SYNTHESIS AND CHARACTERIZATION OF ORDERED CAGE-LIKE SILICEOUS MESOSTRUCTURES WITH ORGANIC PENDANT AND BRIDGING GROUPS

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by

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I. INTRODUCTION

The design of nanoporous materials with desired adsorption and surface properties has become of particular importance from the scientific and technological points of view. Several porous materials are applied as molecular sieves, chemical sensors, selective adsorbents, and shape-selective catalysts due to their high surface area. The International Union of Pure and Applied Chemistry has proposed classification of porous solids into three classes according to their pore size: (i) microporous with pores ranging from 0 and 2 nm, (ii) mesoporous with pore sizes between 2 and 50 nm, and (iii) macroporous with pore sizes exceeding 50 nm. Zeolites, which are members of the microporous family, were found to be very good catalysts and catalytic supports due to the presence of alumina in their framework. Unfortunately, their applicability was greatly restricted by tiny connecting apertures and small micropores. Porous gels and porous glasses extended the pore size from micropores to mesopores; however, pores of these materials were disordered and non-uniform in size. The discovery of ordered mesoporous silicas (OMSs) (M41S) templated by ionic surfactants by Mobil Oil Company researchers in 1992, extended by very important findings from University of California (Santa Barbara) in 1998, was a significant breakthrough in the synthesis and characterization of porous materials such as zeolites, fullerenes, carbon nanotubes, and polymers. Specifically, mesoporous materials, which were synthesized from easily hydrolysable silica (tetraethyl orthosilicate) and organosilica precursors in the presence of nontoxic and biodegradable block copolymer templates, were prepared in a variety of ordered structures with tailorable surface properties. Such polymer-templated adsorbents featured
tunable pore sizes, ordered pore systems and large surface areas. Interestingly, depending on the preparation conditions, the synthesis can lead to ordered mesoporous materials with channel-like and cage-like structures. So far, the development of mesoporous materials was mainly focused on the fabrication of materials with channel-like structures, whereas little or no attention was given to materials with cage-like structures. This dissertation is focused on the synthesis and characterization of materials with cage-like structures, as well as on the incorporation of organic pendant and bridging groups to alter the surface and framework properties, which can be used for many prospective applications in the fields of chromatography, adsorption, gas storage, and catalysis. Several topics such as surfactant-templated and polymer-templated siliceous mesostructures and polymer-templated ordered mesopores organosilicas with organic pendant and bridging groups are presented in the introduction of this dissertation in order to introduce readers into the area of cage-like silica-based materials.

1.1. SURFACTANT-TEMPLATED ORDERED SILICEOUS MESOSTRUCTURES

Initially, research on OMSs [1-7] was mostly focused on the development of materials with two-dimensional (2D) hexagonal arrangement of mesopores such as MCM-41 (Mobil Composition of Matter) \((p6mm)\) [1, 2, 8] and FSM-16 (Folded Sheet Materials) \((p6mm)\) [9, 10], materials with bicontinuous cubic mesostructure such as MCM-48 \((Ia3d)\) [1, 2, 11-13] and lamellar structure such as MCM-50. In particular, MCM-41 [1, 2, 8] was prepared under basic conditions from dilute solutions by
hydrolysis and condensation of inorganic precursors such as tetraethyl orthosilicate (TEOS) or sodium silicate in the presence of amphiphiles such as long alkyl-tri(short alkyl) ammonium surfactants \([C_nH_{2n+1}N(R)\text{}_3]^+ X^-\) (Cl\(^-\) or Br\(^-\)) used as templates; surfactants with various lengths of the alkyl chain \((C_nH_{2n+1}, 6 \leq n \leq 22)\) and different sizes of head groups \([(R: \text{methyl (CH}_3\text{-), ethyl (C}_2\text{H}_5\text{-) and so forth})\] were employed [14, 15]. The self-assembly synthesis of these materials occurs due to electrostatic interactions between negatively charged silica species (I\(^-\)) and positively charged quaternary ammonium micelles (S\(^+\)) [16, 17]. However, FSM-16 [8, 9] was obtained differently; in this case, a layered polysilicate kanemite was intercalated with cetyltrimethylammonium cations, which led to its transformation from lamellar to hexagonal structure.

The pore structure of MCM-41 can be tailored by varying the type of ionic surfactants (pore size in the range from ~2 to ~6 nm) [14, 15] and by addition of auxiliary reagents (2-10 nm) such as 1,3,5-trimethylbenzene, 1,3,5-triisopropylbenzene [18] and long chain trialkylamines [19], or N,N-diethylalkylamines [20] and so forth.

Numerous new structures have emerged based on the analogous approach as that used for the synthesis of MCM-41 [1, 2], however many of them are less ordered. Tanev and co-workers [21] reported the synthesis of HMS (Hexagonal Mesoporous Silica) prepared in the presence of neutral amine as a structure directing agent. In contrast to MCM-41 [1, 2], HMS [21] exhibited weakly ordered hexagonal structure (worm-like) with smaller crystalline sizes and thicker walls. Soon after, Bagshaw and co-workers [22] prepared MSU-n (Michigan State University) materials using polyethylene oxide (PEO), which were weakly ordered with channel-like structure, thick walls and small particle
size. Ryoo et al. [23] reported synthesis of disordered mesoporous silica KIT-1 prepared by addition of different organic polyacids, e.g., ethylenediaminetetraacetic acid tetrasodium salt (EDTANa₄) into the surfactant/TEOS mixture that possessed disordered cylinders with uniform diameter.

1.2. POLYMER-TEMPLATED ORDERED SILICEOUS MESOSTRUCTURES

The surfactant-templated synthesis of OMS was further extended by employing nontoxic and commercially available block copolymers as structure directing agents under acidic conditions [24, 25]. In contrast to the surfactant-templated silicas [1, 2], the polymer-templated materials possess larger pore diameters (~8-15 nm), thicker pore walls and larger pore volumes [24, 25]; however, as in the case of surfactant-assisted synthesis analogous hexagonal and cubic mesostructures are obtained. In particular, 2D hexagonal SBA-15 (Santa Barbara Amorphous) with channel-like mesopores (p6mm) became one of the most popular OMS worldwide due to the successful synthesis reported by Zhao and co-workers [24, 25]. Its simple and reproducible synthesis provides materials with thicker pore walls and larger pores [26]. SBA-15 can be obtained from TEOS [24-26] or sodium silicate [27] under acidic conditions using poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer, Pluronic P123 HO(C₂H₄O)₂₀(C₃H₆O)₇₀(C₂H₄O)₂₀H, having 20 and 70 blocks of hydrophilic EO and hydrophobic PO, respectively. The properties of SBA-15 can be easily tuned by adjusting the synthesis conditions in terms of temperature of initial stirring and hydrothermal treatment [28, 29], time [30], microwave irradiation [31-33], changing ratio
of TEOS/P123 [34-36] and so forth. At first sight, SBA-15 [24, 25] seems to be analogous to MCM-41 [1, 2], but it differs from it due to the presence of large pores (up to 15 nm), thick pore walls and superior thermal and hydrothermal stabilities [37, 38] as well as the presence of microporosity [39, 40]. While both MCM-41 and SBA-15 are 2D structures of hexagonally ordered mesopores, the latter is rather a 3D material due to the presence of irregular interconnecting micropores [39, 40]. SBA-15 OMS has been extensively studied lately, however the main focus of this dissertation is emphasized on cubic structures; therefore it will not be further discussed in this introduction. In addition, several new mesophases were also discovered such as SBA-1 [41], SBA-2 [42], SBA-3 [43, 44], SBA-6, SBA-8 [45], SBA-11 and SBA-12 [25]; a survey of the research in this area can be found in recent review article by Wan and Zhao [46].

Further studies in the area of polymer-templated materials led to the development of body-centered cubic (\textit{Im3m} symmetry) [47] OMS SBA-16 [24, 25] with reproducible synthesis. In contrast to its hexagonal counterpart, 3D cubic SBA-16 exhibits spherical cage-like mesopores, each of them connected with eight similar cages via smaller pores creating multidirectional pore connectivity. Similar to SBA-15 [24-40], the synthesis of SBA-16 [24, 25] is carried out under low (0.5M HCl) acidic conditions using TEOS, trimethyl orthosilicate (TMOS) or sodium silicate as the silica source and a block copolymer (\textit{HO(C}_2\textit{H}_4\textit{O})_{106}(\textit{C}_3\textit{H}_6\textit{O})_{70}(\textit{C}_2\textit{H}_4\textit{O})_{106}\textit{H}) having about five times longer hydrophilic segments than those in the SBA-15 template. Moreover, similarly to SBA-15, the spherical pores of the SBA-16 silica are also interconnected by micropores or small mesopores. Numerous papers have been published on the synthesis [48, 49] and
characterization [47, 50, 51] of SBA-16, which was initially synthesized by Stucky and co-workers [24, 25] in the presence of poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer Pluronic F127, as a structure directing agent; unfortunately, no details regarding the synthesis time and temperature as well as its properties were reported. A few years later, Voort and co-workers [48] provided additional details regarding the stirring and hydrothermal time as well as temperature, but the materials still did not possess well-defined morphology and ordering as evidenced by XRD profiles. To date SBA-16 materials have been synthesized primarily by employing Pluronic F127 [25, 48], however, there are a few reports on the use of copolymer blends of P123 and F127 [52] as well as Pluronic F108 (HO(C$_2$H$_4$O)$_{40}$(C$_3$H$_6$O)$_{141}$(C$_2$H$_4$O)$_{40}$(C$_2$H$_4$O)$_{141}$H) [53] or even non-ionic oligomeric surfactant Brij700 (polyoxyethylene stearyl ether, C$_{18}$H$_{37}$EO$_{100}$) [54], however their synthesis is rarely carried out due to the strict conditions necessary to synthesize high quality material, which often leads to SBA-16 OMS with small pores. In addition, Cheng and co-workers [55] have synthesized SBA-16 OMSs by varying silica concentrations in the range from 0.75 to 1.2 in the final gel composition [55]. It was shown that the spherical particle size can be controlled within 1.5-10 µm, which is important for using these particles as chromatographic packings. It was found that the pore wall thickness and pore diameter can be obtained within 8.57-9.14 nm and 3.1-4.0 nm, respectively. However, such pore sizes with likely narrower pore entrances are relatively too small for many applications. Furthermore, recent studies have demonstrated that SBA-16 can be prepared after one hour of stirring under highly acidic conditions; however, this work does not provide information about hydrothermal
Quite recently, Li and co-workers [57] showed that the use of a mixed template consisting of Pluronic F127 copolymer and sodium dodecyl sulfonate (SDS) anionic surfactant afforded SBA-16 samples with smaller mesopores and enabled some control of microporosity in these materials by varying the SDS/F127 ratio. An analogous approach was also used by Mesa and co-workers [58] who instead of using SDS employed cetyltrimethylammonium bromide (CTMABr) as co-surfactant. However, Kleitz and co-workers [59] were able to obtain the SBA-16 mesostructure over a wide range of compositions of TEOS and Pluronic F127 at low acid concentrations by using n-butanol as an organic additive. Stevens and co-workers [60] also used butanol as an additive to form well-ordered and porous SBA-16 spheres with different sizes by controlling the addition of TEOS during self-assembly. Hwang and co-workers [61] obtained single crystal morphologies for the first time under microwave treatment. The structure and morphologies were controlled by time of microwave irradiation as well as by the temperature of stirring. The mesoporous SBA-16 silica exhibited a broad range of morphologies from a disordered spherical shape to cubic rhombdodecahedral or decaoctahedral shape, depending on the synthesis conditions. Recently Jin and co-workers [62] synthesized single crystal-like SBA-16 mesostructure exhibiting a decaoctahedron shape or a rhomb-dodecahedron shape by finely adjusting the mixture composition of template F127, TEOS and pH under static conditions. Later, Meng and co-workers [63] obtained single crystals with a rhombododecahedron shape using a mixture of F127 template and cationic fluorinated surfactant with short carbon chains. In most cases, the existing recipes afforded SBA-16 with relatively small pore sizes and
quite low pore volumes. There is no clear evidence of how to improve these parameters, especially the pore volume.

It is noteworthy that in the case of SBA-16 cage-like materials containing organic polymer (within 45-55% by weight), the removal of the template is the crucial step in their fabrication and still remains a challenging issue. So far, there are several methods of template removal from the as-synthesized nanomaterials. The most common approach is achieved by conventional ion exchange (extraction), where material is suspended in ethanol solution with a high concentration of ions. The second most popular way is carried out by burning the organic template through heat treatment in an oven under flowing air or nitrogen [24]. However, these two methods are not sufficient to achieve a desired porous structure because extraction leaves a significant template residue, whereas calcination leads to both a high concentration of carbon deposits contaminating the porous silica material and considerable structure contraction. In the case of mesoporous silica films, calcination leads to distortion and cracks due to the stress resulting from structural shrinkage. When the temperature is gradually increased in the oven, a material usually contracts in volume because of the formation of siloxane bonds caused by condensation of silanol groups. Therefore, other procedures have emerged recently to improve the removal of the template; for instance those employing microwave [64, 65] and UV irradiation [66]. In the case of the former microwave generates intensive heat to burn the organic template [64, 65], whereas the latter involves photochemical degradation at a wavelength of 172 nm. In contrast to conventional heating treatment, microwave and photochemical treatments are much more rapid; however they require a microwave and
UV instruments, which are unavailable in many laboratories. Supercritical fluid extraction [67] with CO$_2$ as an extraction fluid at 85 °C was also applied; its benefits are low toxicity, low cost and chemical inertness. However, supercritical fluid extraction turned out to remove only 78 % of the template, which is still unsatisfactory. Unfortunately, the aforementioned procedures do not fulfill all required features at once including a full removal of the polymeric agent, short processing time and minimal distortion of structural and surface characteristics of porous materials. Recently, a two-step removal of Pluronic P123 from as-synthesized mesostructures was proposed by Schüth and co-workers [68, 69] and other researchers [70] indicating some important advantages over other procedures; smaller structural deterioration, larger pore volume and higher surface area as well as higher concentration of Si-OH groups. This procedure involved an initial treatment of as-synthesized samples with 30-60 wt % sulfuric acid solution followed by their calcination at a lower temperature (200 °C or higher). The aforementioned method was shown to be effective for the template removal from channel-like SBA-15 structures and to our knowledge it was not applied to cage-like materials.

An analogous approach was also used for the preparation of ordered 3D cage-like siliceous mesostructure such as FDU-12 materials as reported by Fan and co-workers [71], which have been synthesized using amphiphilic triblock copolymer F127 template similarly to SBA-16 silica and TEOS. However, this rather complicated procedure involves high concentration of hydrochloric acid, the addition of potassium chloride and 1,3,5-trimethylbenzene (swelling agent), different hydrothermal treatment temperature
and extended hydrothermal treatment time up to 72 h. It was suggested [71] that FDU-12 possesses a face-centered-cubic structure ($Fm\overline{3}m$ symmetry group) without 3D hexagonal intergrowth, where each cage is connected with nearest twelve cages. It should be noted that the synthesis of FDU-12 can only be carried out in a narrow range of synthesis conditions, low temperature to avoid structural deterioration and in the presence of 1,3,5-trimethylbenzene and potassium chloride, which are very critical for preparation of FDU-12.

Simultaneously, Ryoo and co-workers [72] reported the synthesis of another 3D cage-like mesoporous silica KIT-5 with cubic $Fm\overline{3}m$ structure. KIT-5 was synthesized using TEOS and F127 triblock copolymer template similarly to FDU-12, however at low acid concentrations and without addition of salts or swelling agents. The authors showed the possibility of tailoring mesopore diameters and size apertures by controlling hydrothermal treatment temperature within 45 and 150 °C, but these materials exhibited moderate specific surface area and total pore volume. In addition, at hydrothermal treatment temperature above 130 °C the structure exhibited enlarged pore openings.

Shortly after, mesoporous cage-like PSU-1 (Pennsylvania State University-1) silica [73] was synthesized in the presence of cetyltrimethylammonium halide and triblock copolymer P123 as a mixed template under microwave–hydrothermal conditions. It was found that the chain length of ionic surfactant affects the size of cage diameter. However, the synthesis required very specific methodology and is not reproducible under conventional hydrothermal treatment conditions resulting in disordered structure with broad pore size distribution.
Numerous attempts were made to obtain ordered siliceous mesostructures with cage-like pores. Fabrication of these materials requires strict control of synthesis conditions, which usually leads to mixed mesophases and lack of ordering. Therefore, the synthesis of 3D cage-like siliceous materials with high quality and high degree of ordering is still very challenging.

A cage-like FDU-1 OMS offers greater flexibility of the synthesis conditions by employing a more hydrophobic triblock copolymer, poly(ethylene oxide)-block-poly(butylene oxide)-block-poly(ethylene oxide); \( \text{HO(C}_2\text{H}_4\text{O})_{39}(\text{C}_4\text{H}_8\text{O})_{47}(\text{C}_2\text{H}_4\text{O})_{39}\text{H} \), instead of poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) used for the synthesis of SBA-16 [24, 25] as reported by Yu and co-workers [74]. Initially this structure was assigned to the \( \text{Im}3\text{m} \) space group, however based on HRTEM and SAXS analysis, Jaroniec and co-workers proposed a face-centered cubic \( \text{Fm}3\text{m} \) symmetry with three-dimensional hexagonal intergrowth [75]. Each cage is connected with twelve neighboring pores via small apertures to form a multidirectional mesopore network. Analogously to the other polymer-templated materials such as SBA-15 and SBA-16 [24, 25], the cage-like pores of FDU-1 are interpenetrated by micropores and smaller mesopores. Subsequently, a new method for evaluation of the pore entrance sizes in the cage-like mesostructures was reported [78]. This method is based on the monitoring of the pore accessibility by nitrogen molecules after modification of the sample with organosilanes of progressively increasing dimensions. These organosilanes form a dense chemically bonded monolayer on the surface of cage-like silica making the structure inaccessible, if the size of organosilanes is able to block the pore openings. This
inexpensive and practical approach is useful to estimate the pore opening sizes in the range of 1 to 5 nm. Jaroniec and co-workers [79] have studied hydrothermal and thermal stabilities of the FDU-1 silica by boiling the material in water at 100 °C between 3 hrs and 32 days and heating in flowing air at 700 and 1000 °C for 5 hrs. It was found out that FDU-1 preserved its uniform cage-like pores even after 32 days of boiling in hot water revealing its unprecedented hydrothermal stability. It was reported that after heating in hot media for a prolonged time the silica layers were progressively peeled off, not affecting the uniformity of the thick cage-like pores as much as pore diameter and the pore entrances, which were enlarged after 12 hrs of boiling and further increased with a heating time leading to an open pore structure. Moreover, they found that the hydrothermal stability can be enhanced by the introduction of an additional layer of silica through post-grafting modification with chemically bonded trimethylchlorosilane on its surface or framework that prevents further erosion in hot aqueous medium. In the case of heat treatment in air at 900 °C, most of the primary pores (70%) were also preserved indicating its extraordinary thermal stability. More recently, a rapid fabrication of FDU-1 OMSs was investigated using hydrothermal treatment in a microwave oven at 100 °C within 15 and 180 minutes [80]. It was shown that ordered silica mesostructures can be synthesized between 15 and 60 minutes of microwave hydrothermal treatment disclosing a new possibility for a short time preparation of the FDU-1 materials. In particular, some attempts have been made to narrow the pore size distribution and tailor the pore size entrances by addition of inorganic salts under different acid concentrations [81].
In comparison to other polymer-templated ordered cage-like siliceous mesostructures, FDU-1 [74] and SBA-16 [24] have attracted a lot of attention that originated from reproducible synthesis procedures, flexible synthesis range and fascinating characteristics reflected by high specific surface area, high pore volume and large mesopore diameter. For 3D type of porous structures the aforementioned properties ensure faster transport of reactants, provide more resistance to blocking of pores and make them accessible from any direction. These features make cage-like FDU-1 and SBA-16 OMSs very promising materials for applications in gas sensing, adsorption, catalysis and separations of molecules.

