*, 3151.

9 W. J. Hunks, G. A. Ozin, *J. Mater. Chem.* **2005**, *15*, 3716.

10 S. L. Burkett, S. D. Sims, S. Mann, *Chem. Commun.* **1996**, 1362.

11 D. J. Macquarrie, *Chem. Commun.* **1996**, 1961.

12 M. H. Lim, C. F. Blanford, A. Stein, *J. Am. Chem. Soc.* **1997**, *119*, 4090.

13 A. Bhaumik, T. Tatsumi, *J. Catal.* **2000**, *189*, 31.

14 F. Babonneau, L. Leite, S. Fontlupt, *J. Mater. Chem.* **1999**, *9*, 175.

15 L. Mercier, T. J. Pinnavaia, *Chem. Mater.* **2000**, *12*, 188.

16 A. Corma, J. L. Jorda, M. T. Navarro, F. Rey, *Chem. Commun.* **1998**, 1899.

17 W. M. V. Rhijin, D. E. D. Vos, B. F. Sels, W. D. Bossaert, P. A. Jacobs, *Chem. Commun.* **1998**, 317.

18 J. Liu, Y. Shin, Z. Nie, J. H. Chang, L. Q. Wang, G. E. Fryxell, W. D. Samuels, G. J. Exarhos, *J. Phys. Chem. A* **2000**, *104*, 8328.

19 S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.* **1999**, *121*, 9611.

20 B. J. Melde, B. T. Holland, C. F. Blanford, A. Stein, *Chem. Mater.* **1999**, *11*, 3302.

21 a) T. Asefa, M. J. MacLachlan, N. Coombs, G. A. Ozin, *Nature* **1999**, *402*, 867. b) C. Yoshina-Ishii, T. Asefa, N. Coombs, M. J. MacLachlan, G. A. Ozin, *Chem. Commun.* **1999**, 2539.

22 S. Guan, S. Inagaki, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.* **2000**, *122*, 5660.

23 A. Sayari, S. Hamoudi, Y. Yang, I. L. Moudrakovski, J. R. Ripmeester, *Chem. Mater.* **2000**, *12*, 3857.

24 M. P. Kapoor, S. Inagaki, *Chem. Mater.* **2002**, *14*, 3509.

25 M. Kruk, M. Jaroniec, S. Guan, S. Inagaki, *J. Phys. Chem. B* **2001**, *105*, 681.

26 T. Asefa, M. J. MacLachlan, H. Grondey, N. Coombs, G. A. Ozin, *Angew. Chem., Int. Ed.* **2000**, *39*, 1808.

27 S. Hamoudi, Y. Yang, I. L. Moudrskovski, S. Lang, A. Sayari, *J. Phys. Chem. B* **2001**, *105*, 9118.

28 Y. Liang, M. Hanzlik, R. Anwander, *Chem. Commun.*

2005, 525.

29 H. I. Lee, C. Pak, S. H. Yi, J. K. Shon, S. S. Kim, B. G. So, H. Chang, J. E. Yie, Y. U. Kwon, J. M. Kim, *J. Mater. Chem.* **2005**, *15*, 4711.

30 T. Ren, X. Zhang, J. Suo, *Microporous Mesoporous Mater.* **2002**, *54*, 139.

31 A. Sayari, Y. Yang, *Chem. Commun.* **2002**, 2582.

32 S. Hamoudi, S. Kaliaguine, *Chem. Commun.* **2002**, 2118.

33 O. Muth, C. Schellbach, M. Fröba, *Chem. Commun.* **2001**, 2032.

34 M. C. Burleigh, M. A. Markowitz, E. M. Wong, J.-S. Lin, B. P. Gaber, *Chem. Mater.* **2001**, *13*, 4411.

35 J. R. Matos, M. Kurk, L. P. Mercuri, M. Jeroniec, T. Asefa, N. Coombs, G. A. Ozin, T. Kamiyama, O. Terasaki, *Chem. Mater.* **2002**, *14*, 1903.

36 C. Yu, Y. Yu, D. Zhao, *Chem. Commun.* **2000**, 575.

37 W. Guo, J.-Y. Park, M.-O. Oh, H.-W. Jeong, W.-J. Cho, I. Kim, C.-S. Ha, *Chem. Mater.* **2003**, *15*, 2295.

38 W. Guo, I. Kim, C.-S. Ha, *Chem. Commun.* **2003**, 2692.

39 K. Nakajima, D. Lu, I. Tomita, S. Inagaki, M. Hara, S. Hayashi, K. Domen, J. N. Kondo, *Chem. Lett.* **2003**, *32*, 950.