Meanwhile analogous methodology was also applied for the fabrication of non-silica mesoporous metal oxides of titanium [82], aluminum [38, 83], zirconium [38], tin [38], manganese [84], niobium [85], germanium [86] metal sulfides and metal phosphates of aluminum [87] and zirconium [88]. The aforementioned synthesis of OMSs is known as soft-templating synthesis, whereas in hard-templating synthesis a nanoporous material can be used as a template similar to that of a surfactant. The empty voids of a mesoporous solid can be impregnated with inorganic precursors, which can be further treated under specific conditions to obtain a negative replica. The “hard” silica template is usually removed by etching with HF or NaOH solution and the resulting inverse replica usually has a high surface area. This method was also successfully applied by Ryoo and co-workers [89] to synthesize ordered mesoporous carbons using carbon precursors such as sucrose and phenol resin to fill MCM-48 (CMK-1) mesoporous silica template. After impregnation, precursors underwent polymerization and stabilization (if needed) as well
as carbonization to create a rigid carbon framework in the 3D mesoporous network of the silica template. Finally, silica template was removed with HF or NaOH solution. Soon after the first publication on the hard-templating synthesis of carbons [89] reports devoted to ordered mesoporous carbons have been published [90]. It is interesting to note that the replication recipe can lead to two different structures of mesoporous carbons, i.e., rod-like and tube-like, depending on the level of impregnation. For example, SBA-15 mesoporous silica template with hexagonal $p6mm$ structure [24] leads to CMK-3 [91] and CMK-5 [92] ordered mesoporous carbons, as a result of complete and incomplete filling of the SBA-15 cylindrical pores, respectively. For cubic mesoporous silica templates such as FDU-1, the resulting mesoporous carbons are known as KIT-5 [93]. This type of mesoporous carbon has received a lot of attention because of 3D connectivity that can be beneficial for applications in gas sensing [94], optics and catalysis [95]. Currently, there are many suitable carbon precursors, which have been successfully used such as sucrose, furfuryl alcohol, acetylene, mesophase pitch, pyrrole, phenol resin and so forth, which have been used for the synthesis of mesoporous carbons [96].
1.3. POLYMER-TEMPLATED ORDERED SILICEOUS MESOSTRUCTURES WITH ORGANIC PENDANT GROUPS

The diversity of mesoporous sieves has been further extended by designing new hybrid inorganic materials [97-101], referred to as ordered mesoporous organosilicas (OMOs), which are OMSs with organic functional groups covalently attached to the mesopore walls. The introduction of various functionalities results in materials with useful optical, mechanical and electrical properties, which make them attractive materials for catalytic and adsorption processes, sensing devices and environmental applications, e.g., removal of toxic heavy metal ions such as mercury and lead from aqueous media [102, 103].

There are two common approaches to the surface functionalization of mesostructured materials: (i) post-synthesis grafting [2, 104-112] and (ii) co-condensation, also known as one-pot synthesis [105, 113-118]. Post-synthesis grafting refers to functionalization of the inner surface of mesoporous silica, which does not contain template such as surfactant or polymer (usually, extraction or calcination is used to remove the template). Modification occurs due to the reaction between free silanol groups and chlorosilane ClSiR₃ or more often organosilanes (R’O)₃SiR in dry toluene or other solvent. In general, various functional ligands can be incorporated using this procedure and appropriate organosilane precursors like mercury-binding ligands such as 1-allyl-3-propylthiourea [119], 1-benzoyl-3-propylthiourea [120-122] and 2,5-dimercapto-1,3,4-thiadiazole [123, 124]. Another option of post-synthesis modification
is grafting of organic functionalities combined with simultaneous template displacement [125], where silica-surfactant mesostructure is reacted with an organosilane in order to displace the surfactant template and to introduce the surface ligand.

Alternatively, ordered mesoporous organosilicas can be also prepared by one-pot synthesis [105, 113-118]. This method allows one to introduce organic ligands to the pore walls during the self-assembly process with all precursors participating in the structure formation. In particular, tetraalkyl orthosilicate [(RO₄)Si; TEOS or TMOS] as a silica precursor is prehydrolyzed and co-condensed together with organotrialkoxysilane (R’O)₃SiR precursor in the presence of a soft template.

In general, post-synthesis grafting [2, 104-112, 119-124] and co-condensation routes usually lead to materials differing in the surface area, surface reactivity [126], pore and binding site accessibility [127, 128], as well as distribution of organic groups [105]. Moreover, the presence of organic groups leads to improved hydrothermal stability of the ordered mesostructure [110]. Post-synthesis modification is convenient for tailoring the pore diameter of OMOs, which is governed by the silica matrix (see Scheme 1A) and the length of the organic groups attached to the pore walls as well as their size and surface coverage [107, 112]. The pore size of the starting silica depends on the nature of the structure directing agent and can be tailored by varying the chain length (in the case of ionic surfactants), by selecting the block copolymer of desired composition of hydrophobic and hydrophilic blocks or by hydrothermal treatment of the self-assembled material for an extended period of time to cause its restructuring [129-134]. Finally, the
pore diameter of organosiliceous materials can be tailored by addition of micelle expanders [18-20, 135-139] and direct high-temperature synthesis [140-142].

Direct one-pot synthesis [105, 113-118], in contrast to the post-synthesis grafting [2, 104-112, 119-124] (even though it offers less possibilities to tune the pore diameter, see Scheme 1B), is particularly prominent because it affords OMOs with relatively high loadings of functional ligands and large pore diameters [143, 144]. This is due to the formation of functionalized mesostructure in the presence of micelles and the elimination of calcination procedure that causes substantial structure shrinkage, often up to 25% of the resulting pore width.

Even though co-condensation [105, 113-118] has some limitations such as possible phase separation at higher loadings (>40%) and the requirement of highly stable organic precursors that have to survive hydrothermal treatment and template removal procedure, it has attracted a lot of attention. This is because of its ability not only to incorporate a relatively high concentration of surface ligands but also to tailor the adsorption and structural properties. Moreover, the one-pot synthesis is simple, efficient and less time-consuming than post-synthesis modification.

Since the first reports published by Stein [114], Macquarie [116] and Mann [113, 115], co-condensation has been successfully applied to the synthesis of a variety of hexagonal OMSs and to a less extent, cubic OMSs with numerous surface groups. Many pendant ligands such as methyl [118, 143, 145, 146], vinyl [105, 114, 146-156], phenyl [113], octyl [113], 2-cyanoethyl [116], mercaptopropyl [115, 157-163], aminopropyl [115, 159, 164-167], ureidopropyl [115, 159, 168, 169], imidazole [115, 170-173],
carboxylic [174-176], propylsulfonic [144, 177-179] and so forth have been introduced by the use of appropriate organosilanes. Some of the most attractive ligands are described here.

Among many surface groups, vinyl [105, 114, 146-156] and mercaptopropyl [115, 157-163] continue to attract a considerable interest due to the possibility of achieving high ligand concentrations [147]. In addition, the vinyl surface group due to its double bond, which is preserved during the synthesis, can undergo a number of chemical transformations including bromination [114], alcoholysis, hydroboration and epoxidation [148]. On the other hand, mercaptopropyl surface groups attached to the silica framework have been very popular due to their strong and selective binding affinity towards heavy metal ions such as Hg (II) [160, 180] and their ability to complex AuCl\(^-\), which can be converted via reduction reaction to gold nanoparticles inside the pores [181-183]. In addition, mercaptopropyl groups can be used for the immobilization of size-selective proteins [184] and as an intermediate in the mild oxidation reactions of propylsulfonic groups with H\(_2\)O\(_2\) [177-179], which are used in acid catalysis [158].

Some of the mesoporous materials prepared via one-pot synthesis with vinyl and mercaptopropyl groups undergo some structural transformations. Wei and co-workers [163] studied the effects of vinyl and mercaptopropyl addition on the pore structure of the SBA-15 material, concluding that in order to avoid major structural changes, the amount of TEVS and MPTMS should not exceed 20%. Schüth and co-workers [150] examined the influence of vinyl incorporation on the structure of the SBA-15 silica in the presence of NaCl, showing that the incorporation of a low percentage of TEVS (10%) does not
alter the hexagonal $p6mm$ structure, however at higher percentages (>15%) a well-ordered cubic $Ia3d$ structure is formed.

The ureidopropyl ligand [115, 159, 168, 169] possesses two amines combined with carbonyl groups, therefore it has attracted a considerable attention due to the potential for creating chelate complexes with proteins, heavy metal ions such as $\text{Zn}^{2+}$, $\text{Cr}^{6+}$ and $\text{Ni}^{2+}$ and other reactants. More recently, Gong and co-workers [168] have studied the incorporation of ureidopropyl ligands into the 3D worm hole-like porous MSU-n material by a one-pot route, as well as the synthesis of a bi-functional MSU-n containing the ureidopropyl group along with small alkyl and aromatic groups such as methyl and phenyl. Later, Huh and co-workers [159] have reported a co-condensation synthesis of ureidopropyl-functionalized MCM-41 silicas templated by cetyltrimethylammonium bromide (CTAB) ionic surfactant under basic pH. In comparison to mercapto propyl groups [115, 157-163], relatively little research was published in the literature regarding the incorporation of ureidopropyl groups into polymer-templated materials.

Imidazole [115, 170-173] is a relatively large organic group that can be attached to the surface of silica-based materials via post-synthesis modification as reported by Yi and co-workers [170] and Ratnasamy and co-workers [172] for SBA-15 OMS or via one-pot synthesis route as reported by Mann and co-workers [115] in 1997 for MCM-41. Quite recently, Moreau and co-workers [171] proposed the co-condensation synthesis of alkylimidazolium salts with short and longer alkyl chains leading to lamellar and hexagonal mesostructures, respectively. The covalent bonding of chemically active
imidazole groups to the pore walls of silica materials modifies their surface properties and extends the range of potential applications. Also, Yi and co-workers [170] reported that imidazole ligands immobilized on the pore walls of SBA-15 can selectively bind some precious metal ions such as Pt$^{2+}$ and Pd$^{2+}$ in the presence of other metal ions such as Cd$^{2+}$, Cu$^{2+}$, and Ni$^{2+}$. Moreover, Yi and co-workers [170] showed a simple way for recovering precious metal ions by treating organosilica with adsorbed ions with nitric acid solution. The aforementioned method was shown to be an effective and a relatively safe for the adsorbent. Furthermore, the imidazole-organosilica is a good alternative to ligand-immobilized organic polymers, which are currently used for recovery of precious metals. Ratnasamy and co-workers [172] demonstrated that SBA-15 functionalized with imidazole and Ti$^{4+}$ species possesses active sites for the binding of carbon dioxide.

So far, studies of vinyl, mercaptopropyl, ureidopropyl and imidazole-containing OMSs have been limited to 2D hexagonal mesostructures [105, 113-118, 143-154, 157-179] with channel-like pores such as MCM-41 and SBA-15 and only few publications regarding 3D cubic FDU-12 [155] and SBA-1 [156] silicas containing vinyl pendant groups. There are no reports on the introduction of surface groups into cage-like materials such as SBA-16 [24] and FDU-1 [74], which are believed to be more favorable than those with 2D hexagonal structures because of the presence of larger pores, thicker walls, enhanced hydrothermal and thermal stabilities and the ability to obtain higher loading of functional groups, which is desirable for industrial applications.
Scheme 1. Schematic illustration of incorporation of organic surface groups into mesoporous structure by two main methods: (A) post-synthesis modification (top scheme) and (B) direct co-condensation (bottom scheme).
1.4. POLYMER-TEMPLATED SILICEOUS MESOSTRUCTURES WITH ORGANIC BRIDGING GROUPS

In 1999 three independent research groups of Ozin [185, 186], Inagaki [187] and Stein [188] simultaneously showed the possibility of the formation of ordered mesostructures by using bridged silsequioxane precursors, \((\text{RO})_3\text{-Si-R}^-\text{-Si-(RO)}_3\), that undergo hydrolysis and condensation to form an integrated organic-inorganic framework similar to sol-gel chemistry, which has been known for a long time [189, 190]. This synthetic approach led to a new type of ordered mesoporous materials, denoted as periodic mesoporous organosilicas (PMOs). It has eliminated the multistep protocol required for post-synthesis grafting [11] and avoided problems related to different hydrolysis rates of the precursors. PMOs [185-188] can be prepared by catalyzed hydrolysis of appropriately selected bis(trialkoxy)silyl) organic precursors in the presence of various structure directing agents such as ionic surfactants [185-188, 191], oligomeric surfactants [192-195] and nonionic block copolymers [196-200].

In contrast to silica-based materials with functionalized surfaces, the framework of PMOs [185-188] contain, in addition to Si-O-Si bonds, Si-R^-Si linkages with the functional groups located within the mesopore walls, whereas the surface-modified silicas exhibits Si-O-Si linkages only with functional groups hanging on the surface. PMOs [185-188] possess a high degree of structural order and homogenous distribution of organic bridging groups inside the mesopore walls with a maximum loading, which was not achievable with organic terminal groups. Furthermore, integrated bridging
groups inside the pore walls do not block the entrances to the mesopores, thus allowing different chemical reactions to take place, which were impossible with higher loadings of surface groups. The hybrid of organic-inorganic chemistry also gives the opportunity to design the mechanical properties of PMOs because of the structural rigidity provided by the siloxane linkages and flexibility resulting from organic fragments [110]. Because of these properties, as well as the increased hydrothermal and thermal stabilities [200, 201], PMOs have become very promising materials for potential applications ranging from highly selective adsorbents [202], catalysts [203, 204], sensing devices [205, 206], hosts for biomolecule immobilization [207, 208] to environmental technology [209, 210].

Initially, research on PMOs was focused on the incorporation of short aliphatic and rigid aromatic bridging groups such as methylene [211], ethane [187], ethene [185], ethylene [188], acetylene [186], vinyl [212], totyl [213], xylyl [213], benzene [186], thiophene [186], ferrocene [186], bithiophene [186], dimethoxyphenyl [213] and so forth. Some of the selected large bridging groups are described in this chapter. Ozin and co-workers [186] reported the first PMO containing aryl bridging groups using 1,4-bis(triethoxysilyl)benzene and 2,5-bis(triethoxysilyl)thiophene as organosilica precursors and cetyltrimethylammonium bromide ionic surfactant as the structure directing agent but due to the presence of ammonia in the reaction mixture almost all of the Si-C bonds were cleaved. Later, Inagaki and co-workers [214] successfully reported PMO in the presence of octadecyltrimethylammonium chloride as a template under basic conditions using phenylene and thiophene as bridging groups. The resulting 2D hexagonal benzene-bridged PMO exhibited periodicity on the molecular level, confirming crystal-like
arrangement. Soon after, Bion and co-workers [215] confirmed crystal like-like pore walls by synthesizing 1,4-benzene-bridged PMO in the presence of trimethylammonium halide surfactant with different hydrocarbon lengths from C_{14} to C_{18}. Inagaki and co-workers [216] prepared similar PMOs with benzene linked to two silicon atoms using 4,4’-bis(triethoxysilyl)biphenyl and octadecyltrimethylammonium chloride as the template under basic conditions. The resulting biphenyl-bridged PMO exhibited hexagonally ordered pore structure with crystal-like organization of biphenyl units within the pore walls, which was confirmed by wide-angle XRD and HRTEM images and high thermal and hydrothermal stabilities. These various bridging groups were incorporated mostly into the channel-like structures, i.e., MCM-41 and SBA-15 [198, 199] using both ionic surfactants and nonionic block copolymers. There are only a few reports on PMOs with cage-like mesostructured materials such as KIT-5 [190], FDU-1 [196] and SBA-16 [197, 217] containing small aliphatic ethane groups.

Recently, Sayari and Wang [218] synthesized a PMO containing crystal-like pore walls using 1,4-bis[(E)-2-(triethoxysilyl)vinyl]benzene as the organosilica precursor and octadecyltrimethylammonium chloride as the structure directing agent under basic conditions. The resulting PMO exhibited 2D hexagonal arrangement of cylindrical pore and crystalline pore walls.

More recently, several efforts were made to synthesize PMOs with larger bridging spacers, such as bipyridine with neither well-defined structure nor high stability, and biphenylene that displays crystal-like walls (similar to phenylene), which form simultaneously during hydrothermal treatment as reported by Morell and co-workers
Ozin and co-workers [220] reported PMOs with 4-phenyl ether and 4-phenyl sulfide bridge-bonded silsesquioxanes using salt-assisted self-assembly with non-ionic oligomeric surfactants for the removal of toxic metals. Further development on PMOs with long and flexible spacers was extended [210] through the one-pot co-condensation of 1,4-bis(triethoxysilyl)propane tetrasulfide and TEOS that resulted in the formation of thioether functionalized composite as an environmentally friendly, highly-selective adsorbent for heavy metal ions. PMO-tetrasulfide exhibits very high affinity towards mercury ions from aqueous solutions (1.5 g/g) with very weak adsorption to similar ions such as lead, cadmium, zinc and copper. In addition, this hydrothermally stable thioether-PMO is also an efficient adsorbent for phenols with a maximum adsorption of 76 mg/g [201]. Similar research was shown by Hossain and Mercier [221], where HMS mesostructure was prepared with different concentrations of ethylenediamine bridging groups via one-pot synthesis with TEOS and N,N’-(bis(3-trimethoxysilyl)propyl)ethylenediamine (TMSEN) in the presence of dodecyloamine surfactant as template. TMSEN contains nitrogen atoms, which are known as efficient chelators for transition metal ions. Even though the HMS-TMSEN material exhibited only up to 5% loading of TMSEN, it showed high affinity to Cu$^{2+}$ with very low adsorption of Ni$^{2+}$ and Zn$^{2+}$. It has to be noted that if the synthesis is carried out with such precursors without addition of TEOS, these organosilane are too flexible to preserve the structure after removal of template, therefore materials carry the risk of structural collapse. Precursors containing amines or sulfides, usually lead to disordered structures with relatively low surface area. Corriu and co-workers [222] reported PMO containing
cyclam chelating moieties in a two step synthesis; a chlorpropyl-containing material was prepared first and then was treated with 1,4,8,11-tetraazacyclotetradecane attached to four silicone linkages that anchored cyclam moieties to the pore walls. Such bridging groups localized on the surface are well-known for their remarkable complexation ability to bind transition metal salts such as Cu (II) and Co (II), possibly applicable in magnetism and photoluminescence. The series of various PMO materials was further extended by Ozin and co-workers [223] who synthesized PMO with a benzene ring linked with three silicon atoms, 1,3,5-tris(triethoxysilyl)benzene. The resulting PMO exhibited crystal-like order in the walls of the benzene-silica framework containing micropores of moderate surface area with enhanced thermal stability due to the three siloxane linkages. Cornelius and co-workers [224] prepared PMO containing 1,4-divinylbenzene bridging groups for potential hydroboration reactions to form diols due to the presence of the double bond. The aforementioned spacers were prepared with the channel-like structure only (see reviews and references therein [225-229]).

In 2005, bulky heterocyclic bridging groups, isocyanurate (ICS) ring attached to three trimethoxysilyls via flexible propyl chains, was successfully incorporated into the siliceous SBA-15 mesostructure as reported by Olkhovyk and Jaroniec [229]. This PMO was obtained by co-condensation of tri[3-(trimethoxysilyl)propyl]isocyanurate (ICS) and TEOS in the presence of triblock copolymer Pluronic P123 under acidic conditions. It is worth noting that ICS is a commercially available organosilane often used as a coupling agent for metal oxides and glass reinforcement, as a cross-linker and a sol-gel precursor [230, 231]. The PMO obtained with 25% loading of the incorporated bridging groups
(ICS-25) exhibited good structural ordering (P6mm space group), high BET specific surface area of 622 m²/g, total pore volume of 0.81 cc/g and a narrow pore size distribution. The results estimated from elemental analysis showed that PMO-25 contained 0.81 mmol/g of ICS. It was also shown that 75% or even 90% of ICS can be incorporated into the SBA-15 hexagonal structure with 1.38 and 1.68 mmol/g of ICS groups, respectively; the resulting PMOs exhibited the pore volume of 0.5 and 0.37 cc/g and the specific surface area of 515 and 266 m²/g, respectively. Interestingly, the presence of isocyanurate moieties in the framework led to unexpectedly high affinity towards heavy metal ions, which was evidenced by high adsorption capacity of 1.8 g of mercury per gram of adsorbent in aqueous solution. Such strong ability to adsorb toxic pollutants from contaminated water makes this PMO very attractive from the viewpoint of environmental protection. Fischer and co-workers [232] have incorporated isocyanurate bridging groups into the framework of SBA-15 mesoporous ethane-silica leading to a bifunctional material consisting of two different organic moieties; small inert aliphatic ethane and large active heterocyclic isocyanurate bridging groups, using P123 as template and the addition of salts such as NaCl and NH₄F. The addition of NH₄F is believed to accelerate the hydrolysis rate of 1,2-bis(trimethoxysilyl)ethane organosilane, matching the rate of ICS, which facilitates the preparation of high quality PMO. The resulting bifunctional PMO with 0.75 mole fraction of ICS exhibited well-ordered structure with hexagonal P6mm symmetry and a surface area of 331 m²/g, relatively small pore volume of 0.35 cc/g and pore size of 5.9 nm. Such PMO displayed the possibility for chemical adsorption of H₂PtCl₆, which then was subsequently transformed
into platinum nanoparticles within the mesoporous framework. The platinum nanocrystals encapsulated in bifunctional PMO can be used as a selective heterogeneous catalyst in platinum-catalyzed reactions, e.g., hydrocarbon conversion such as ethylene [233] and toluene hydrogenation [234]. There is also a growing interest in the synthesis of PMOs with more than one functional group. Such materials containing specific functional pendant ligands located on the mesopore walls and bridging groups incorporated into the framework can show completely new physical and chemical properties; thus, novel and interesting applications can be anticipated for material obtained by careful selection of appropriate organosilanes. Recently, a bifunctional PMO was synthesized by co-condensation of ICS and mercaptopropyl organosilanes together with TEOS using P123 as template under acidic medium [235]. This well-ordered bifunctional PMO showed the BET specific surface area of 514 m$^2$/g, pore volume of 0.54 cc/g and pore diameter of 7.26 nm. In addition, high contents of ICS bridging groups (0.99 mmole/g) and mercaptopropyl pendant ligands (0.59 mmol/g), estimated on the basis of elemental analysis, make this material a very good adsorbent for removal of heavy metal ions with 4.23 mmol/g of adsorbed mercury from aqueous media. Subsequently, Fischer and co-workers [236] reproduced the synthesis of this bifunctional PMO with up to 40% of mercaptopropyl groups, the BET specific surface area of 147 m$^2$/g, pore diameter of 3.5 nm and pore volume of 0.19 cc/g. Recently, the co-condensation syntheses of bifunctional PMOs containing ICS with ureidopropyl pendant ligands, ICS with imidazole pendant ligands and ICS along with thioether bridging groups were reported [237]. All of these materials were prepared in the presence of
Pluronic P123, under acidic conditions and with addition of TEOS for structural support. This approach revealed the endless possibilities of bifunctionalization of not only the framework but also the pore walls, offering new practical applications in environmental cleanup, sensing and other related disciplines.

In the last decade, advances achieved in the synthesis and characterization of organic-inorganic hybrid nanocomposite structures have focused intensively on novel types of functionalized PMOs with 2D hexagonal structures such as MCM-41 and SBA-15 with cylindrical pores ($P6mm$ space group). However, only a few kinds of ordered organosilicas with 3D cubic structures like FDU-1 ($Fm3m$ space group) [196], SBA-16 ($Im3m$ space group) [197, 217] and other related less popular materials [155, 156, 190] with spherical pores (supercages) have been reported so far.

There is a notable driving force towards the development of new adsorbents. The ability to synthesize novel 3D cubic mesostructures containing desired multifunctional pendant and bridging groups may lead to untold advances in the area of adsorption, catalysis, chromatography, sensors and environmental technology. In general, the extraordinary hydrothermal and thermal stability (FDU-1), high surface area and large pore volume of these 3D PMO-SBA-16 and PMO-FDU-1 mesostructures, which exhibit large spherical pores and much smaller connections, are currently of great interest. This interest is driven by their prospective applications, such as separation of molecules with certain dimensions, as hosts for immobilization and encapsulation of biomolecules and as drug delivery systems due to their decreased susceptibility to pore blockage.
1.5. RESEARCH OBJECTIVES AND SUMMARY

The main objective of my Ph.D. research was to study the functionalization of cubic PMO mesostructures, such as SBA-16 and FDU-1, with cage-like pores via co-condensation of the appropriate organosilanes in the presence of block copolymers as structure directing agents. For that purpose, this study explored various organic pendant ligands and organic bridging groups to obtain novel hybrid organic-inorganic mesostructures. The key issue of this research was to control the surface, structural and adsorption properties of the resulting porous solids. Extraction, a typical template removal procedure, was found to be not a suitable method for the complete removal of the template from the spherical pores interconnected by narrow apertures; therefore, a special emphasis was put on the development of an effective method for the complete removal of the polymer templates from composite mesostructures without degradation of organic groups and deterioration of structural ordering.

Since high quality ordered siliceous mesostructures with cage-like pores such as SBA-16 and FDU-1 are still uncommon, the first stage of my dissertation (chapter 3) is focused on the improvement of the synthesis conditions and monitoring of the structural changes, which may occur during their preparation. In order to achieve this objective, there was a need to study the influence of different synthesis parameters on the structural properties of cage-like mesoporous materials (Schemes 2A, 2B). The effect of TEOS/template ratio was examined in order to establish optimal conditions for the synthesis of materials with ordered mesopores and uniform pore entrances. Further
studies were focused on the effect of inorganic salt and pH on the development of ordered mesoporosity. Also the effect of time on the self-assembly of the FDU-1 materials was examined. It was shown that the synthesis of FDU-1 can be greatly improved by controlling the stirring time, optimal ratio of TEOS to template and addition of inorganic salt under low acidic conditions.

The second phase of this chapter is devoted to the template removal. The objective was to find a solution that effectively removes the structure directing agent while allowing for open porosity of the cage-like materials by combining extraction and temperature-controlled calcination in flowing air at various temperatures. As a result of this study, we have outlined a method that efficiently removes the template and prevents structure shrinkage at elevated temperatures.

In the second part of this dissertation (chapter 4), the acquired knowledge from chapter 3 was utilized to fabricate cage-like SBA-16 and FDU-1 siliceous mesostructures with various small and large functional “hanging” groups (Scheme 2C). The objective of this part was to obtain ordered inorganic supports containing high loadings of organic groups with uniform pores and narrow PSDs. The hanging groups were carefully chosen from the viewpoint of their potential reactivity, thermal/hydrothermal stabilities, commercial availability and affinity towards mercury (II) ions. Also, the adsorption properties of the resultant functionalized materials, including specific surface area, pore size and pore volume, were taken into consideration in order to provide materials with desired characteristics. Surface ligands containing nitrogen and sulfur heteroatoms were employed such as mercaptopropyl, ureidopropyl and imidazole groups, however vinyl
groups were also used due to their double bond properties and small size. By gradually adding alkyltrialkoxy silane it was possible to study the structural transformation from 3D cubic mesostructures with spherical pores to 2D hexagonal mesostructures with cylindrical ones. The observed systematic changes in their physical properties were examined by argon and nitrogen adsorption, powder X-ray diffraction and electron microscopy, whereas incorporation of organic ligands was monitored by elemental analysis, spectroscopy and high resolution thermogravimetry. The observed structural changes were related to the nature and amount of alkyltrialkoxy silane under the conditions studied. Several other issues related to the synthesis of organosilicas were addressed such as addition of sodium chloride, adjustment of pH and variation of the TEOS/template ratio.

Another part of this chapter was devoted to the synthesis of bifunctional organosiliceous mesostructures with high concentration of both ligands (Scheme 2E). The main objective of this study was the incorporation of two different organic surface groups in order to obtain high quality materials with a large concentration of both organics. Several issues were examined with respect to their prospective environmental applications including ligands that possess multifunctional binding sites and strong chelating properties to achieve high adsorption capacity.

Finally, we synthesized cage-like periodic mesoporous organosilicas with organic bridging groups via a one-pot synthesis of the desired bridged organosilanes in the presence of F127 and B50-6600 templates (Scheme 2D). The main objective of this portion of research (chapter 5) was to maximize the incorporation of isocyanurate
bridging moieties into the framework, which led to the enhancement of adsorption capacity of these materials making them applicable for environmental cleanup. The amount of incorporated bridging groups, surface area, porosity and stability of organic groups were monitored and assessed by using diffraction and spectroscopic measurements, elemental analysis, high resolution thermogravimetry, and nitrogen and argon adsorption. It was shown that the bulky heterocyclic bridging rings can be incorporated into the cage-like silica framework of Im3m symmetry. The resulting ordered materials possessed relatively high loading of bridging groups, large total pore volume and increased surface area. Also, due to the high curvature of 3D cubic mesostructures, the template removal procedure was re-examined in order to sufficiently remove the polymer without decomposition of organic spacers. As a result of this study, a more effective procedure for the template removal method was proposed in order to avoid the decomposition of organic groups and structural shrinkage of both SBA-16 and FDU-1 materials.

The final section of this chapter was devoted to the optimization of the synthesis of bifunctional PMOs with cage-like structures (Scheme 2F). Therefore, we explored the incorporation of bulky heterocyclic bridged silsequioxanes along with small aliphatic ethane bridged precursors to achieve well-defined pores and highly ordered structures. The studies showed that a high isocyanurate concentration was successfully introduced along with ethane bridging groups without diminishing the quality of the resulting mesostructures.
Scheme 2. Schematic illustration of cage-like mesoporous SBA-16 (A) and FDU-1 (B) silicas and organosilicas containing single and double pendant (C, E) and bridging (D, F) groups.
This dissertation is based on the following publications:


In addition, several articles closely related to those mentioned above have been published:


II. EXPERIMENTAL SECTION

2.1. TECHNIQUES USED FOR CHARACTERIZATION OF MESOPOROUS MATERIALS

Several different analytical methods were used for the characterization of the porous adsorbents described in this dissertation. One of the most important techniques that is often employed to obtain structural and surface characteristics of porous solids is gas physisorption. Typical information that can be generated from adsorption data includes specific surface area, pore volume, pore diameter, pore size distribution, pore uniformity, pore accessibility, and pore chemistry; the latter can be deduced from the low-pressure portion of adsorption data. Gas adsorption provides information about the overall quality of porous solids; however it is not useful for assessment of the structural ordering, particle morphology, thermal stability or template removal. Therefore, other methods are employed such as small angle X-ray scattering (SAXS), low and wide angle powder X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and thermogravimetric analysis (TG). In order to confirm the incorporation of surface pendant and bridging groups, usually an additional set of methods is used such as elemental analysis, infrared spectroscopy, Raman spectroscopy, solid state nuclear magnetic resonance (NMR) and thermogravimetric analysis as well as gas adsorption.
Nitrogen and argon adsorption analysis

Nitrogen and argon adsorption was the primary method used to characterize the porous solids studied; therefore, presentation of this technique will be more extensive. All adsorption measurements were performed using ASAP 2010 and ASAP 2020 volumetric analyzers manufactured by Micromeritics, Inc. (Norcross, GA). Adsorption isotherms were measured at -196 °C over the interval of relative pressures from $10^{-6}$ to 0.995 using high purity 99.999% adsorbates. Prior to each adsorption analysis all materials were outgassed under vacuum in the port of the adsorption instrument for at least 2 hours at either 200 or 110 °C for silicas and organosilicas, respectively, until the residual pressure dropped to 6 or less μmHg. The outgassing temperature for organosilicas (110 °C) was used to avoid thermal decomposition/degradation of organic pendant and bridging groups and to remove physically adsorbed species including ethanol and water.

There are five important quantities required to measure adsorption isotherms; sample weight, warm free space, cold free space, temperature and pressure. The latter two quantities are recorded by instrument automatically. The warm free space is the volume of the sample tube at room temperature, whereas the cold free space is the volume of this tube at the temperature of liquid nitrogen. Since the tube for adsorption measurement contains the porous material, the cold free space has to be corrected using the following equation:

$$CFS = CFS_{empty\ tube} - \frac{m_{sample} \cdot 3.533}{\rho_{sample}},$$

(1)
where $CFS_{\text{empty tube}}$ represents the cold free space without the analyzed material, $m_{\text{sample}}$ reflects the weight of the analyzed material and $\rho_{\text{sample}}$ is the density of the material. Another possibility is to use helium for measurement of CFS of the tube with the sample. The density of mesoporous silica was assumed to be 2.2 g/cm$^3$. The weight of the analyzed material was calculated by subtracting the weight of the tube containing the analyzed material after outgassing from the weight of empty tube.

The collected adsorption-desorption isotherm usually contains between 100 and 150 data points. Each point is represented as the amount of nitrogen or argon adsorbed per gram of material (cm$^3$ STP g$^{-1}$, where STP reflects standard temperature (0 °C) and pressure (760 mmHg)) at the corresponding equilibrium pressure. The adsorption isotherm were recorded by using two options: (i) the first one refers to the range of 10$^{-6}$ and 10$^{-1}$ relative pressure, in which points are recorded using the incremental doses of adsorbate usually between 1 and 10 cm$^3$ depending on the surface area and (ii) the second option refers to the range of 0.1 and 0.995, in which data points are collected according to the pressure table set by the user. The instrument measures the pressure before and after dosing the gaseous adsorbate when the equilibrium is reached. The volume adsorbed at a particular relative pressure is obtained by subtracting the equilibrium pressure from the initial pressure and converting the resulting difference to the volume by using gas law. After measuring adsorption branch of the isotherm, desorption branch is recorded.

IUPAC [7] defines three types of pores according to their size: (i) macropores, mesopores and micropores with pore sizes greater than 50 nm, 2 nm and 50 nm and smaller than 2 nm, respectively. It is noteworthy to mention that the term gas adsorption
refers to the accumulation of molecules (adsorbate) on the surface of a solid (adsorbent) [7, 239].

Adsorption of molecules in mesopores consists of the following physical events: (i) at low relative pressures molecules adsorb on the surface creating a single layer (monolayer formation), (ii) at higher pressures molecules form subsequent adsorbed layers (multilayer formation) and (iii) at the pressure reaching the critical value for a given pore diameter molecules instantly fill the remaining pore space, which is called the capillary condensation. There are several factors affecting capillary condensation, which in turn influences the overall shape of the adsorption isotherm. The latter depends on the type of adsorbate (nitrogen or argon), temperature, pore size, and type of pores including cylindrical, spherical, and slit-like, as well as their organization. On the other hand, the process of instantaneous emptying of the pore void is known as capillary evaporation, which occurs during desorption and for the most part, does not overlap with the capillary condensation step, resulting in the hysteresis loop. In contrast, when the pore voids are exclusively micropores, the small space is thoroughly filled at low pressures. This process is known as micropore filling.

According to IUPAC classification [7, 240] of adsorption isotherms and hysteresis loops, there are six different types of adsorption isotherms (Scheme 3) and four types of hysteresis loops (Scheme 4). Type I is characteristic for microporous materials; in this case the isotherm usually shows a steep adsorption at low relative pressures and then levels off. In contrast, Type II and III are characteristic for macroporous or nonporous materials, where adsorption proceeds through mono- and multilayer formation
that leads to abrupt adsorption close to saturation vapor pressure. Desorption for Type I, II and III isotherms overlap with adsorption, and thus they do not have hysteresis loops. Type IV and V isotherms are characteristic for mesoporous materials where in addition to monolayer and multilayer formation the capillary condensation takes place in mesopores. Therefore, the first part of the type IV isotherm is very similar to Type I and II; however at higher pressures the isotherm follows through a steep step due to adsorption in mesopores (capillary condensation) and then levels off. Usually capillary condensation and capillary evaporation do not coincide, thus giving rise to a pronounced hysteresis loop. The difference between IV and V refers to the initial part of the isotherm and is similar to II and III. Type IV and IVc isotherms refer to mesoporous solids; however the latter takes place in materials with small mesopores, below 4 nm in the case of nitrogen at -196 °C.

The irreversibility of desorption and adsorption at high pressures leads to the hysteresis loop, which is related to two different events [7, 240, 241]. The first one is related to the thermodynamics of adsorption resulting in the delayed capillary condensation in relation to the capillary evaporation. The second effect is related to the pore connectivity (network effect) and it affects mainly the desorption branch. For instance, the adsorbate molecules for the adsorbents studied, such as SBA-16 and FDU-1 can enter the large cage-like pores via narrow constrictions. Only when the pressure on the desorption branch reaches the pressure corresponding to their capillary evaporation, the large cage-like pores cannot be evacuated because the pressure required to empty the small constrictions should be smaller. Therefore, the large cage-like pores of SBA-16 and
Scheme 3. The IUPAC classification of adsorption isotherms [7, 240].
Scheme 4. The IUPAC classification of adsorption-desorption hysteresis loops [7, 240].
FDU-1 materials are evacuated at the pressure that is related to the small connecting apertures. The hysteresis loops, which are observed for cage-like materials such as SBA-16 and FDU-1, are due to both network and thermodynamic effects. IUPAC recommends four types of hysteresis loops [7, 240]. The H1 loop shows almost vertical adsorption and desorption steps, which suggests highly uniform pore sizes with facile pore connectivity. This type of hysteresis loop often occurs for materials such as SBA-15 with cylindrical channel-like pores and uniform pore entrances. Some of the FDU-1 organosilicas with pendant vinyl and mercaptopropyl groups studied in chapter IV show the transformation from cubic $Fm3m$ to hexagonal $P6mm$, therefore this type of hysteresis H1 will be discussed later.

Hysteresis with H2 loop displays a triangular shape with an abrupt desorption step, such hysteresis shape was associated with network effects and was reported for materials with spherical cage-like pores such as SBA-16 and FDU-1. The H3 and H4 hysteresis loops were observed for materials with slit-like pores; however for the H3 loop, the adsorption branch does not level off close to the saturation vapor pressure, whereas the Type H4 loop shows parallel and almost horizontal branches.

**Powder X-ray diffraction (XRD) measurements**

The materials for X-ray diffraction (XRD) analysis were deposited on a glass plate and recorded at room temperature using X'Pert Pro (MPD) Multi Purpose Diffractometer using monochromated Cu K\(\alpha\) radiation of wavelength $\lambda = 1.5418$Å, operating voltage of 40 kV, 0.01° step size and 10 s step time (PANanalytical, Inc). The diffraction angle, $2\theta$, was varied between 0.4° and 3.5°.
**Small angle X-ray scattering (SAXS) measurements**

Synchrotron X-ray scattering experiments were conducted at the SAXS beam line on NanoSTAR system (Bruker AXS). The instrument was equipped with pinhole collimation and a two-dimensional detector (HiSTAR), which was mounted on a micro focus X-ray tube with copper anode, operating with X-ray wavelength of 0.1541 nm and equipped with crossed Göbel mirrors. The sample-to-detector distance was 650 mm. The exposure time for a single frame was 5000-10000 s. All measurements were carried out at room temperature.

**Transmission electron microscopy (TEM) analysis**

Scanning and transmission electron microscopy images were recorded on a Hitachi HD-2000 Scanning and Transmission Electron Microscope (STEM) operating at an accelerate voltage of 200kV and a current of 30 mA. The samples for analysis were dispersed in ethanol by a moderate sonication at concentrations of 5 wt% of solids. A lacy carbon coated 200-mesh copper TEM grid was first dipped into the sample suspension and then dried under vacuum at 80 ºC for 12 hours prior to microscopic studies.

**Fourier-transform infrared spectroscopy (FT-IR)**

FT-IR spectra were collected using a Digilab FTS-3000 spectrometer equipped with a liquid nitrogen cooled mercury-cadmium-telluride detector, operating at 4 cm\(^{-1}\) nominal resolution by co-addition of 64 scans. Diffuse reflectance spectra were obtained using an optical accessory from Harrick Scientific (Ossining, NY, DRA-2CN). Samples
were prepared by mixing a 10% (w/w) dispersion of modified silica in dried, pre-ground KCl after adjustment of the sample height to obtain the maximum interferogram signal. All spectra were ratioed to that of pure KCl and converted to the Kubelka-Munk (KM) units using standard instrument software.