40 W. Wang, S. Xie, W. Zhou, A. Sayari, *Chem. Mater.* **2004**, *16*, 1756.

41 K. Nakajima, I. Tomita, M. Hara, S. Hayashi, K. Domen, J. N. Kondo, *J. Mater. Chem.* **2005**, *15*, 2362.

42 G. Temtsin, T. Asefa, S. Bittner, G. A. Ozin, *J. Mater. Chem.* **2001**, *11*, 3202.

43 Y. Goto, S. Inagaki, *Chem. Commun.* **2002**, 2410.

44 M. P. Kapoor, N. Setoyama, Q. Yang, M. Ohashi, S. Inagaki, *Langmuir* **2005**, *21*, 443.

45 M. Kuroki, T. Asefa, W. Whitnal, M. Kruk, C. Yoshina-Ishii, M. Jaroniec, G. A. Ozin, *J. Am. Chem. Soc.* **2002**, *124*, 13886.

46 K. Landskron, B. D. Hatton, D. D. Perovic, G. A. Ozin, *Science* **2003**, *302*, 266.

47 K. Landskron, G. A. Ozin, *Science* **2004**, *306*, 1529.

48 W. J. Hunks, G. A. Ozin, *Chem. Commun.* **2004**, 2426.

49 W. J. Hunks, G. A. Ozin, *Chem. Mater.* **2004**, *16*, 5465.

50 J. Morell, G. Wolter, M. Fröba, *Chem. Mater.* **2005**, *17*, 804.

51 M. E. Devis, *Nature* **2002**, *417*, 813.

52 S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, *Nature* **2002**, *416*, 304.

53 N. Bion, P. Ferreira, A. Valente, I. S. Goncalves, J. Rocha, *J. Mater. Chem.* **2003**, *13*, 1910.

54 B. Onida, L. Borello, C. Busco, P. Ugliengo, Y. Goto, S. Inagaki, E. Garrone, *J. Phys. Chem.* **2005**, *109*, 11961.

55 B. Onida, B. Camarota, P. Ugliengo, Y. Goto, S. Inagaki, E. Garrone, *J. Phys. Chem.* **2005**, *109*, 21732.

56 J. Morell, C. T. Teixeira, M. Cornelius, V. Rebbin, M. Tiemann, H. Amenitsch, M. Fröba, M. Linden, *Chem. Mater.* **2004**, *16*, 5564.

57 K. Okamoto, Y. Goto, S. Inagaki, *J. Mater. Chem.* **2005**, *15*, 4136.

58 Y. Goto, K. Okamoto, S. Inagaki, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 932.

59 Y. Xia, W. Wang, R. Mokaya, *J. Am. Chem. Soc.* **2005**, *127*, 790.

60 W. Wang, W. Zhou, A. Sayari, *Chem. Mater.* **2003**, *15*, 4886.

61 M. P. Kapoor, Q. Yang, S. Inagaki, *Chem. Mater.* **2004**, *16*, 1209.

62 A. Sayari, W. Wang, *J. Am. Chem. Soc.* **2005**, *127*, 12194.

63 M. P. Kapoor, Q. Yang, S. Inagaki, *J. Am. Chem. Soc.* **2002**, *124*, 15176.

64 E. F. Vansant, P. VanDerVoort, K. C. Vrancken, *Stud. Surf. Sci. Catal.* **1995**, *93*, 3.

65 T. Shimada, K. Aoki, Y. Shinoda, T. Nakamura, N. Tokunaga, S. Inagaki, T. Hayashi, *J. Am. Chem. Soc.* **2003**, *125*, 4688.

66 K. Aoki, T. Shimada, T. Hayashi, *Tetrahedron: Asymmetry* **2004**, *15*, 1771.

67 M. P. Kapoor, S. Inagaki, S. Ikeda, K. Kakiuchi, M. Suda, T. Shimada, *J. Am. Chem. Soc.* **2005**, *127*, 8174.

68 T. H. Chan, I. Feming, *Synthesis* **1979**, 761.

69 L. H. Sommer, L. J. Tyler, F. C. Whitmore, *J. Am. Chem. Soc.* **1948**, *70*, 2872.

70 T. Morita, Y. Okamoto, H. Sakurai, *Tetrahedron Lett.* **1980**, *21*, 835.

71 K. Okamoto, M. P. Kapoor, S. Inagaki, *Chem. Commun.* **2005**, 1423.

72 S. C. Christiansen, D. Zhao, M. T. Janicke, C. C. Landry, G. D. Stucky, B. F. Chmelka, *J. Am. Chem. Soc.* **2001**, *123*, 4519.