**Elemental analysis**

Quantitative estimation of organic groups was performed by carbon, hydrogen, nitrogen and sulphur (CHNS) analysis using a LECO model CHNS-932 elemental analyzer from St. Joseph, MI. For each material, three measurements were carried out with a relative error of less than 0.1%

**High resolution thermogravimetric analysis**

Pure silica, organosilica with pendant organic groups and organosilica with bridging groups were analyzed in various forms, such as-synthesized, extracted, extracted-calcined and calcined, depending on the information needed. All thermogravimetric measurements were carried out in flowing nitrogen or air using a TA Instruments Inc. (New Castle, DE, USA) model TGA 2950 high-resolution thermogravimetric analyzer. The weight change (TG) patterns were recorded as a function of temperature in the range from 35 to 900 °C. The instrument was equipped with an open platinum pan and an automatically programmed temperature controller. The high-resolution mode was used to record the TG data. The heating rate was adjusted automatically during measurements to achieve the best resolution; its maximum was 5 °C min⁻¹. The resolution and sensitivity parameters were 4 and 6, respectively. The flow rate
of nitrogen gas in the system was 100 and 60 cm³ min⁻¹ on the furnace and balance, respectively. The weight of the analyzed sample was typically within 5-10 mg.

2.2. CALCULATION METHODS

**Determination of the ligand bonding density**

The surface coverage of functional groups expressed per gram of the entire sample (C_{lig}, mmol/g) was calculated from nitrogen and sulphur contents obtained from elemental analysis.

**Determination of the specific surface area**

The specific surface area (S_{BET}, m²/g) for the materials under study was calculated by employing the Brunauer-Emmett-Teller (BET) method [244] from adsorption data at -196 °C in the range of relative pressures from 0.05 to 0.2. Typically, gas molecules are adsorbed gradually on the surface by forming a monolayer, its capacity (n_m, moles/g) is used to obtain the specific surface area, S_{BET} [7, 239]. The calculations are carried out according to the following equation:

\[
S_{BET} = n_m \cdot N_A \cdot \omega_{N_2},
\]

where \(N_A\) is Avogadro’s number (6.23 \cdot 10^{23} \text{ molecules/mol}), \(\omega_{N_2}\) is the cross-sectional area of nitrogen or argon at -196 °C, which is estimated to be 0.162 \cdot 10^{-18} \text{ m}^2 / \text{ molecule} or 0.138 \cdot 10^{-18} \text{ m}^2 / \text{ molecule}, respectively, and \(n_m\) is the aforementioned monolayer capacity.
The monolayer capacity, $n_m$, and the BET constant $C$ can be calculated from the slope and intercept from the linear BET equation:

$$\frac{p}{p_o} = \frac{1}{n_m \cdot C} + \frac{(C-1)}{n_m \cdot C} \cdot \left(\frac{p}{p_o}\right)$$

(3)

where $n$ is the amount adsorbed expressed in cm$^3$ STP/g and $\frac{p}{p_o}$ is the relative pressure (dimensionless). $C$ is the BET constant associated with adsorption energy that provides information about surface characteristics. In order to obtain these parameters, it is necessary to plot $\frac{p}{p_o} \cdot \left(1 - \frac{p}{p_o}\right)$ vs $\left(\frac{p}{p_o}\right)$. The slope of the straight line and intercept are equal to $\frac{(C-1)}{n_m \cdot C}$ and $\frac{1}{n_m \cdot C}$, respectively. It is noteworthy that the BET method takes into consideration the following assumptions: (i) energetically homogenous surface, (ii) localized adsorption, i.e., molecules once adsorbed on the surface are motionless, (iii) no lateral interactions on the surface between adsorbate molecules and (iv) infinite number of layers is formed.

**Determination of single-point pore volume**

The single-point total pore volume ($V_t$, cm$^3$ g$^{-1}$) [7] was estimated from the amount adsorbed at a relative pressure $p/p_o$ of 0.99, where $p$ and $p_o$ denote the equilibrium pressure and saturation vapor pressure, respectively.
Determination of pore size distribution

The pore size distributions (PSDs) were calculated from the adsorption branches of nitrogen or argon adsorption-desorption isotherms using the Kruk-Jaroniec-Sayari (KJS) method [243]. The KJS method employs the Barrett-Joyner-Halenda (BJH) algorithm [246] for cylindrical pores with the relation between the pore width and capillary condensation pressure derived on the basis of adsorption data for high quality MCM-41 materials with pore diameters within 2 and 6.4 nm, fitted by a Kelvin-type equation [243]:

$$r = \frac{2 \cdot \gamma \cdot V_L}{R \cdot T \cdot \ln \left( \frac{P_o}{P} \right)} + t \left( \frac{P}{P_o} \right) + 0.3 \tag{4}$$

where \( r \) is the pore radius, \( V_L \) is the molar volume of the liquid adsorbate, which for liquid nitrogen is 34.68 cm\(^3\)/mol, \( \gamma \) is the surface tension, which is 8.88 \( \times \) 10\(^{-3} \) N m\(^{-1} \) for liquid nitrogen at -196 °C, \( T \) is the absolute temperature (-196 °C for liquid nitrogen), \( R \) is the universal gas constant (8.314 J/mol·K) and \( t(p/p_o) \) is the statistical film thickness (nm) for nitrogen adsorption on the reference silica, which is expressed using the following equation, accurate in the relative pressure range within 0.1 and 0.95:

$$t \left( \frac{P}{P_o} \right) = 0.1 \cdot \left[ \frac{60.65}{0.03071 - \log \left( \frac{P}{P_o} \right)} \right]^{-0.3968} \tag{5}$$

The pore radius expression is obtained after substitution of all numerical values into equation (4):
\( r \left( \frac{p}{p_o} \right) = \frac{0.416}{\log \left( \frac{p_e}{p} \right)} + t \left( \frac{p}{p_o} \right) + 0.3 \)  

(6)

The primary mesopore diameter \( (w_{KJS}, \text{nm}) \) was defined at the maximum of the PSD. It should be noted that FDU-1 synthesized with pendant vinyl groups (20-40%) and mercaptoropyl groups (10-40%) exhibit cylindrical pores, therefore PSDs were calculated from the adsorption branches using the improved KJS method [247].

The volume of complementary pores [7] for the FDU-1 and SBA-16 silicas and organosilicas was calculated by integration of the pore size distributions (PSDs) in the pore width range up to 4 nm. This volume, denoted as \( V_c \) \( (\text{cm}^3 \text{ g}^{-1}) \), includes the volume of irregular micropores present in the spherical cage-like walls as well as small mesopores connecting ordered spherical pores. \( V_{co} \) \( (\text{cm}^3 \text{ g}^{-1}) \) includes the volume of complementary and ordered (primary) pores.

**Determination of unit cell parameter**

The unit-cell \( (a, \text{nm}) \) parameter was calculated using the interplanar spacing \( (d, \text{nm}) \) from the position of the (111), (110) or (100) first diffraction peak on either XRD or SAXS patterns for \( Fm3m, Im3m \) or \( P6mm \) space groups, respectively, using the following formulas [248]:

\[ a = d_{111} \sqrt{3} \]  

(7)

\[ a = d_{110} \sqrt{2} \]  

(8)

\[ a = d_{100} \frac{2}{\sqrt{3}} \]  

(9)
The interplanar spacing was calculated as follows:

\[ d = \frac{\lambda}{2 \sin \theta} \]  

(10)

where \( d \) is the interplanar distance (nm), \( \lambda \) is the wavelength (0.154056 nm in this study), \( \theta \) (degrees) is the position of the (111), (110) or (100) first diffraction peak.

**Determination of pore diameter**

The PSD analysis was performed under the assumption of cylindrical pore geometry, while cage-like SBA-16 and FDU-1 mesopores are rather spherical; thus, the KJS method leads to a systematic underestimation of the size of spherical cages by approximately 2 nm [76]. Therefore, the primary mesopore diameters were evaluated by using the proper geometrical relations [75, 76, 248] correlating the pore size \( (w_d, \text{nm}) \), volume of complementary pores \( (V_c, \text{cm}^3 \text{ g}^{-1}) \), volume of ordered mesopores \( (V_o, \text{cm}^3 \text{ g}^{-1}) \) and unit cell parameter \( (a, \text{nm}) \) derived for the \( Fm3m \) (Equation 11), \( P6mm \) (Equation 12) and \( I \) \( m3m \) (Equation 13) symmetry groups, respectively. The symbol \( \rho \) denotes the pore wall density, which is 2.2 g\(^{-1}\) cm\(^3\) for amorphous silica; 2.0 g\(^{-1}\) cm\(^3\) value was assumed for organosilicas studied.

\[ w_d = 0.78 \cdot a \cdot \left( \frac{V_o}{1/\rho + V_c + V_o} \right)^{1/3} \]  

(11)

\[ w_d = 1.05 \cdot a \cdot \left( \frac{V_o}{1/\rho + V_c + V_o} \right)^{1/2} \]  

(12)

\[ w_d = 0.985 \cdot a \cdot \left( \frac{V_o}{1/\rho + V_c + V_o} \right)^{1/3} \]  

(13)
2.3. MATERIALS AND REAGENTS

Structure directing agents: poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) triblock copolymer Pluronic F127 (EO$_{106}$PO$_{70}$EO$_{106}$) and poly(ethylene oxide)-b-poly(butylene oxide)-b-poly(ethylene oxide) triblock copolymer template B60-5500 (EO$_{39}$BO$_{47}$EO$_{39}$) were from BASF Corporation and Dow Chemicals, respectively. Silica source: tetraethyl orthosilicate (TEOS) was from Fluka Chemical Corp., St. Louis, MO. Triethoxyvinylsilane was from Acros Organics, Morris Plains, NJ, whereas (3-mercaptopropyl)trimethoxysilane, ureidopropyltrimethoxysilane and N-(3-trithoxysilylpropyl)-4,5-dihydroimidazole were from Gelest, Inc., Morrisville, PA. Bridging organosilanes: 1,2-bis(triethoxysilyl) ethane (BTESE) and tri[3-(trimethoxysilyl)propyl] isocyanurate (ICS) were from Gelest, Inc., Morrisville, PA. The chemical structures of the organosilanes used are shown in Table 1. Concentrated sulphuric acid (97 %), fuming hydrochloric acid (37%), ethanol (95 %) and sodium chloride were obtained from Fischer Scientific (Pittsburgh, PA). Deionized water (DW; conductivity < 17.5 MΩcm) was obtained using in-house Ionpure Plus 150 Service Deionization ion-exchange purification system. All chemicals were used as received without further purification.
Table 1. Description of adsorbents employed in the syntheses of the materials studied.

<table>
<thead>
<tr>
<th>Organic Group</th>
<th>Abbr.</th>
<th>Organosilane structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ureidopropyl</td>
<td>U</td>
<td><img src="image" alt="Ureidopropytrimethoxysilane" /></td>
</tr>
<tr>
<td>Mercaptopropyl</td>
<td>SH</td>
<td><img src="image" alt="3-mercaptotropyl)trimethoxysilane" /></td>
</tr>
<tr>
<td>Imidazole</td>
<td>IM</td>
<td><img src="image" alt="N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole" /></td>
</tr>
<tr>
<td>Vinyl</td>
<td>V</td>
<td><img src="image" alt="Triethoxyvinylsilane" /></td>
</tr>
<tr>
<td>Isocyanurate</td>
<td>ICS</td>
<td><img src="image" alt="Tri[3-(trimethoxysilyl)propy]isocyanurate" /></td>
</tr>
<tr>
<td>Ethane</td>
<td>E</td>
<td><img src="image" alt="1,2-bis(triethoxysilyl)ethane" /></td>
</tr>
</tbody>
</table>
III. IMPROVEMENT OF THE SYNTHESIS CONDITIONS OF CAGE-LIKE SILICEOUS MESOSTRUCTURES

Since the discovery of ordered mesostructured materials [1, 2], the worldwide research has been intensively focused on the fabrication and improvement of 2D hexagonal structures with channel-like pores such as MCM-41 and SBA-15 [46]. In contrast, smaller progress has been made in the direction of 3D siliceous cubic structures with cage-like pores such as SBA-16 (Im3m) and FDU-1 (Fm3m) prepared in the presence of triblock copolymer templates [25, 74]. These materials exhibit spherical voids interconnected with either 8 (SBA-16) or 12 (FDU-1) neighboring cages via smaller apertures forming multidirectional porous systems. Optimization of the synthesis conditions and enhancement of their structural and adsorption properties is a paramount issue from the view point of their potential applications ranging from diffusion and separation of molecules, as hosts for immobilization and encapsulation of biomolecules to drug delivery systems. The cubic cage-like structures are usually characterized by relatively small pores, low surface area and small pore volume. Therefore, the intention of the current study was the improvement of the fabrication procedures such as reduction of the self-assembly time, optimization of the polymer-silica ratio and enhancement of structural ordering and uniformity of mesopores. In addition, the aim of the last section of

* This Chapter is based on the following publications:

this chapter was to elaborate a simple and effective method for the removal of triblock copolymer template, F127, from as-synthesized SBA-16 silica by combining extraction and temperature-controlled calcination. The cage-like OMSs were characterized using SAXS/XRD, argon and nitrogen adsorption, high resolution TG and elemental analysis.

3.1. EXPERIMENTAL

Synthesis of FDU-1 silica: variation of time and template-silica ratio

The FDU-1 samples were synthesized from tetraethyl orthosilicate (TEOS) by using poly(ethylene oxide)-poly(butylene oxide)-poly(ethylene oxide) triblock copolymer (EO\textsubscript{39}BO\textsubscript{47}EO\textsubscript{39}; B50-6600) as soft template in an analogous way to that reported by Yu and co-workers [74]. The overall synthesis mixture composition was as follows: 1 TEOS: 0.00735 B50-6600: 6 HCl: 155 H\textsubscript{2}O. In a typical synthesis (Scheme 5) batch 2g of triblock copolymer was dissolved in 120 ml of 2M HCl followed by addition of 8.32g (8.9 cm\textsuperscript{3}) of TEOS under vigorous stirring for 1, 3, 4, 6, 8, 12 and 24 hours at room temperature. On the other hand, for optimization of the template-silica ratio, the specified weight of triblock copolymer ranging from 0.5 to 4g was combined with 120 ml of 2M HCl under constant stirring for 4 hr to form a clear mixture at room temperature. Later, 8.9 ml of TEOS was added dropwise to the B50-6600-HCl solution under vigorous stirring at room temperature. The resulting mixtures were subsequently aged at 100 °C for 6 hours under static conditions. The powder was filtered and washed with deionized water and dried overnight followed by calcination in air at 540 °C for 4 hours to remove
the template. The FDU-1 silicas were denoted as Ft-x and Fr-y, where x and y stand for the stirring time and polymer-silica ratio, respectively.

**Synthesis of FDU-1 silica prepared using double amount of template and NaCl at low pH**

The recipe reported by Yu and co-workers [74] was modified (see Scheme 6) to achieve high quality samples using the following molar composition: 1 TEOS : 0.0147 Polymer : 1.4074 HCl : 2.57 - 6.09 NaCl : 165.68 H₂O. In a typical synthesis, 4g of EO₃⁹BO₄⁷EO₃⁹ was dissolved in 90 ml of distilled water and 30 ml of 2M HCl followed by addition of different amounts of sodium chloride (NaCl) under vigorous stirring at 45 °C to obtain the NaCl : polymer mass ratio = 0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0, where zero refers to the synthesis without salt addition. The synthesized FDU-1 samples are denoted as Fs-z, where z indicates the salt/polymer weight ratio. After one hour mixing, the synthesis gel was cooled down to room temperature and 8.30 g of tetraethylorthosilicate (TEOS) was added dropwise under vigorous stirring, which was continued for 6 hours. The resulting gel was subsequently aged at 100 °C for 6 hrs under static conditions. The white solid was washed with deionized water, filtered and dried at 80 °C. The template was removed by calcination in air at 540 °C for 4 hrs.

**Synthesis of SBA-16 silica: template removal**

A large pore cubic silica, SBA-16, was prepared by using copolymer surfactant (EO₁₀₆PO₇₀ EO₁₀₆, F127) as a structure directing agent, tetraethylorthosilicate (TEOS) as a silica source and sodium chloride at low acid concentrations.
Scheme 5. Chart illustrating the synthesis procedure for cage-like mesoporous FDU-1 silica.
Scheme 6. Schematic comparison of the synthesis conditions for FDU-1 with about twice the pore volume and a narrower pore size distribution and those for previously reported FDU-1 samples.
Scheme 7. Chart illustrating the synthesis procedure for cage-like mesoporous SBA-16 silica.
The synthesis procedure was based on the recipe reported earlier by Qiu and co-workers (Scheme 7) [217]. In the typical synthesis batch, 2 g of F127 and 7.05 g of NaCl were dissolved in 80 ml 0.5M HCl at 40 °C. After 2-3 hours stirring 8.4 g TEOS was added dropwise.

The resulting mixture of the following molar composition: 1 TEOS: 0.00367 F127: 0.864 HCl: 2.7699 NaCl: 100.231 H₂O was stirred for 20 h at 40 °C, and subsequently subjected to the hydrothermal treatment for 24 h at 100 °C. The product was filtered, washed with deionized water and dried at 80 °C. The resulting white solid was divided into two parts; the first one (0.5 g) was extracted with a mixture of 100 ml ethanol and 2 ml 36% HCl at 60-70 °C for 24 h (75 % of polymer was removed) followed by drying, whereas the second one was dried only. After drying in oven at 80 °C both parts were calcined in the flowing air at various temperatures: 200, 250, 300, 350, 400, 450, 500 and 550 °C for 4 h with a heating rate of 3 °C min⁻¹. The template-free SBA-16 mesosilicas are denoted as S-ex and S-cx, where ex refers to the samples initially extracted followed by calcination at temperature x, whereas cx denotes the samples subjected directly to calcination at temperature x.

### 3.2. EFFECT OF VARIOUS SYNTHESIS CONDITIONS FOR CAGE-LIKE SILICEOUS MESOSTRUCTURES

**Variation of time**

Shown in Fig. 1 is the SAXS pattern for calcined Ft-6 sample with four reflections: 111, 220, 311 and 420 characteristic for a face-centered cubic \( Fm\bar{3}m \)
structure. This SAXS pattern is quite similar to that for Ft-24 reported elsewhere [76]. The average value of the unit cell parameter, \(a\), calculated from the observed reflections is about 22.2 nm. Shown in Fig. 2A is a comparison of argon adsorption isotherms for calcined FDU-1 samples synthesized by varying the time of the room temperature synthesis. Table 2 contains the values of the BET specific surface area, total pore volume, volume of primary mesopores, micropore volume and pore diameter at the maximum of pore size distribution, which were evaluated from adsorption isotherms shown in Fig. 2A. All adsorption isotherms are type IV and feature a pronounced hysteresis loop with the capillary condensation step at a relative pressure of about 0.80-0.90 and capillary evaporation step at \(\sim\)0.35, which is typical for cage-like mesoporous materials. For the samples prepared during shorter time (1h and 3h) the capillary condensation step is less steep indicating broader distribution of pore sizes. The corresponding pore size distributions (PSD) are shown in Fig. 2B. As can be seen from this figure the PSD curves for the samples synthesized from 6 to 24 hours are similar and narrower than those for the remaining samples. This shows that 6 hour stirring is sufficient to yield high quality FDU-1 samples with uniform and well ordered mesopores. The Ft-6 sample had the BET specific surface area of 862 m\(^2\)g\(^{-1}\), the total pore volume of 0.79 cm\(^3\)g\(^{-1}\) and the pore diameter at the maximum of the KJS PSD curve of about 10 nm. As can be seen from Table 2, a decrease in the stirring time of the first synthesis step caused a decrease in the values of the total pore volume, BET specific surface area and micropore volume. These data show that 6 hour stirring at room temperature followed by 6 hour hydrothermal
Table 2. Adsorption parameters determined from argon adsorption isotherms measured at -196 °C for the calcined cage-like FDU-1 mesoporous silicas prepared at room temperature using various stirring times (Figures 1 and 2).a

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stirring Time [h]</th>
<th>$S_{\text{BET}}$ [m$^2$ g$^{-1}$]</th>
<th>$V_c$ [cm$^3$ g$^{-1}$]</th>
<th>$V_t$ [cm$^3$ g$^{-1}$]</th>
<th>$w_{\text{KJS}}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ft-24</td>
<td>24</td>
<td>841</td>
<td>0.20</td>
<td>0.78</td>
<td>9.6</td>
</tr>
<tr>
<td>Ft-12</td>
<td>12</td>
<td>1103</td>
<td>0.23</td>
<td>1.03</td>
<td>10.9</td>
</tr>
<tr>
<td>Ft-8</td>
<td>8</td>
<td>835</td>
<td>0.20</td>
<td>0.78</td>
<td>10.1</td>
</tr>
<tr>
<td>Ft-6</td>
<td>6</td>
<td>862</td>
<td>0.20</td>
<td>0.79</td>
<td>10.0</td>
</tr>
<tr>
<td>Ft-4</td>
<td>4</td>
<td>855</td>
<td>0.18</td>
<td>0.83</td>
<td>10.1</td>
</tr>
<tr>
<td>Ft-3</td>
<td>3</td>
<td>810</td>
<td>0.17</td>
<td>0.76</td>
<td>10.6</td>
</tr>
<tr>
<td>Ft-1</td>
<td>1</td>
<td>756</td>
<td>0.14</td>
<td>0.75</td>
<td>9.8</td>
</tr>
</tbody>
</table>

a $S_{\text{BET}}$, BET specific surface area; volume of complementary pores calculated from PSD by integration between 0 and 4 nm; $V_c$, single-point pore volume; $w_{\text{KJS}}$, mesopore cage diameter calculated by the KJS method [243].
Figure 1. Small angle X-ray scattering (SAXS) pattern for the calcined cage-like FDU-1 mesoporous silica synthesized at room temperature by using 6 hour stirring time and hydrothermal treatment at 100 °C for 6 hours.
Figure 2. Argon adsorption isotherms measured at -196 °C (A) and the corresponding pore size distributions (PSDs) (B) calculated according to KJS method [243] for the calcined cage-like FDU-1 mesoporous silicas synthesized at room temperature by using different stirring times from 1h to 24h and performing hydrothermal treatment at 100 °C for 6 hours. The isotherm curves and PSDs for the Ft-3, Ft-4, Ft-6, Ft-8, Ft-12 and Ft-24 samples were offset vertically by 265, 540, 875, 1190, 1480 and 1805 cm$^3$ STP g$^{-1}$ and by 0.12, 0.22, 0.34, 0.55, 0.7 and 0.89 cm$^3$ g$^{-1}$ nm$^{-1}$, respectively.
treatment is sufficient to synthesize highly ordered FDU-1 samples with uniform cage-like mesopores. It is worthy to mention that the PSD curves shown in Fig. 2B were calculated from argon adsorption isotherms using the modified BJH method calibrated for cylindrical mesopores with diameter between 2 and 6.5 nm \[246\]. This method underestimates the diameter of cage-like mesopores by about 2 nm \[76\].

**Variation of TEOS/template ratio**

Structural characterization of the calcined FDU-1 silicas studied was determined by using SAXS data shown in Fig. 3. As can be seen from this figure, the SAXS patterns feature one peak at the scattering vector \( q = 0.5 \) that is visible and quite narrow for the Fr-1, Fr-1.5, Fr-2, Fr-2.5, Fr-3 samples and it becomes much broader for the Fr-3.5 and Fr-4 samples. In addition to this first reflection the SAXS patterns possess also other peaks, which are the best resolved for the Fr-2, Fr-2.5 and Fr-3 samples. The SAXS patterns for all these samples were assigned according to the face-centered cubic \( Fm\bar{3}m \) symmetry analogously as it was done elsewhere for the FDU-1 mesostructures \[76\]. Thus, the observed reflections were indexed as 111, 220, 311, 400, 420 and 600, respectively. The unit cell parameter values calculated for each reflection are similar (see Table 3) indicting that the assumed symmetry group provides a reasonable representation for the FDU-1 mesostructure. A detailed comparison of the peak intensities for the 220, 311 and 420 reflections present on the SAXS patterns provide some information about structural differences between various samples. This comparison shows that the best structural ordering is observed for the Fr-2, Fr-2.5 and Fr-3 samples. The structural ordering is poor for Fr-1 and Fr-1.5 samples and becomes the worst for the Fr-3.5 and Fr-4 samples.
**Figure 3.** Small angle X-ray scattering (SAXS) patterns for the calcined cage-like FDU-1 mesoporous silicas synthesized with different triblock copolymer-silica ratios.
This finding suggests that the structure deterioration is much more intense when the polymer concentration is too high; this effect is smaller at low polymer concentrations.

Apart from the observed changes in the mesostructural ordering reflected by changes in the peak intensities, one more interesting phenomenon is observed. As can be seen from Fig. 3, the intensity of 220 reflection in relation to 310 peak is rising with the increasing polymer concentration and it becomes the highest for the Fr-2 (0.0074 ratio) sample, whereas it decreases meaningfully for the Fr-2.5 and Fr-3 samples and totally disappears for the Fr-3.5 and Fr-4 samples. It is noteworthy that the 220 reflection originates from the lattice plane, which lies on the diagonal of the unit cell [76] so its intensity can be related to the entrance size of cage-like mesopores. The aforementioned observation of the changes in the intensity of 220 peak for the samples studied shows that FDU1-2 should have the smallest entrances to the spherical cages in comparison to the other samples, which is confirmed by a delayed desorption and the abrupt closure of the hysteresis loop at the lower limit of relative pressure for argon at -196 °C (see Fig. 4).

Nitrogen adsorption-desorption isotherms of type IV with a pronounced hysteresis loop are shown in Fig. 4, where the BET specific surface area, micropore volume, volume of the primary mesopores and mesopore diameter derived from these adsorption isotherms are listed in Table 3 and shown in Fig. 5.
Figure 4. Argon adsorption-desorption isotherms measured at -196 °C for the calcined cage-like FDU-1 mesoporous silicas synthesized with different triblock copolymer-silica ratios. The isotherms for Fr-1.5, Fr-2, Fr-2.5, Fr-3, Fr-3.5 and Fr-4 samples were offset vertically by 160, 380, 680, 1070, 1310 and 1460 cm$^3$ STP g$^{-1}$, respectively.
Figure 5. Evolution of the BET specific surface area (A), volume of the primary mesopores (B) and mesopore cage diameter (C) for the calcined cage-like FDU-1 mesoporous silicas synthesized using different triblock copolymer-silica ratios.
Figure 6. Pore size distributions (PSDs) (A, B) calculated according to the KJS method [243] from argon adsorption isotherms for the calcined cage-like FDU-1 mesoporous silicas synthesized with different triblock copolymer-silica ratios.
The first part of argon adsorption isotherms (Fig. 4) depicts micropore filling and multilayer film formation on the pore walls. Like most of mesoporous materials templated by block copolymers, the FDU-1 silicas studied also contain microporosity formed by occlusion of hydrophilic chains of copolymer in the walls of as-synthesized nanocomposites. Looking at Table 3, one can clearly see that the micropore volume underwent through certain optimum, and it was the highest for Fr-2 with 0.34 cm$^3$g$^{-1}$, i.e., increased with increasing amount of block copolymer and later it decreased slowly with lowering this ratio. The second part of the adsorption isotherm represents the capillary condensation of adsorbate molecules in mesopores. As can be seen from Fig. 4, all samples except Fr-1, Fr-3.5 and Fr-4 feature sharp capillary condensation steps at relative pressure of 0.8. This indicates the presence of uniform mesopores as evidenced by the corresponding PSDs (Figs. 6A and 6B). The higher and lower copolymer-to-silica ratios than 135:1 (see isotherms for Fr-1, Fr-1.5 Fr-3.5 and Fr-4 as well as the w values in Table 3) resulted in a shift towards smaller values of relative pressures, which reflect the reduction of mesopore diameter from ~9.6 to ~6.5 nm, respectively. On the other hand higher values of this ratio from 135:1 to 90:1 caused the mesopore enlargement (see Fr-2, Fr-2.5 and Fr-3 as well as the w values in Table 3). This agrees with PSDs in Figs. 6A and 6B and the mesopore sizes listed in Table 3. The third part of adsorption-desorption isotherm is the capillary evaporation branch that is delayed to the lower limit of hysteresis. This is typical for materials with cage-like structures, where large cavities are connected through narrow entrances that delay desorption of gas molecules from
mesopores. As can be seen from Fig. 4, only the sample synthesized with the 135:1 ratio
displayed steep capillary evaporation step indicating high uniformity of the pore opening
sizes. The samples synthesized with higher ratio than 135:1 (Fr-1 and Fr-1.5) featured
two distinct steps on the desorption branch. The first broad step occurred somewhere
between 0.47-0.6 and the second step, which was due to the metastability of the adsorbate
film, occurred near 0.34-0.36 of the relative pressure that corresponds to the opening
sizes of 4.4-5.5 nm and below 4 nm, respectively. On the other hand, samples with the
ratio lower than 135:1 featured one broad desorption that reflected wide distribution of
entrance sizes. The Fr-2 sample exhibited the BET specific surface area of 760 m^2 g^-1, the
single-point total pore volume of 0.85 cm^3 g^-1 and the pore width of 15.6 nm.

The amount of the polymeric template used in the synthesis was determined by
high resolution thermogravimetry (TG) as shown in Fig. 7. The TG curves recorded
under flowing nitrogen in the range from 100 and 800 °C for the as-synthesized FDU-1
materials with progressively increasing amount of the polymeric template (from Fr-1 to
Fr-4) exhibit a gradual increase in the total weight loss, i.e., 29.13, 37.5, 44.52, 41.56,
49.30, 56.21 and 54.43 %, respectively.

**Variation of NaCl, pH and template concentration**

Fig. 8 shows argon adsorption-desorption isotherms for two calcined FDU-1
samples (with and without optimized amount of sodium chloride), denoted as Fs-2.5 and
Fs-0, respectively. These isotherms are type IV with a pronounced hysteresis loop
starting at the relative pressure of about 0.80-0.85 and abruptly ending at ~0.35 that is
typical for a good quality of large pore cage-like structures.
Table 3. Adsorption and structural parameters determined from argon adsorption isotherms measured at -196 °C and small angle X-ray scattering (SAXS) for the calcined cage-like FDU-1 mesoporous silicas prepared at room temperature using various triblock copolymer-silica ratios (Figures 3-7).^a

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratio</th>
<th>$S_{\text{BET}}$ [m$^2$ g$^{-1}$]</th>
<th>$V_c$ [cm$^3$ g$^{-1}$]</th>
<th>$V_t$ [cm$^3$ g$^{-1}$]</th>
<th>$w_{\text{KJS}}$ [nm]</th>
<th>$w_d$ [nm]</th>
<th>$a$ [nm]</th>
</tr>
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<tbody>
<tr>
<td>Fr-1</td>
<td>0.0037</td>
<td>651</td>
<td>0.22</td>
<td>0.67</td>
<td>9.6</td>
<td>-</td>
<td>23.1</td>
</tr>
<tr>
<td>Fr-1.5</td>
<td>0.0055</td>
<td>859</td>
<td>0.30</td>
<td>0.77</td>
<td>9.8</td>
<td>13.4</td>
<td>23.3</td>
</tr>
<tr>
<td>Fr-2</td>
<td>0.0074</td>
<td>760</td>
<td>0.34</td>
<td>0.85</td>
<td>15.6</td>
<td>13.5</td>
<td>23.3</td>
</tr>
<tr>
<td>Fr-2.5</td>
<td>0.0093</td>
<td>539</td>
<td>0.33</td>
<td>1.05</td>
<td>14.6</td>
<td>14.4</td>
<td>23.3</td>
</tr>
<tr>
<td>Fr-3</td>
<td>0.0111</td>
<td>561</td>
<td>0.28</td>
<td>0.97</td>
<td>13.5</td>
<td>14.1</td>
<td>22.9</td>
</tr>
<tr>
<td>Fr-3.5</td>
<td>0.0129</td>
<td>518</td>
<td>0.23</td>
<td>1.08</td>
<td>12.3</td>
<td>14.2</td>
<td>22.1</td>
</tr>
<tr>
<td>Fr-4</td>
<td>0.0148</td>
<td>404</td>
<td>0.21</td>
<td>0.98</td>
<td>6.5</td>
<td>-</td>
<td>19.2</td>
</tr>
</tbody>
</table>

^a Ratio, copolymer-to-silica ratio; $S_{\text{BET}}$, BET specific surface area; $V_c$, volume of complementary pores calculated from PSD by integration between 0 and 4 nm; $V_t$, single-point pore volume; $w_{\text{KJS}}$, mesopore cage diameter calculated by the KJS method [243]; $w_d$, pore width calculated on the basis of unit cell parameter and pore volumes according to the relations derived for the cubic $Fm3m$ (Equation 11) structure [248]; $a$, unit cell parameter calculated from the first observed characteristic Bragg’s reflection.
Figure 7. Thermogravimetric weight curves measured in flowing nitrogen for the as-synthesized cage-like FDU-1 mesoporous silicas obtained with different triblock copolymer-silica ratios.
**Figure 8.** Comparison of argon adsorption isotherms measured at -196 °C for two calcined cage-like FDU-1 mesoporous silicas: Fs-0 synthesized without sodium chloride using 2M HCl and a typical amount of polymer, Fs-2.5 synthesized with sodium chloride using 0.5M HCl and a double amount of polymer.
Figure 9. Pore size distributions (PSDs) calculated according to the KJS method [243] for two calcined cage-like FDU-1 mesoporous silicas: Fs-0 synthesized without sodium chloride using 2M HCl and a typical amount of polymer, Fs-2.5 synthesized with sodium chloride using 0.5M HCl and a double amount of polymer.
As can be seen from this figure the capillary condensation step for Fs-2.5 is about twice higher and shaper than that for the sample FDU-1 obtained without salt addition, which reflects better uniformity of the mesoporous structure and about twice larger pore volume. A comparison of the pore size distributions (Fig. 9) shows that the distribution peak for Fs-2.5 is not only narrower but also about three times higher than that for the sample without salt addition. The sample Fs-2.5 exhibited the BET specific surface area of 830 m$^2$g$^{-1}$, total pore volume of 1.1 cm$^3$g$^{-1}$, and pore diameter of about 10 nm estimated according the KJS method [243] elaborated for the cylindrical pore geometry (Table 4).

Fig. 10 shows a comparison of argon adsorption isotherms for a series of the Fs-z samples synthesized using different salt/polymer mass ratios. As can be seen from this figure the optimal salt/polymer ratio lies between 2 and 3. There is almost no difference among isotherms for the samples synthesized at this salt/polymer ratio range except less steep desorption branch for Fs-2, which suggests some nonuniformity in the size of the cage entrances. Fig. 11 shows the pore volume plotted against the salt/polymer ratio for the samples studied, which clearly indicates the best range for this ratio between 2 and 3.

The samples synthesized below and above the optimal salt/polymer mass ratio region exhibit less steep capillary condensation step and consequently broader PSD as shown in Fig. 12. Moreover, the volume of micropores and primary mesopores for the aforementioned samples are lower than those for the Fs-z samples with z between 2 and 3. In addition, the mesopore diameter for those samples was about 1-2 nm smaller in comparison to the samples synthesized at optimal conditions (Table 4).
Figure 10. Comparison of argon adsorption-desorption isotherms at -196 °C for a series of calcined cage-like FDU-1 mesoporous silicas synthesized at different salt/polymer mass ratios. The isotherms for Fs-2, Fs-2.5, Fs-3, Fs-3.5 and Fs-4 were offset vertically by 170, 680, 1220, 1770 and 2110 cm$^3$ STP g$^{-1}$, respectively.
Figure 11. Dependence of the total pore volume on the salt/polymer mass ratio for a series of calcined cage-like FDU-1 mesoporous silicas synthesized at different salt/polymer mass ratios.
Figure 12. Pore size distributions (PSDs) calculated according to the KJS method [243] for a series of calcined cage-like FDU-1 mesoporous silicas synthesized at different salt/polymer mass ratios.
Also, the PSD peak for the samples synthesized beyond the optimal range of the salt/polymer ratio is about 2-3 times smaller than that for the Fs-z samples (z = 2, 2.5, 3) and sometimes shifted in direction of smaller pores.

SAXS patterns shown in Fig. 13 for selected samples indicate that the samples synthesized in the presence of sodium chloride exhibit analogous structure as samples synthesized without addition of salt.

This study shows that the synthesis of highly ordered nanoporous silicas with spherical cage-like pores synthesized using self-assembly of B50-6600 triblock copolymer template and TEOS can be greatly improved over wide range of synthesis conditions including reduction of stirring time, optimization of polymer-to-silica ratio and addition of sodium chloride using a double amount of the template. The structural ordering, the high surface area of up to 1103 m²g⁻¹ and large pore size about 6.5 and 15.6 nm were thoroughly confirmed by XRD and argon adsorption analysis.

**Template removal from cage-like siliceous mesostructure**

Nitrogen adsorption–desorption isotherms for two SBA-16 samples denoted as S-e350 and S-c550 are shown in Fig. 14. The BET specific surface area, total pore volume, volume of primary mesopores, pore diameter, carbon percentage and unit cell parameter for those samples are listed in Table 5. These isotherms are type IV with a broad hysteresis loop starting at a relative pressure at ~ 0.6 - 0.7 and abruptly ending at ~ 0.45, which indicates the presence of good-quality cage-like pores. As can be seen from Fig. 14, S-e350 features steeper capillary condensation step and much larger volume of mesopores than those in S-c550. Moreover, the capillary condensation step for S-e350 is
Table 4. Adsorption parameters determined from argon adsorption isotherms measured at -196 °C for the calcined cage-like FDU-1 mesoporous silicas prepared with addition of sodium chloride, low pH and a double amount of template (Figures 8-13).a

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratio</th>
<th>$S_{\text{BET}}$ [m$^2$ g$^{-1}$]</th>
<th>$V_c$ [cm$^3$ g$^{-1}$]</th>
<th>$V_t$ [cm$^3$ g$^{-1}$]</th>
<th>$w_{\text{KJS}}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fs-0</td>
<td>0</td>
<td>801</td>
<td>0.16</td>
<td>0.80</td>
<td>10.1</td>
</tr>
<tr>
<td>Fs-1.5</td>
<td>1.5</td>
<td>650</td>
<td>0.09</td>
<td>0.61</td>
<td>8.0</td>
</tr>
<tr>
<td>Fs-2</td>
<td>2</td>
<td>830</td>
<td>0.11</td>
<td>1.10</td>
<td>10.1</td>
</tr>
<tr>
<td>Fs-2.5</td>
<td>2.5</td>
<td>811</td>
<td>0.12</td>
<td>1.10</td>
<td>10.0</td>
</tr>
<tr>
<td>Fs-3</td>
<td>3</td>
<td>708</td>
<td>0.10</td>
<td>1.06</td>
<td>10.0</td>
</tr>
<tr>
<td>Fs-3.5</td>
<td>3.5</td>
<td>558</td>
<td>0.08</td>
<td>0.66</td>
<td>8.4</td>
</tr>
<tr>
<td>Fs-4</td>
<td>4</td>
<td>455</td>
<td>0.05</td>
<td>0.62</td>
<td>9.0</td>
</tr>
</tbody>
</table>

a Ratio, salt-to-polymer weight ratio; $S_{\text{BET}}$, BET specific surface area; volume of complementary pores calculated from PSD by integration between 0 and 4 nm; $V_t$, single-point pore volume; $w_{\text{KJS}}$, mesopore cage diameter calculated by the KJS method [243].
Figure 13. Small angle X-ray scattering (SAXS) for selected calcined cage-like FDU-1 mesoporous silicas synthesized at different salt/polymer mass ratios.
**Figure 14.** Comparison of nitrogen adsorption-desorption isotherms at –196 °C for two cage-like SBA-16 mesoporous silicas studied: extracted (S-e350) and as-synthesized (S-c550) samples calcined in flowing air at different temperatures.
Figure 15. Pore size distributions (PSDs) calculated according to the KJS method [243] for two cage-like SBA-16 mesoporous silicas studied: extracted (S-e350) and as-synthesized (S-c550) samples calcined in flowing air at different temperatures.
shifted to higher relative pressures, indicating larger pore size as shown in the corresponding pore size distributions in Fig. 15. As expected, calcination process at 550°C (S-c550) caused a significant shrinkage of the structure compared to the step by step template removal (S-e350), which can be seen by the offset of the micropore peak (~2.2 nm) towards smaller values, which resulted in the decrease of the micropore volume from 0.45 to 0.37 cm³g⁻¹ as well as the reduction of the mesopore size and the volume of mesopores (see PSD in Fig. 15) (Scheme 8). The S-e350 sample exhibited the BET specific surface area of 1187 m²g⁻¹, total pore volume of 0.84 cm³g⁻¹, and the pore width of 8.56 nm calculated according to the KJS method calibrated for cylindrical pores [243] (Table 5).