73 N. Hedin, R. Graf, S. C. Christiansen, C. Gervais, R. C. Hayward, J. Eckert, B. F. Chmelka, *J. Am. Chem. Soc.* **2004**, *126*, 9425.

74 X. Feng, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, J. Liu, K. M. Kemner, *Science* **1997**, *276*, 923.

75 L. Mercier, T. J. Pinnavaia, *Adv. Mater.* **1997**, *9*, 500.

76 J. Brown, L. Mercier, T. J. Pinnavaia, *Chem. Commun.* **1999**, 69.

77 A. M. Liu, K. Hidajat, S. Kawi, D. Y. Zhao, *Chem. Commun.* **2000**, 1145.

78 W. D. Bossaert, D. E. De Vos, W. M. Van Rhijn, J. Bullen, P. J. Grobet, P. A. Jacobs, *J. Catal.* **1999**, *182*, 156.

79 M. A. Harmer, W. E. Farneth, Q. Sun, *Adv. Mater.* **1998**, *10*, 1255.

80 T. Asefa, M. Kruk, M. J. MacLachlan, N. Coombs, H. Grondey, M. Jaroniec, G. A. Ozin, *J. Am. Chem. Soc.* **2001**, *1235*, 8520.

81 M. C. Burleigh, M. A. Markowitz, M. S. Spector, B. P. Gaber, *J. Phys. Chem. B* **2001**, *105*, 9935.

82 R. Voss, A. Thomas, M. Antonietti, G. A. Ozin, *J. Mater. Chem.* **2005**, *15*, 4010.

83 Q. Yang, M. P. Kapoor, S. Inagaki, *J. Am. Chem. Soc.* **2002**, *124*, 9694.

84 M. P. Kapoor, Q. Yang, Y. Goto, S. Inagaki, *Chem. Lett.* **2003**, *32*, 914.

85 T. Kamegawa, T. Sakai, M. Matsuoka, M. Anpo, *J. Am. Chem. Soc.* **2005**, *127*, 16764.

86 K. Nakajima, I. Tomita, M. Hara, S. Hayashi, K. Domen, J. N. Kondo, *Adv. Mater.* **2005**, *17*, 1839.

87 S. S. Park, C. H. Lee, J. H. Cheon, D. H. Park, *J. Mater. Chem.* **2001**, *11*, 3397.

88 S. S. Park, C. H. Lee, J. H. Cheon, S. J. Choe, D. H. Park, *Bull. Korean Chem. Soc.* **2001**, *22*, 948.

89 C. H. Lee, S. S. Park, S. J. Choe, D. H. Park, *Microporous Mesoporous Mater.* **2001**, *46*, 257.

90 M. P. Kapoor, S. Inagaki, *Chem. Lett.* **2004**, *33*, 88.

91 V. Rebbin, M. Jakubowski, S. Pötz, M. Fröba, *Microporous Mesoporous Mater.* **2004**, *72*, 99.

92 D.-J. Kim, J.-S. Chung, W.-S. Ahn, G.-W. Kang, W.-J. Cheongy, *Chem. Lett.* **2004**, *33*, 422.

93 X. Y. Bao, X. S. Zhao, *J. Phys. Chem. B* **2005**, *109*, 10727.

94 Q. Yang, M. P. Kapoor, N. Shirokura, M. Ohashi, S. Inagaki, J. N. Kondo, K. Domen, *J. Mater. Chem.* **2005**, *15*, 666.

95 Q. Yang, M. P. Kapoor, S. Inagaki, N. Shirokura, J. N. Kondo, K. Domen, *J. Mol. Catal. A: Chem.* **2005**, *230*, 85.