Figs. 16A and 16B show a comparison of nitrogen adsorption isotherms for a series of the S-ex and S-cx samples calcined at different temperatures, respectively. As can be seen from Fig. 16A the optimal temperature of the template removal is between 200 and 500 °C. Comparing the two extreme samples from this series, one can conclude that the extracted sample calcined at 200 °C (denoted as e-200) has the largest pore diameter and contains a small amount of polymer residue (C = 1.88 %, see Table 5) that reduces slightly its total pore volume. Note that the carbon percentage decreased with increasing calcination temperature, so for the S-e350 sample it was 0.38 % only. However, the pore size of the extracted and calcined sample at 550 °C (S-e550) dramatically decreased and consequently reached the value obtained for the sample calcined at 550 °C (S-c550) due to the structure shrinkage (see Fig. 16B). This pore size reduction is confirmed by the pore size distributions shown in Figs. 17A and 17B.
Scheme 8. Schematic illustration of the polymeric template removal from as-synthesized SBA-16 by two different methods: (i) commonly used calcination at 550 °C (top scheme) and (ii) combined extraction followed by controlled-temperature calcination at 350 °C (bottom scheme). The large circles connected with straight channels represent interconnected spherical cages (ordered mesopores), whereas curved thin ribbons denote irregular micropores within walls of ordered mesopores.
Table 5. Structural parameters determined from argon adsorption isotherms measured at -196 °C, powder X-ray diffraction (XRD) and elemental analysis for the cage-like SBA-16 mesoporous silicas studied (Figures 14-20).\(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{BET}) [m(^2) g(^{-1})]</th>
<th>(V_o) [cm(^3) g(^{-1})]</th>
<th>(V_t) [cm(^3) g(^{-1})]</th>
<th>(w_{KJS}) [nm]</th>
<th>(a) [nm]</th>
<th>C [%]</th>
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</thead>
<tbody>
<tr>
<td>S-c200</td>
<td>1084</td>
<td>0.29</td>
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<td>7.66</td>
<td>16.74</td>
<td>1.70</td>
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<tr>
<td>S-e200</td>
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<td>0.86</td>
<td>8.74</td>
<td>17.47</td>
<td>1.88</td>
</tr>
<tr>
<td>S-c250</td>
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<td>0.75</td>
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<td>1.60</td>
</tr>
<tr>
<td>S-e250</td>
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<td>0.89</td>
<td>8.73</td>
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<td>1.18</td>
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<td>0.89</td>
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<td>16.90</td>
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<td>8.30</td>
<td>16.42</td>
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<td>0.60</td>
<td>7.02</td>
<td>15.02</td>
<td>0.04</td>
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<td>S-e550</td>
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<td>0.63</td>
<td>7.26</td>
<td>15.23</td>
<td>0.04</td>
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<tr>
<td>S-e</td>
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<td>0.73</td>
<td>8.56</td>
<td>17.22</td>
<td>5.13</td>
</tr>
</tbody>
</table>

\(^a\) \(S_{BET}\), BET specific surface area; \(V_o\), volume of ordered pores; \(V_t\), single-point pore volume; \(w_{KJS}\), mesopore diameter calculated by the KJS method [243]; \(a\), unit cell parameter calculated from the first observed characteristic Bragg’s reflection, \(\%C\), carbon percentage obtained from elemental analysis.
Figure 16. Comparison of nitrogen adsorption-desorption isotherms at -196 °C for a series of extracted (A) and as-synthesized (B) cage-like SBA-16 mesoporous silicas calcined at different temperatures. The isotherms on Panel A for S-e450, S-e350, S-e250 and S-e are offset vertically by 110, 235, 400 and 680 cm$^3$ STP g$^{-1}$; whereas the isotherms on Panel B for S-c450, S-c350 and S-c250 are offset vertically by 193, 418 and 678 cm$^3$ STP g$^{-1}$, respectively.
**Figure 17.** Pore size distributions (PSDs) calculated according to the KJS method [243] for a series of extracted (A) and as-synthesized (B) cage-like SBA-16 mesoporous silicas calcined at different temperatures.
Note that each of those distributions contains two well-resolved peaks. The first peak having maximum at ~2 nm reflects irregular micropores present in the mesopore walls and small pores that interconnect ordered spherical cages (mesopores) as shown in Scheme 8. The second peak reflects the distribution of ordered spherical mesopores. The temperature range for removal of polymeric template from SBA-16 is in the range of 200 and 500 °C, however, the sample prepared at 200 °C contains a small polymer residue, so the most effective temperature is somewhere at 300-350 °C to achieve desired quality of mesostructures.

Fig. 18 shows the X-ray diffraction patterns for the samples studied (S-c, S-e, S-e350 and S-c550) in the low angle region (2θ (Cu-Kα) = 0.4 - 5°), which exhibit intensive peak at 2θ = ~ 0.77 attributed to the (110) reflection and two minor less-resolved peaks at 2θ = ~ 1.05 and 1.5 attributed to the (200) and (211) reflections, respectively. This is consistent with the formation of ordered mesoporous materials with Im3m cubic symmetry. As can be seen from Table 5 the unit cell parameter for the S-cx samples gradually decreases with increasing temperature (which is seen from the shift of the diffraction peaks towards higher 2θ values), whereas this decrease is smaller for the S-ex samples and becomes more pronounced at temperatures close to 550 °C.

Shown in Figs. 19A and 19B are thermogravimetric curves that exhibit the weight loss between 100 and 800°C related to the polymer removal/decomposition, which is about 38, 23 and 3% for the S-c, S-e and S-e350 samples, respectively. Elemental analysis indicated that the extracted sample retained about 5.13 % of the carbon residue, which after calcination at 350 °C was reduced to 0.38 %.
Figure 18. Powder X-ray diffraction (XRD) patterns for extracted (S-e), as-synthesized (S-p) and calcined (S-e350 and S-c550) cage-like SBA-16 mesoporous silicas. XRD patterns for S-e, S-e350 and S-c550 were offset horizontally by 0.15, 0.8 and 1.2 (°), respectively.
Figure 19. Thermogravimetric weight change curves measured in flowing nitrogen (A) and corresponding differential DTG curves (B) for extracted (S-e), as-synthesized (S-p) and calcined (S-e350 and S-c550) cage-like SBA-16 mesoporous silicas heated at different temperatures.
Figure 20. Evolution of the mesopore diameter as a function of calcination temperature for two series of the extracted and as-synthesized cage-like SBA-16 mesoporous silicas calcined at various temperatures; the other parameters are held constant (calcination time = 240 minutes, temperature rate = 5 degrees per minute, flowing gas = air; extraction time = 24 hours).
The extraction step is very important for the template removal from cage-like mesostructures. At least 70-75 % of the polymer should be removed to achieve high pore volume and large pore size of SBA-16. When the polymer removal was 50 % the resulting SBA-16 was similar to the calcined sample without prior extraction.

In summary, an effective method for the removal of polymeric template, which combines extraction and temperature-controlled calcination is proposed to obtain high pore volume and large pore size of ordered mesoporous silicas, SBA-16 (*Im3m* symmetry group), which was synthesized in the presence of sodium chloride at low acid concentrations using poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (Pluronic F127) as a structure directing agent and tetraethylorthosilicate as a silica source.
IV. ORDERED SILICEOUS MESOSTRUCTURES WITH ORGANIC PENDANT GROUPS

An incorporation of various small and large pendant groups into the walls of ordered mesoporous SBA-16 and FDU-1 silicas via co-condensation method with maximized concentrations of organic ligands and high quality materials is a paramount issue from the viewpoint of possible applications of these adsorbents. The structural and adsorption characteristics were undertaken into consideration to obtain these adsorbents with desired properties. The effect of structural transformation resulted from addition of various organic pendant groups were carefully studied. The OMOs were analyzed by means of SAXS/XRD, TEM, argon and nitrogen adsorption, high resolution TG, FTIR, and elemental analysis.

4.1. EXPERIMENTAL

Synthesis of FDU-1 organosilica with organic pendant groups using a typical amount of polymer

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* This Chapter is based on the following publications:
Grudzien R. M.; Grabicka B. E.; Jaroniec M. *Adsorption* 2006, 12, 293 [256].

The synthesis of mesoporous materials with organic pendant groups was carried out according to the procedure of Yu et al. [74] employing poly(ethylene oxide)-block-poly(butylene oxide)-block-poly(ethylene oxide) triblock copolymer B50-6600 (EO_{39}BO_{47}EO_{39}) template under highly acidic conditions. In a typical procedure, 2 g of polymer B50-6600 was dissolved in 120 ml of 2M HCl aqueous solution with a fast stirring for 4 h at room temperature and then either using triethoxyvinylsilane (TEVS) or (3-mercaptopropyl)trimethoxysilane (MPTMS) as reagents together with prehydrolyzed TEOS (15 minutes) using the molar ratio ranging from 10 to 30% (see experimental details given in subsequent chapter). After stirring for another 6 h, the mixture was transferred to polypropylene bottle, sealed and aged for 6 h at 100 °C. The product was filtered, washed with DW and dried followed by polymer removal via extraction with acidic ethanol solution (2 ml of HCl and 100 ml of 95% EtOH) at 70 °C. Vinyl- and mercaptopropyl-containing organosilicas fabricated using this procedure are designated as F-Vx-2 or F-SHx-2, where V, SH, x and 2 refer to vinyl group, mercaptopropyl group, molar concentration of organosilane and 2M HCl solution, respectively.

**Synthesis of FDU-1 organosilica with organic pendant groups using a double amount of polymer**

In the synthesis of the FDU-1 silica, 4 g of B50-6600 and 10 g of NaCl were added to 90 ml of DW solution, which has been acidified with 30 ml of HCl 2M. A clear B50-6600-NaCl-HCl-DW solution was kept under vigorous stirring before a 8.32 g of TEOS was pipetted slowly to the mixture at 45 °C. FDU-1 organosilicas were prepared in a similar way to pure FDU-1 silica with addition of sodium chloride that was synthesized
using the procedure reported in our previous communication [251]. Various organosilica precurso rs were employed such as triethoxyvinylsilane (TEVS), 3-mercaptopropyl trimethoxysilane (MPTMS), N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (TESPDI), ureidopropyltrimethoxysilane (UPTMS) together with TEOS using different molar ratio of organosilanes up to 40% (see experimental details given in subsequent chapter). The TEOS prehydrolysis time was 15 minutes before addition of organosilane followed by another 6h at 100 °C of hydrothermal treatment. The precipitate was filtered, washed with DW and dried at 70 °C in the oven. The materials were extracted with 2 ml of HCl and 100 ml of 95% EtOH at 70 °C to remove the polymer (Scheme 9). The extracted vinyl-, mercaptopropyl-, imidazole-, ureidopropyl- and bifunctional ureidopropyl- with mercaptopropyl-containing FDU-1 OMOs synthesized with addition of NaCl at 0.5M HCl are denoted as F-Vx-0.5s, F-SHx-0.5s, F-IMx-0.5s, F-Ux-0.5s and F-USHx-0.5s where V, SH, IM, UR, x, 0.5 and s refer to vinyl group, mercaptopropyl group, imidazole group, ureidopropyl, organosilane molar concentration, molar concentration of HCl and addition of salt, respectively.

In addition, the samples with 20% of vinyl groups were also synthesized with addition of NaCl at various HCl molar concentrations; 0.5, 1, 1.5 and 2M, thus their names are as follows: F-V20-0.5s, F-V20-1s, F-V20-1.5s and F-V20-2s. The F-V20-0.5 sample was synthesized using 0.5M HCl without addition of salt. The as-synthesized samples with vinyl and mercaptopropyl groups are denoted as F-V40-0.5s-p and F-SH40-0.5s-p.
Synthesis of SBA-16 organosilica with organic pendant groups

Cage-like mesoporous silica, SBA-16, with imidazole, ureidopropyl, and bifunctional ureidopropyl and mercaptopropyl pendant groups was synthesized by co-condensation of N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (TESPDI), ureidopropyltrimethoxysilane (UPTMS), (3-mercaptopropyl)trimethoxysilane (MPTMS) and TEOS in the presence of poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer (Pluronic F127, EO\textsubscript{106}PO\textsubscript{70}EO\textsubscript{106}) under low acidic concentrations and with addition of sodium chloride. The recipe used was similar to the procedure reported by Qiu at al [217]. In a typical synthesis, 2 g of F127 and 7.05 g of sodium chloride were dissolved in 20 ml 2M HCl and 60 ml deionized water at 40 °C. After 4 hours stirring a specified volume of TEOS was pipetted dropwise to this solution under vigorous mixing, and next after 15 minutes organosilica reagent was added to achieve the desired molar composition of both silanes. After further stirring for 20 hrs at 40 °C, the resulting white precipitate was transferred into a polypropylene bottle and subsequently heated at 100 °C for 24 hrs. The product was filtered, washed with DW, and dried in the oven at 80 °C. To remove the polymeric template from mesopores, the as-synthesized nanocomposites were extracted three times with 2 ml of 36 % wt. HCl and 100 ml of 95 % ethanol at 70 °C (see experimental details given in subsequent chapter).

The extracted SBA-16 silicas containing imidazole, ureidopropyl and ureidopropyl along with mercaptopropyl groups are denoted as S-IMx-0.5s, S-Ux-0.5s S-USHx-0.5s where IM, U, SH refers to imidazole, ureidopropyl and ureidopropyl with mercaptopropyl
Scheme 9. Chart illustrating the synthesis procedure for cage-like mesoporous FDU-1 organosilica containing ureidopropyl and mercaptopropyl pendant groups.
pendant groups, whereas x, 0.5 and s denote molar concentration of organosilane, HCl concentration and sodium chloride. The letter p refers to a sample containing polymeric template. The SBA-16 sample subjected to calcination at 550 °C in flowing air for 4 hours was denoted as S-0.5s.

4.2. CAGE-LIKE OMO CONTAINING SINGLE VINYL AND MERCAPTOPROPYL PENDANT GROUPS

OMO obtained using a typical amount of polymer without NaCl

Figs. 21A and 22A show argon adsorption isotherms measured at -196 °C for two sets of OMOs with vinyl and mercaptopropyl pendant groups synthesized without addition of NaCl using 2M HCl and regular amount of B50-6600, whereas Figs. 21B and 22B depict the corresponding pore size distributions calculated according to the KJS method [243]. The structural parameters for these materials are shown in Tables 6-9. As can be seen from Fig. 21A, the OMO sample with up to 20% of vinyl groups exhibit type IV isotherm with apparent hysteresis loop having a steep capillary condensation step and a delayed steep desorption step. This indicates the presence of cage-like mesopores and uniform pore openings smaller than 4 nm. However, for the samples prepared with 30% of TEVS, the isotherm exhibits both continuously increasing capillary condensation and decreasing capillary evaporation steps suggesting a broad PSD and non-uniform pore entrance sizes (see PSD Fig. 21B). As regards to mercaptopropyl-containing materials shown in Fig. 22A, all samples with mercaptopropyl groups show isotherms similar to that for F-V30-2, which reflects broad PSD.
Figure 21. Comparison of argon adsorption-desorption isotherms (A) measured at -196 °C and the corresponding pore size distributions (PSDs) (B) calculated according to the KJS method [243] from adsorption branches for the extracted mesoporous organosilicas with vinyl (V) pendant groups obtained using 2M HCl without addition of NaCl and a typical amount of triblock copolymer. The isotherms and the PSD curves for F-V10-2, F-V20-2, F-V30-2 were offset by 380, 710, 820 cm$^3$ STP g$^{-1}$ and by 0.19, 0.4, 0.55 cm$^3$ g$^{-1}$ nm$^{-1}$, respectively.
Figure 22. Comparison of argon adsorption-desorption isotherms measured at -196 °C (A) and the corresponding pore size distributions (PSDs) (B) calculated according to the KJS method [243] from adsorption branches for the extracted mesoporous organosilicas with mercaptopropyl (SH) pendant groups obtained using 2M HCl without addition of NaCl and a typical amount of triblock copolymer. The isotherms and the PSD curves for F-SH10-2, F-SH20-2 were offset by 300, 575 cm$^3$ STP g$^{-1}$ and by 0.17, 0.32 cm$^3$ g$^{-1}$ nm$^{-1}$, respectively.
Figure 23. Small angle X-ray scattering (SAXS) patterns for the extracted mesoporous organosilicas with vinyl (V) pendant groups obtained using 2M HCl without addition of NaCl and a typical amount of triblock copolymer.
Figure 24. Small angle X-ray scattering (SAXS) patterns for the extracted mesoporous organosilicas with mercaptopropyl (SH) pendant groups obtained using 2M HCl without addition of NaCl and a typical amount of triblock copolymer.
As can be seen from Figs. 21B and 22B, PSD for the sample synthesized without addition of organic groups (pure silica) is narrow, however after gradual addition of TEVS above 30% and MPTMS above 10% the PSD curves become very broad with the peak maximum shifted progressively towards smaller values.

Figs. 23 and 24 depict small angle X-ray scattering (SAXS) patterns for OMOs with vinyl groups up to 30% and mercaptopropyl groups up to 20%. The pure silica sample (FDU1-2) exhibits one major reflection (111) and three minor reflections (220), (311) and (420), which were assigned according to the face-centered cubic \( Fm\overline{3}m \) structure [75]. As can be seen from Fig. 23, an introduction of vinyl functionality of 10 % leads to the disappearance of (420) reflection, nevertheless, the \( Fm\overline{3}m \) symmetry group can still be assigned. An additional introduction of TEVS (20%) causes some structural deterioration, thus assigning \( Fm\overline{3}m \) becomes problematic. In contrary, the sample with 30% groups possesses only one broad peak at 0.78 2\( \theta \), which probably was formed by overlapping of few other broad peaks. In the case of even longer surface group, i.e. mercaptopropyl (see Fig. 24), the results indicate that both concentrations of mercaptopropyl ligands lead to a significant deterioration of the structure with one broad peak (see Tables 6 and 7 for the d spacing values and unit cell).

**OMO obtained using a double amount of polymer with NaCl**

Comparisons of argon adsorption-desorption isotherms measured at -196 °C for the extracted OMOs with vinyl and mercaptopropyl groups prepared with addition of NaCl under low acidic conditions and a double amount of polymer are shown in Figs. 25A and 26A, respectively.
Figure 25. Comparison of argon adsorption-desorption isotherms measured at -196 °C (A) and the corresponding pore size distribution (PSDs) (B) calculated according to the KJS method [243] from adsorption branches for the extracted mesoporous organosilicas with various vinyl (V) loadings (0-40 %) obtained using 0.5M HCl concentration with NaCl addition and a double amount of triblock copolymer. The isotherms and the PSD curves for F-V15-0.5s, F-V20-0.5s, F-V30-0.5s, F-V35-0.5s, F-V40-0.5s were offset by 500, 930, 1400, 1800, 2040 cm$^3$ STP g$^{-1}$ and by 0.4, 0.8, 1.3, 1.8, 2.3 cm$^3$ g$^{-1}$ nm$^{-1}$, respectively.
Figure 26. Comparison of argon adsorption-desorption isotherms measured at -196 °C (A) and the corresponding pore size distributions (PSDs) (B) calculated according to the KJS method [243] from adsorption branches for the extracted mesoporous organosilicas with various mercaptopropyl (SH) loadings (0-40 %) obtained using 0.5M HCl with addition of NaCl and a double amount of triblock copolymer. The isotherms and the PSD curves for F-SH10-0.5s, F-SH15-0.5s, F-SH20-0.5s, F-SH25-0.5s, F-SH30-0.5s, F-SH35-0.5s, F-SH40-0.5s were offset by 560, 660, 1050, 1250, 1380, 1600, 1700 cm$^3$ STP g$^{-1}$ and by 0.4, 0.8, 1.1, 1.4, 1.7, 2.1, 2.3 cm$^3$ g$^{-1}$ nm$^{-1}$, respectively.
As can be seen from Fig. 25A, both pure silica (F-0.5s) and the vinyl OMO with 15% loading (F-V15-0.5s) exhibit very sharp capillary condensation branches at high relative pressure, which reflects large mesopore sizes (see PSDs in Fig. 25B). In contrast to the other samples, the isotherms of F-V15-0.5s and F-0.5s also show delayed capillary evaporation on desorption branches, which is characteristic for the materials with cage-like pores, for which hysteresis closes at lower pressure limit typical for argon at -196 °C [10]. This type of adsorption hysteresis suggests that the pore openings are uniform and smaller than 4 nm. The hysteresis of F-V15-0.5s looks slightly different at higher pressures than that of F-0.5s.

As can be seen from the desorption branch of F-V15-0.5s sample, the capillary evaporation progresses through a minor step similarly as in the case of the vinyl samples synthesized with higher amounts of TEVS, however the capillary evaporation does not descend but gradually decreases until it reaches argon desorption limit. This type of desorption behaviour suggests a non-uniformity of the pore openings.

Introduction of higher concentrations of TEVS results in the shift of capillary condensation towards lower relative pressures and in the closure of the capillary evaporation step at higher pressures. These isotherms are distinctive for materials with cylindrical channel-like pores such as SBA-15 [24, 25]. Therefore, based on the shapes of argon adsorption-desorption isotherms it is suggested that the introduction of vinyl at the concentration higher then 15% induces a structural change from cubic \( Fm\text{3m} \) to hexagonal \( p6\text{mm} \). A similar behaviour is observed for mercaptopropyl-containing OMO materials; however in this case there are no intermediates of cubic structures. Even a
relatively low concentration of MPTSE such as 10% under the conditions studied proceeds the transformation of the structure from cubic to hexagonal. Contrary to the vinyl-functionalized materials, the isotherms for OMOs with mercaptopropyl groups show capillary condensation at lower pressures, which is attributed to smaller mesopores and the capillary evaporation does not close instantly but exhibits tailing that relates to a non-uniformity of pore entrances.

In addition, these isotherms were used to calculate the PSD curves by the KJS method [243] shown in Figs. 25B and 26B. All OMOs studied show narrow pore size distributions, which are systematically decreasing with increasing concentration of organotrialkoxysilanes (see Tables 8 and 9).

The changes in the porous structure with increasing concentration of organic groups were also monitored by the small angle X-ray scattering (SAXS). Shown in Fig. 27 are the SAXS patterns for a series of extracted OMOs with up to 40% of vinyl groups. As can be seen from this figure, the pure FDU-1 silica (F-0.5s) and the sample prepared with 15% of vinyl groups exhibit one intensive reflection at 0.66 q and some minor reflections associated with ordered porosity. These reflections were indexed as (111), (220), (311), (420) and (422) assuming the $Fm\overline{3}m$ (face-centered) structure [75]. However, a progressive increase in the relative amount of TEVS in the synthesis gel led to a decrease in the intensity of minor peaks, and to the shift of major reflection towards higher values. FWHM value for the sample with 15% of TEVS is 0.134, whereas for those OMOs with 20%, 30% and 40% of TEVS are 0.1, 0.1 and 0.09, respectively, which suggests an induced structural change. Therefore, the reflection on the SAXS patterns for
the samples with 20%, 30% and 40% of vinyl groups were indexed as (100), (110) and (200) according to the \textit{p6mm} hexagonally ordered structure, which is in a good agreement with the shape of argon adsorption isotherms, as discussed earlier. In the case of the extracted mercaptopropyl-containing OMOs shown in Fig. 28, the SAXS profiles are similar as those for OMOs with vinyl groups. Even though, the SAXS curves for the sample with 10% loading of MPTMS exhibits similar pattern to the XRD of the pure FDU-1 silica (F-0.5s), the intensities of the second and third peak are different. Also, argon isotherm indicates a typical shape for hexagonally ordered structure confirming the \textit{p6mm} symmetry group. Therefore, one intensive peak at 0.73 \( \theta \) and two minor reflections at 1.25 and 1.44 \( \theta \) were indexed as (100), (110) and (200) reflections. The samples synthesized with higher molar ratios of MPTSE in the synthesis gel of 15% and 20% sustain the \textit{p6mm} structure. However, the samples with the molar ratio higher then 20% exhibit rather a hexagonal mixed structure.

The SAXS analysis is further verified by the representative TEM images presented in Fig. 29 that provide an additional evidence for the structural changes. The TEM image showed in Fig. 29A for a low molar percentage of TEVS (15%) in the synthesis gel demonstrates clearly the arrays of highly-ordered uniform cages, which show a very good cubic structural ordering according to a three-dimensional \textit{Fm3m} symmetry group. An additional increase of vinyl groups of up to 35% (F-V35-0.5s) resulted in the structural changes. The TEM images showed in Fig. 29B and 29C depict a good long-range order characteristic for two-dimensional \textit{p6mm} hexagonal structure.
Table 6. Synthesis gel composition and structural parameters obtained from SAXS patterns for the extracted organosilicas with various vinyl (V) pendant groups obtained under conditions studied (Figures 21-34).^a

<table>
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<th>Sample</th>
<th>TEVS [%]</th>
<th>HCl [M]</th>
<th>[NaCl] [wt]</th>
<th>d [nm]</th>
<th>a [nm]</th>
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<td>0</td>
<td>13.40</td>
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</tr>
<tr>
<td>F-V10-2</td>
<td>10</td>
<td>2.0</td>
<td>0</td>
<td>13.40</td>
<td>23.20</td>
<td>Fm3m</td>
</tr>
<tr>
<td>F-V20-2</td>
<td>20</td>
<td>2.0</td>
<td>0</td>
<td>12.18</td>
<td>21.10</td>
<td>Fm3m^a</td>
</tr>
<tr>
<td>F-V30-2</td>
<td>30</td>
<td>2.0</td>
<td>0</td>
<td>11.20</td>
<td>19.40</td>
<td>Fm3m^b</td>
</tr>
<tr>
<td>F-0.5s</td>
<td>0</td>
<td>0.5</td>
<td>2.5</td>
<td>12.40</td>
<td>21.46</td>
<td>Fm3m</td>
</tr>
<tr>
<td>F-V15-0.5s</td>
<td>15</td>
<td>0.5</td>
<td>2.5</td>
<td>13.22</td>
<td>22.90</td>
<td>Fm3m</td>
</tr>
<tr>
<td>F-V20-0.5s</td>
<td>20</td>
<td>0.5</td>
<td>2.5</td>
<td>12.55</td>
<td>14.49</td>
<td>p6mm</td>
</tr>
<tr>
<td>F-V20-1s</td>
<td>20</td>
<td>1.0</td>
<td>2.5</td>
<td>12.67</td>
<td>14.63</td>
<td>p6mm</td>
</tr>
<tr>
<td>F-V20-1.5s</td>
<td>20</td>
<td>1.5</td>
<td>2.5</td>
<td>12.41</td>
<td>14.33</td>
<td>p6mm</td>
</tr>
<tr>
<td>F-V20-2s</td>
<td>20</td>
<td>2.0</td>
<td>2.5</td>
<td>11.81</td>
<td>13.64</td>
<td>p6mm</td>
</tr>
<tr>
<td>F-V20-0.5</td>
<td>20</td>
<td>0.5</td>
<td>0</td>
<td>12.29</td>
<td>14.19</td>
<td>p6mm</td>
</tr>
<tr>
<td>F-V30-0.5s</td>
<td>30</td>
<td>0.5</td>
<td>2.5</td>
<td>11.84</td>
<td>13.67</td>
<td>p6mm</td>
</tr>
<tr>
<td>F-V30-0.5sc</td>
<td>30</td>
<td>0.5</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>p6mm</td>
</tr>
<tr>
<td>F-V35-0.5s</td>
<td>35</td>
<td>0.5</td>
<td>2.5</td>
<td>11.37</td>
<td>13.13</td>
<td>p6mm</td>
</tr>
<tr>
<td>F-V40-0.5s</td>
<td>45</td>
<td>0.5</td>
<td>2.5</td>
<td>11.27</td>
<td>13.01</td>
<td>p6mm</td>
</tr>
</tbody>
</table>

^a TEVS %, mole percentage of vinyl precursor in the initial synthesis gel mixture, HCl/M, molar concentration of HCl; [NaCl]/wt, weight ratio of NaCl to triblock copolymer; d, interplanar spacing obtained on the basis of SAXS pattern corresponding to the first Bragg’s reflection; a, unit cell parameter calculated on the basis of the first reflection of SAXS peak. ^Isotherm is characteristic for the cage-like structures but the SAXS pattern can not be assigned to one cubic phase. ^Disordered structure with one major peak.
**Figure 27.** Small angle X-ray scattering (SAXS) for the extracted mesoporous organosilicas with various vinyl (V) loadings (0-40 %) obtained using 0.5M HCl concentration with NaCl addition and a double amount of triblock copolymer.
Figure 28. Small angle X-ray scattering (SAXS) patterns for the extracted mesoporous organosilicas with various mercaptopropyl (SH) loadings (0-40 %) obtained using 0.5M HCl with addition of NaCl and a double amount of triblock copolymer.
Figure 29. Transmission electron microscopy (TEM) images recorded on a Hitachi HD-2000 with a voltage of 200 kV and current of 30 mA for extracted mesoporous organosilicas obtained using different concentration of vinyl (V) pendant groups: (A) 15% and (B and C) 35%. The panel B corresponds to the top view (perpendicular to the pore orientation), whereas the panel C corresponds to the side view (parallel to the pore orientation).
Table 7. Synthesis gel composition and structural parameters obtained from SAXS patterns for the extracted organosilicas with various mercaptopropyl (SH) pendant groups obtained under conditions studied (Figures 21-34).a

<table>
<thead>
<tr>
<th>Sample</th>
<th>MPTMS [%]</th>
<th>HCl [M]</th>
<th>[NaCl] [wt]</th>
<th>d [nm]</th>
<th>a [nm]</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-2</td>
<td>0</td>
<td>2.0</td>
<td>0</td>
<td>13.40</td>
<td>23.20</td>
<td>Fm3m</td>
</tr>
<tr>
<td>F-SH10-2</td>
<td>10</td>
<td>2.0</td>
<td>0</td>
<td>9.00</td>
<td>15.60</td>
<td>Fm3m(^a)</td>
</tr>
<tr>
<td>F-SH20-2</td>
<td>20</td>
<td>2.0</td>
<td>0</td>
<td>9.00</td>
<td>15.60</td>
<td>Fm3m(^a)</td>
</tr>
<tr>
<td>F-0.5s</td>
<td>0</td>
<td>0.5</td>
<td>2.5</td>
<td>12.40</td>
<td>21.46</td>
<td>Fm3m</td>
</tr>
<tr>
<td>F-SH10-0.5s</td>
<td>10</td>
<td>0.5</td>
<td>2.5</td>
<td>12.13</td>
<td>14.00</td>
<td>p6mm</td>
</tr>
<tr>
<td>F-SH15-0.5s</td>
<td>15</td>
<td>0.5</td>
<td>2.5</td>
<td>10.45</td>
<td>12.07</td>
<td>p6mm</td>
</tr>
<tr>
<td>F-SH20-0.5s</td>
<td>20</td>
<td>0.5</td>
<td>2.5</td>
<td>10.87</td>
<td>12.55</td>
<td>p6mm</td>
</tr>
<tr>
<td>F-SH25-0.5s</td>
<td>25</td>
<td>0.5</td>
<td>2.5</td>
<td>10.10</td>
<td>11.66</td>
<td>p6mm(^b)</td>
</tr>
<tr>
<td>F-SH30-0.5s</td>
<td>30</td>
<td>0.5</td>
<td>2.5</td>
<td>10.06</td>
<td>11.62</td>
<td>p6mm(^b)</td>
</tr>
<tr>
<td>F-SH35-0.5s</td>
<td>35</td>
<td>0.5</td>
<td>2.5</td>
<td>9.63</td>
<td>11.10</td>
<td>p6mm(^b)</td>
</tr>
<tr>
<td>F-SH40-0.5s</td>
<td>45</td>
<td>0.5</td>
<td>2.5</td>
<td>9.54</td>
<td>11.01</td>
<td>p6mm(^b)</td>
</tr>
</tbody>
</table>

\(^a\) MPTMS %, mole percentage of mercaptopropyl precursor in the initial synthesis gel mixture, HCl/M, molar concentration of HCl; [NaCl]/wt, weight ratio of NaCl to triblock copolymer; d, interplanar spacing obtained on the basis of SAXS pattern corresponding to the first Bragg’s reflection; a, unit cell parameter calculated on the basis of the first reflection of SAXS pattern. \(^b\)Disordered structure with one major peak. \(^b\)Mixed hexagonal structure.
In order to determine if the change from cubic structure to hexagonal one is facilitated by varying the acidity of the synthesis gel and by adding sodium chloride, OMO with 20% of TEVS was synthesized using optimal amount of NaCl over a wide range of acid concentrations; 0.5M (F-V20-0.5s), 1M (F-V20-1s), 1.5M (F-V20-1.5s) and 2M HCl (F-V20-2s) and a double amount of polymer, see Figs. 30 and 31. In addition, one sample (F-V20-0.5) was prepared using 0.5M HCl and a double amount of polymer without NaCl. As can be seen from Fig. 30A, all the samples synthesized with NaCl under different acidic conditions show isotherms that are characteristic for materials with cylindrical pores. It can be noticed that the best sample was formed using 0.5M HCl, the other samples synthesized by using 1M, 1.5M and 2M display less steep capillary condensation and tailing of capillary evaporation steps, which suggests broad PSD (see Fig. 30B) and different pore openings. In regards to the sample synthesized at 0.5M HCl without NaCl (F-V20-0.5), its isotherm also exhibits sharp capillary condensation and evaporation steps and consequently narrow PSD. As can be seen from the SAXS patterns (Fig. 31), all samples display one intensive peak and some minor peaks. A careful SAXS analysis revealed that all patterns belong to the hexagonal \textit{p6mm} structure. Therefore, it can be concluded that for the polymer/precursor ratio studied the structural change depends mostly on the concentration of TEVS, whereas the addition of NaCl and the pH reduction improve only PSD and uniformity of pore openings.

The thermal stability of vinyl- and mercaptopropyl-containing materials was evaluated using thermogravimetric analysis.
Figure 30. Comparison of argon adsorption-desorption isotherms measured at -196 °C (A) and the corresponding pore size distributions (PSDs) (B) calculated according to the KJS method [243] from adsorption branches for the extracted mesoporous organosilicas with 20 % of vinyl (V) pendant groups obtained using a double amount of triblock copolymer and various HCl concentrations without NaCl (F-V20-0.5; at 0.5M HCl) and with NaCl. The isotherms and the PSD curves for F-V20-0.5s, F-V20-1s, F-V20-1.5s, F-V20-2s were offset by 250, 685, 1040, 1430 cm$^3$ STP g$^{-1}$ and by 0.3, 0.8, 1.05, 1.3 cm$^3$ g$^{-1}$ nm$^{-1}$, respectively.
Figure 31. Small angle X-ray scattering (SAXS) patterns for the extracted mesoporous organosilicas with 20 % of vinyl (V) pendant groups obtained using a double amount of triblock copolymer and various HCl concentrations without NaCl (F-V20-0.5; at 0.5M HCl) and with NaCl.
The TGA data were recorded from room temperature to 800 °C under flowing air for the selected polymer-containing and polymer-free samples. The TGA and DTG profiles for the vinyl- and mercaptopropyl-containing samples are shown in Figs. 32 and 33, respectively. A minor weight loss for the polymer-containing OMOs with vinyl and mercaptopropyl groups in the range of 30 °C and 100 °C reflects the removal of physisorbed water, whereas the major weight loss for F-V40-0.5s-p and F-SH40-s-p, 65.02% and 65.18%, respectively, is observed between 100 °C and 800 °C. This large weight loss results mostly from thermodesorption and decomposition of the polymeric template as well as from the degradation of organic groups. A small weight loss in the range of 400 °C and 800 °C is attributed to the condensation of silanol groups. Similarly, the weight loss of the extracted OMOs with vinyl and mercaptopropyl groups follows an analogous behaviour, i.e. the weight loss below 100 °C is due to the desorption of water, whereas the respective weight losses of 17.17 % and 39.93 % in the range of 100 °C and 800 °C are due to the decomposition of the remaining template and organic groups. As can be seen from the DTG curves for OMOs with vinyl and mercaptopropyl groups shown on the panels 32B and 33B, the peak reflecting the removal of the polymer at 150 and 204°C almost completely disappears. The decomposition of vinyl and mercaptopropyl groups began above 200 °C with their maximum corresponding to 239 °C and 306°C, respectively. The quantity of the polymeric template estimated by TG seems to be very low. In fact, the elemental analysis recorded for extracted OMOs with vinyl groups up to 20% and 40% of TEVS indicates the carbon contents of less then 6%
and 2%, respectively, whereas for OMOs with mercaptopropyl groups less then 7% and 1%, which could be either from the remaining polymer or unhydrolyzed alkoxy groups.

A successful introduction of vinyl ligands to the mesoporous materials was confirmed by the FT-IR spectroscopy in the range of 4000 and 550 cm\(^{-1}\). Fig. 34A shows the IR spectra of two polymer-extracted vinyl-functionalized samples containing two various contents, i.e., 15% (F-V15-0.5s) and 35% (F-V35-0.5s). A characteristic bump visible in the range of 3200 to 3500 cm\(^{-1}\) corresponds to hydrogen-bonded OH stretching vibrations originated from surface OH groups and molecularly adsorbed water. The materials studied (15 % and 35% of vinyl groups) exhibit typical symmetric and asymmetric stretching vibrations bands of -Si-O-Si- at 790 and 1110 cm\(^{-1}\), which are attributed to the formation of a condensed silica network. However a small peak at 950 cm\(^{-1}\) corresponding to the asymmetric stretching vibrations of -SiOH, suggests that a non-condensed silica is also present.