96 Q. Yang, J. Liu, J. Yang, M. P. Kapoor, S. Inagaki, C. Li, *J. Catal.* **2004**, *228*, 265.

97 J. Liu, Q. Yang, M. P. Kapoor, N. Setoyama, S. Inagaki, J. Yang, L. Zhang, *J. Phys. Chem.* **2005**, *109*, 12250.

98 P. L. Dhepe, M. Ohashi, S. Inagaki, M. Ichikawa, A. Fukuoka, *Catal. Lett.* **2005**, *102*, 163.

99 M. P. Kapoor, A. Bhaumik, S. Inagaki, K. Kuraoka, T. Yazawa, *J. Mater. Chem.* **2002**, *12*, 3078.

100 M. P. Kapoor, A. K. Sinha, S. Seelan, S. Inagaki, S. Tsubota, H. Yoshida, M. Haruta, *Chem. Commun.* **2002**, 2902.

101 A. Bhaumik, M. P. Kapoor, S. Inagaki, *Chem. Commun.* **2003**, 470.

102 B. J. Hughes, J. B. Guilbaud, M. Allix, Y. Z. Khimyak, *J. Mater. Chem.* **2005**, *15*, 4728.

103 Q. Yang, J. Yang, Z. Feng, Y. Li, *J. Mater. Chem.* **2005**, *15*, 4268.

104 L. Zhang, W. Zhang, J. Shi, Z. Hua, Y. Li, J. Yan, *Chem. Commun.* **2003**, 210.

105 O. Olkhovyk, M. Jaroniec, *J. Am. Chem. Soc.* **2005**, *127*, 60.

106 A. Fukuoka, Y. Sakamoto, S. Guan, S. Inagaki, N. Sugimoto, Y. Fukushima, K. Hirahara, S. Iijima, M. Ichikawa, *J. Am. Chem. Soc.* **2001**, *123*, 3373.

107 Y. Sakamoto, A. Fukuoka, T. Higuchi, N. Shimomura, S. Inagaki, M. Ichikawa, *J. Phys. Chem. B* **2004**, *108*, 853.

108 A. Fukuoka, H. Araki, Y. Sakamoto, S. Inagaki, Y. Fukushima, M. Ichikawa, *Inorg. Chim. Acta* **2003**, *350*, 371.

109 Y. Lu, H. Fan, N. Doke, D. A. Loy, R. A. Assink, D. A. LaVan, C. J. Brinker, *J. Am. Chem. Soc.* **2000**, *122*, 5258.

110 Ö. Dag, C. Yoshina-Ishii, T. Asefa, M. J. MacLachlan, H. Grondey, N. Coombs, G. A. Ozin, *Adv. Funct. Mater.* **2001**, *11*, 213.

111 S. S. Park, C.-S. Ha, *Chem. Commun.* **2004**, 1986.

112 B. D. Hatton, K. Landskron, W. Whitnall, D. D. Perovic, G. A. Ozin, *Adv. Funct. Mater.* **2005**, *15*, 823.

113 S. Hamoudi, S. Royer, S. Kaliaguine, *Microporous Mesoporous Mater.* **2004**, *71*, 17.

114 O. Ohtani, Y. Goto, K. Okamoto, S. Inagaki, *Mater. Lett.* **2006**, *60*, 177.

115 O. Ohtani, Y. Goto, K. Okamoto, S. Inagaki, *Chem. Lett.* **2005**, *34*, 1342.

116 J. Pang, V. T. John, D. A. Loy, Z. Yang, Y. Lu, *Adv. Mater.* **2005**, *17*, 704.

Mahendra P. Kapoor received his B.S. (chemistry) in 1984 and M.S. (organic chemistry) in 1986 from HNB Garhwal University, India. In 1990, he obtained his Ph.D. (petroleum chemistry) from the Indian Institute of Petroleum (CSIR). After post-doctoral work at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, in Moscow (1989–1992), he joined the Chemical Engineering Department at the University of Laval as a research associate (1992–1998) in the group of Prof. S. Kaliaguine. In 1998, he joined the Osaka National Research Institute (AIST-Kansai) as a STA fellow (1998–2000) and was an AIST research fellow until 2001. He joined Toyota Central R&D Labs., Inc. in 2001 as a visiting researcher, where he worked with Dr. S. Inagaki until 2004. Since, he has joined the Nano-Function Division of the Taiyo Kagaku Co., Ltd in Yokkaichi, Mie as a senior scientist. The focus of his research is on the design of organic–inorganic hybrid mesoporous materials and functionalized porous solids for high-throughput experimentation in catalysis, optoelectronics, membrane technology, and other diverse material science related applications.

Award recipient

Shinji Inagaki was born in Nagoya, Japan, in 1959. He received a B.S. degree in 1982 and a M.S. degree in 1984 from Nagoya University. He joined Toyota Central R&D Labs., Inc. in 1984. He received a Dr. degree in 1998 from Nagoya University. He is presently a principal researcher at Toyota Central R&D Labs., Inc., leading a research group devoted to mesoporous materials. He received the Chemical Society of Japan Award for Creative Work for 2004 and the Minister Award of Education, Culture, Sport, Science and Technology (2005). His current research has focused on the synthesis and applications of organic–inorganic hybrid mesoporous materials.