The introduction of vinyl groups is verified by the presence of double bond (C=C) stretching mode at 1600 cm\(^{-1}\). In order to determine that a higher concentration of vinyl groups was successfully incorporated, the IR spectra of the F-V15-0.5s and F-V35-0.5s samples were depicted in the inset in Fig. 34A. As can be seen from panel A, the inset shows an enlarged portion of the spectra within 1760 and 1540 cm\(^{-1}\). There are two peaks, one at 1620 cm\(^{-1}\) corresponding to the molecularly adsorbed water and the second one at 1600 cm\(^{-1}\) related to double bond originated from vinyl groups. The 1600 cm\(^{-1}\) band for the F-V35-0.5s sample has higher intensity compared to the (F-V15-0.5s) sample having lower concentration of vinyl.
Figure 32. Thermogravimetric weight change (TG) profiles (A) measured in flowing air and the corresponding differential thermogravimetric (DTG) patterns (B) for the selected mesoporous organosilicas with 40 % of vinyl (V) pendant groups: the as-synthesized (F-V40-0.5s-p, dash line) and extracted (F-V40-0.5s, solid line) samples.
Figure 33. Thermogravimetric weight change (TG) profiles (A) measured in flowing air and the corresponding differential thermogravimetric (DTG) patterns (B) for the selected mesoporous organosilicas with 40% of mercaptopropyl (SH) pendant groups: the as-synthesized (F-SH40-0.5s-p, dash line) and extracted (F-SH40-0.5s, solid line) samples.
Table 8. Adsorption parameters determined from argon adsorption isotherms measured at -196 °C for the extracted organosilicas with various vinyl (V) pendant groups obtained under conditions studied (Figures 21-34).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ [m$^2$ g$^{-1}$]</th>
<th>$V_c$ [cm$^3$ g$^{-1}$]</th>
<th>$V_t$ [cm$^3$ g$^{-1}$]</th>
<th>$w_{\text{KJS}}$ [nm]</th>
<th>$w_d$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-2</td>
<td>862</td>
<td>0.28</td>
<td>0.79</td>
<td>10.0</td>
<td>13.47</td>
</tr>
<tr>
<td>F-V10-2</td>
<td>635</td>
<td>0.20</td>
<td>0.63</td>
<td>9.5</td>
<td>13.33</td>
</tr>
<tr>
<td>F-V20-2</td>
<td>483</td>
<td>0.14</td>
<td>0.55</td>
<td>8.2</td>
<td>12.23</td>
</tr>
<tr>
<td>F-V30-2</td>
<td>730</td>
<td>0.12</td>
<td>1.20</td>
<td>7.6</td>
<td>13.16</td>
</tr>
<tr>
<td>F-0.5s</td>
<td>811</td>
<td>0.20</td>
<td>1.10</td>
<td>10.0</td>
<td>13.99</td>
</tr>
<tr>
<td>F-V15-0.5s</td>
<td>849</td>
<td>0.22</td>
<td>1.14</td>
<td>10.4</td>
<td>14.90</td>
</tr>
<tr>
<td>F-V20-0.5s</td>
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<td>0.23</td>
<td>1.12</td>
<td>10.0</td>
<td>11.44</td>
</tr>
<tr>
<td>F-V20-1s</td>
<td>877</td>
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<td>1.10</td>
<td>9.7</td>
<td>11.43</td>
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<tr>
<td>F-V20-1.5s</td>
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<td>0.98</td>
<td>9.9</td>
<td>10.88</td>
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<td>F-V20-2s</td>
<td>589</td>
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<td>8.75</td>
<td>9.66</td>
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<tr>
<td>F-V20-0.5</td>
<td>762</td>
<td>0.22</td>
<td>0.89</td>
<td>9.4</td>
<td>10.52</td>
</tr>
<tr>
<td>F-V30-0.5s</td>
<td>817</td>
<td>0.23</td>
<td>0.99</td>
<td>9.7</td>
<td>10.41</td>
</tr>
<tr>
<td>F-V30-0.5sc</td>
<td>490</td>
<td>0.14</td>
<td>0.47</td>
<td>6.6</td>
<td>-</td>
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<tr>
<td>F-V35-0.5s</td>
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<td>0.22</td>
<td>0.83</td>
<td>8.9</td>
<td>9.50</td>
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<tr>
<td>F-V40-0.5s</td>
<td>823</td>
<td>0.25</td>
<td>0.86</td>
<td>8.4</td>
<td>9.31</td>
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$S_{\text{BET}}$, BET specific surface area; $V_c$, volume of complementary pores (including micropores) of the diameter below 4 nm; $V_t$, single-point pore volume; $w_{\text{KJS}}$, mesopore diameter calculated by the improved KJS method [243]; $w_d$, pore width calculated on the basis of unit cell parameter and pore volumes according to the relations derived for the cubic $Fm\overline{3}m$ (Equation 11) and $P6\overline{3}m$ (Equation 12) structures [248].
Table 9. Adsorption parameters determined from argon adsorption isotherms measured at -196 °C for the extracted organosilicas with various mercaptopropyl (SH) pendant groups obtained under conditions studied (Figures 21-34).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ [m$^2$ g$^{-1}$]</th>
<th>$V_c$ [cm$^3$ g$^{-1}$]</th>
<th>$V_t$ [cm$^3$ g$^{-1}$]</th>
<th>$w_{KJS}$ [nm]</th>
<th>$w_d$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-2</td>
<td>862</td>
<td>0.28</td>
<td>0.79</td>
<td>10.0</td>
<td>13.47</td>
</tr>
<tr>
<td>F-SH10-2</td>
<td>762</td>
<td>0.20</td>
<td>0.89</td>
<td>9.4</td>
<td>9.76</td>
</tr>
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<td>F-SH20-2</td>
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<td>0.89</td>
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<td>9.94</td>
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<tr>
<td>F-0.5s</td>
<td>811</td>
<td>0.2</td>
<td>1.10</td>
<td>10.0</td>
<td>13.99</td>
</tr>
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<td>0.82</td>
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<td>10.74</td>
</tr>
<tr>
<td>F-SH15-0.5s</td>
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<td>0.25</td>
<td>0.76</td>
<td>7.0</td>
<td>8.21</td>
</tr>
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<td>F-SH20-0.5s</td>
<td>497</td>
<td>0.14</td>
<td>0.50</td>
<td>7.5</td>
<td>7.7</td>
</tr>
<tr>
<td>F-SH25-0.5s</td>
<td>365</td>
<td>0.09</td>
<td>0.36</td>
<td>6.6</td>
<td>7.05</td>
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<tr>
<td>F-SH30-0.5s</td>
<td>386</td>
<td>0.10</td>
<td>0.40</td>
<td>6.6</td>
<td>7.22</td>
</tr>
<tr>
<td>F-SH35-0.5s</td>
<td>192</td>
<td>0.03</td>
<td>0.22</td>
<td>5.8</td>
<td>6.2</td>
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<tr>
<td>F-SH40-0.5s</td>
<td>251</td>
<td>0.06</td>
<td>0.26</td>
<td>5.6</td>
<td>6.11</td>
</tr>
</tbody>
</table>

$S_{BET}$, BET specific surface area; $V_c$, volume of complementary pores (including micropores) of the diameter below 4 nm; $V_t$, single-point pore volume; $w_{KJS}$, mesopore diameter calculated by the improved KJS method [243]; $w_d$, pore width calculated on the basis of unit cell parameter and pore volumes according to the relations derived for the cubic $Fm\bar{3}m$ (Equation 11) and $P\bar{6}mm$ (Equation 12) structures [248].
Figure 34. Infrared spectra for mesoporous organosilicas with vinyl (V) pendant groups: a comparison of two extracted samples with 15% (F-V15-0.5s) and 35% (F-V35-0.5s) TEVS loadings (A) as well as extracted (F-V35-0.5s) and as-synthesized (F-V35-0.5s-p) samples containing the same concentration of TEVS (B). (1) Corresponds to free –OH, (2) to double bond (vinyl) C=C stretching at 1600 cm\(^{-1}\), (3) to molecularly absorbed water at 1620 cm\(^{-1}\), (4) to silica network –Si-O-Si- asymmetric stretching, Si-OH mode and (5) to alkyl CH stretches from polymeric template.
The removal of the polymeric template B50-6600 from the mesostructures was also monitored using the FT-IR spectroscopy. Fig. 34B shows a part of the spectra for the polymer-extracted (F-V35-0.5s) and polymer-containing (F-V35-0.5s-p) samples in the region of 3900 and 2400 cm\(^{-1}\). As can be seen from the spectrum of the latter (dotted line), the high-intensity bands present at around 2900 cm\(^{-1}\) are related to the symmetric and asymmetric alkyl stretching vibrations originating from the polymeric template, which are insignificant for the extracted sample (solid line), suggesting almost complete removal of the template.

This study shows that ordered mesoporous organosilicas (OMOs) with vinyl and mercaptopropyl groups can be synthesized by co-condensation of tetraethyl orthosilicate (TEOS) and either triethoxyvinylsilane (TEVS) or 3-mercaptopropyltrimethoxysilane (MPTMS) with addition of sodium chloride under low acidic concentrations in the presence of poly(ethylene oxide)-block-poly(butylene oxide)-block-poly(ethylene oxide) (EO\(_{39}\)BO\(_{47}\)EO\(_{39}\)) triblock copolymer template B50-6600 as a structure-directing agent. A direct evidence of successful incorporation of vinyl and mercaptopropyl groups was provided by the FTIR and elemental analysis. The OMOs samples with 15% of vinyl groups showed a typical large-pore cubic \(Fm\overline{3}m\) structure, whereas at higher molar percentage of vinyl group (>20%), the structure has changed to \(p\overline{6}mm\) symmetry, which was further verified by the SAXS and TEM analysis. The TEM studies revealed that the samples with 15% and 35% of vinyl groups exhibited highly ordered nanoporous structures with \(Fm\overline{3}m\) and \(p\overline{6}mm\) symmetries, respectively. As regards to mercaptopropyl-containing materials, any addition of MPTMS led to the formation of
It is shown that OMOs with vinyl and mercaptopropyl groups can be synthesized using triblock copolymer B50-6600 (EO$_{39}$BO$_{47}$EO$_{39}$), which in the case of pure silica TEOS condensation gives the $Fm3m$ structure but the co-condensation of TEOS with addition of TEVS (>15%) or MPTMS results in the formation of the hexagonal $p6mm$ structure identical with that of SBA-15 templated by poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer Pluronic P123 (EO$_{20}$PO$_{70}$EO$_{20}$).

4.3. CAGE-LIKE OMO CONTAINING IMIDAZOLE PENDANT GROUPS

Fig. 35 shows the XRD patterns for the extracted imidazole-functionalized SBA-16 (A) and FDU-1 (B) organosilicas having gradually increasing concentration of imidazole pendant groups (Scheme 10). As can be seen from Figs. 35A and 35B, all SBA-16 and FDU-1 OMOs show a single distinct reflection at $2\theta$ about 0.85° and 0.8°, respectively. However, for the FDU-1 samples this peak is much broader than that for SBA-16. The XRD spectra for calcined pure SBA-16 and FDU-1 silicas show more reflections than those for the corresponding functionalized silicas. Similarly as in the previous works devoted to SBA-16 [47] and FDU-1 [75], the XRD patterns were assigned according to the cubic $Im3m$ (body-centered packing) (Fig. 35A) and $Fm3m$ (Fig. 35B) (face-centered packing) symmetry, respectively. As can be seen from Fig. 35 the intensity of secondary reflections decrease gradually with increasing imidazole concentration, indicating a decrease in the structural ordering of the samples, which is also confirmed by the shape of nitrogen adsorption-desorption isotherms.
Nitrogen adsorption-desorption isotherms measured at – 196 °C for the SBA-16 and FDU-1 samples studied are shown in Figs. 36A and 36B, respectively. As can be seen from these figures both series of the samples studied exhibit type IV isotherms with apparent hysteresis loops [75], indicating the presence of cage-like mesopores with small openings. For calcined SBA-16 (S-0.5s) and FDU-1 (F-0.5s) silica samples the capillary condensation steps are located at different relative pressures ~0.65 and ~0.80, respectively, indicating a pronounced difference in the diameter of mesopores for these cage-like structures (see Table 10). The cages of FDU-1 are about 4 nm larger than mesopores of SBA-16. In addition to the mesopore diameters, Table 10 contains the BET specific surface area, volume of complementary pores and total pore volume, which were evaluated from adsorption isotherms shown in Fig. 36.

Also, adsorption isotherms for the SBA-16 and FDU-1 silicas exhibit sharp capillary condensation steps, which are generally attributed to the presence of uniform mesopores as evidenced by narrow pore size distributions (PSDs) shown in Figs. 37A and 37B. The maximum of PSD for SBA-16 and FDU-1 samples shifts gradually to lower pore diameter with increasing content of imidazole groups. Moreover, the PSD peaks become less narrow, which is consistent with decreasing sharpness of the capillary condensation step. This is especially observed for the SBA-16 samples, for which the pore diameter decreased substantially from 7 nm (pure silica) to 4.7 nm (S-IM10-0.5s), while for FDU-1 the change in the pore diameter was rather insignificant. The total pore volume and BET specific surface area for the SBA-16 samples were also affected by increasing concentration of imidazole groups; they decreased meaningfully from 0.60 to
0.06 cm$^3$g$^{-1}$ and from 941 to 100 m$^2$g$^{-1}$, respectively. Thus, the sample with the highest content (S-IM10-0.5s) exhibited just small fraction of mesopores (see Fig. 37A), whereas it is not the case for the FDU-1 sample (F-IM20-0.5s).

It suggests that twice as higher amount of imidazole groups can be incorporated to the FDU-1 structure; however it is accompanied by a gradual decrease in the uniformity of cage-like mesopores as well as the uniformity of their entrances. For the FDU-1 samples with high concentration of imidazole groups, e.g., F-IM20-0.5s, the pore openings become less uniform as evidenced by decreasing capillary evaporation branch that closes at the lower pressure limit characteristic for nitrogen at -196 °C. The latter behavior of adsorption hysteresis indicates that the pore opening diameters are below 5 nm [75]. If some applications require pore openings of larger sizes, there is a possibility to enlarge them by synthesizing materials at room temperature and extending duration of their hydrothermal treatment for an appropriate period of time at 100 °C or higher temperature as reported previously for cage-like pure silicas [76]. The same approach can be used for cage-like FDU-1 organosilicas.

Introduction of imidazole ligands into the silica structure was monitored by elemental analysis (see nitrogen content data in Table 11). Although this analysis gave somewhat smaller values than those predicted on the basis of initial gel mixture composition, in general the incorporation of imidazole ligand into this structure was good. A comparison of the N% values listed in Table 11 shows a slightly better incorporation of imidazole ligand into mesopores of FDU-1.
**Scheme 10.** Schematic illustration of interconnected spherical pores (large circle with straight channels) of cage-like mesoporous organosilica containing imidazole surface groups.
Figure 35. Powder X-ray diffraction (XRD) patterns for the extracted cage-like SBA-16 (A) and FDU-1 (B) mesoporous organosilicas containing various concentrations of imidazole (IM) pendant groups.
Figure 36. Nitrogen adsorption-desorption isotherms measured at – 196 °C for extracted cage-like SBA-16 (A) and FDU-1 (B) mesoporous organosilicas containing various concentrations of imidazole (IM) pendant groups. The isotherms for S-IM2.5-0.5s, S-IM5-0.5s, F-0.5s, F-IM5-0.5s, F-IM10-0.5s and F-IM15-0.5s were offset vertically by 95, 30, 900, 600, 400 and 280 cm$^3$ STP g$^{-1}$, respectively.
Figure 37. Pore size distributions (PSDs) calculated according to the KJS method [243] for extracted cage-like SBA-16 (A) and FDU-1 (B) mesoporous organosilicas containing various concentrations of imidazole (IM) pendant groups.
Table 10. Adsorption and structural parameters determined from nitrogen adsorption isotherms measured at -196 °C and powder X-ray diffraction (XRD) for the extracted cage-like SBA-16 and FDU-1 mesoporous organosilicas containing various concentrations of imidazole (IM) pendant groups (Figures 35-39).a

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ [m$^2$ g$^{-1}$]</th>
<th>$V_c$ [cm$^3$ g$^{-1}$]</th>
<th>$V_t$ [cm$^3$ g$^{-1}$]</th>
<th>$w_{KJS}$ [nm]</th>
<th>$w_d$ [nm]</th>
<th>$d$ [nm]</th>
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</thead>
<tbody>
<tr>
<td>S-0.5s</td>
<td>941</td>
<td>0.23</td>
<td>0.60</td>
<td>7.00</td>
<td>10.27</td>
<td>10.6</td>
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<tr>
<td>S-IM2.5-0.5s</td>
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<td>0.27</td>
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<td>7.65</td>
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<td>S-IM5-0.5s</td>
<td>356</td>
<td>0.10</td>
<td>0.22</td>
<td>6.16</td>
<td>7.90</td>
<td>10.3</td>
</tr>
<tr>
<td>S-IM7.5-0.5s</td>
<td>299</td>
<td>0.11</td>
<td>0.16</td>
<td>5.70</td>
<td>6.07</td>
<td>10.3</td>
</tr>
<tr>
<td>S-IM10-0.5s</td>
<td>100</td>
<td>0.05</td>
<td>0.06</td>
<td>4.70</td>
<td>3.57</td>
<td>9.8</td>
</tr>
<tr>
<td>F-0.5s</td>
<td>789</td>
<td>0.23</td>
<td>0.89</td>
<td>10.80</td>
<td>12.47</td>
<td>11.8</td>
</tr>
<tr>
<td>F-IM5-0.5s</td>
<td>711</td>
<td>0.22</td>
<td>0.91</td>
<td>11.29</td>
<td>11.84</td>
<td>11.1</td>
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<tr>
<td>F-IM10-0.5s</td>
<td>549</td>
<td>0.17</td>
<td>0.74</td>
<td>10.36</td>
<td>12.33</td>
<td>11.8</td>
</tr>
<tr>
<td>F-IM15-0.5s</td>
<td>443</td>
<td>0.14</td>
<td>0.53</td>
<td>9.26</td>
<td>10.48</td>
<td>10.7</td>
</tr>
<tr>
<td>F-IM20-0.5s</td>
<td>538</td>
<td>0.17</td>
<td>0.69</td>
<td>9.97</td>
<td>12.74</td>
<td>12.4</td>
</tr>
</tbody>
</table>

a $S_{BET}$, BET specific surface area; $V_c$, volume of complementary pores calculated from PSD by integration between 0 and 4 nm; $V_t$, single-point pore volume; $w_{KJS}$, mesopore cage diameter calculated by the KJS method [243]; $w_d$, pore width calculated on the basis of unit cell parameter and pore volumes according to the relations derived for the cubic Im$\bar{3}$m (Equation 13) structure [248]; $d$, interplanar spacing obtained on the basis of SAXS pattern corresponding to the first Bragg’s reflection.
Table 11. Molar composition in the synthesis gels used and the subsequent elemental analysis data for cage-like SBA-16 and FDU-1 mesoporous organosilicas containing various concentrations of imidazole (IM) pendant groups (Figures 35-39).\(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthesis gel mixture</th>
<th>Elemental analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(n_{\text{TEOS}}) [mmol]</td>
<td>(n_{\text{IM}}) [mmol]</td>
</tr>
<tr>
<td>S-0.5s</td>
<td>40.3</td>
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<tr>
<td>S-IM2.5-0.5s</td>
<td>39.3</td>
<td>1.0</td>
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<td>S-IM5-0.5s</td>
<td>38.3</td>
<td>2.0</td>
</tr>
<tr>
<td>S-IM7.5-0.5s</td>
<td>37.3</td>
<td>3.0</td>
</tr>
<tr>
<td>S-IM10-0.5s</td>
<td>36.3</td>
<td>4.0</td>
</tr>
<tr>
<td>F-0.5s</td>
<td>19.9</td>
<td>0.0</td>
</tr>
<tr>
<td>F-IM5-0.5s</td>
<td>19.4</td>
<td>0.5</td>
</tr>
<tr>
<td>F-IM10-0.5s</td>
<td>18.9</td>
<td>1.0</td>
</tr>
<tr>
<td>F-IM15-0.5s</td>
<td>18.4</td>
<td>1.5</td>
</tr>
<tr>
<td>F-IM20-0.5s</td>
<td>17.9</td>
<td>2.0</td>
</tr>
</tbody>
</table>

\(^a\) \(n_{\text{TEOS}}\), number of moles of TEOS; \(n_{\text{IM}}\), number of moles of N-(3-triethoxysilylpropyl)-4,5-dihydro-imidazole; \(C_{\text{IM}^*}\), concentration of imidazole groups predicted on the basis of \(\%N^*\) in the synthesis gel mixture; \(C_{\text{IM}}\), concentration of imidazole groups in the resulting material calculated on the basis of \(\%N\) obtained by elemental analysis; \(\%N\), nitrogen percentage.
As shown in Fig. 38 the incorporation of imidazole ligands into SBA-16 (Fig. 38A) and FDU-1 (Fig. 38B) was monitored by high resolution thermogravimetry (TG) measurements carried out in flowing nitrogen for as-synthesized (S-IM5-0.5s-p and F-IM10-0.5s-p) and extracted (S-IM5-0.5s and F-IM10-0.5s). In general, the observed weight loss in the range of 35 to 150 °C is referred to the evaporation of adsorbed water, whereas the next temperature range is related to thermodesorption of triblock copolymer template and degradation of imidazole groups. Thermogravimetric events reflecting the removal of polymeric template and imidazole groups partially overlap in the range of 200 to 600 °C. Thus, a more detailed analysis of these profiles is difficult.

A qualitative identification of successful incorporation of the organic groups into the mesostructures studied was confirmed by FT-IR spectroscopy. Fig. 39 illustrates the FT-IR spectra of the polymer-free mesostructured organosilicas with imidazole pendant ligands. FT-IR spectrum is presented in the range from 4000 and 550 cm\(^{-1}\). The spectrum exhibits characteristic bands (*) attributed to the formation of a condensed silica network at around 1060 cm\(^{-1}\) and 790 cm\(^{-1}\), which relate to asymmetric and symmetric vibrations of Si-O-Si, respectively. A weak absorbance (●) at around 950 cm\(^{-1}\) is typical of non-condensed silica resulting from the asymmetric Si-O stretching mode of Si-O-H group. All spectra exhibit two other bands at about 3200-3500 cm\(^{-1}\) (+) and 1620 cm\(^{-1}\) corresponding to hydrogen-bonded O-H stretching vibrations from silanols and the bending mode of molecularly adsorbed water, respectively. Moreover, the spectrum shows absorbances in the 2900-3000 cm\(^{-1}\) and 1450 cm\(^{-1}\) regions assigned to the asymmetric stretching and bending C-H vibrations, respectively.
Figure 38. Thermogravimetric weight change (TG) profiles measured in flowing nitrogen and the corresponding differential thermogravimetric (DTG) patterns for cage-like SBA-16 (A) and FDU-1 (B) mesoporous organosilica containing various concentrations of imidazole (IM) pendant groups: as-synthesized (S-IM5-0.5s-p and F-IM10-0.5s-p) and extracted (S-IM5-0.5s and F-IM10-0.5s).
Figure 39. Infrared spectra of the extracted cage-like FDU-1 mesoporous organosilica containing imidazole (IM) pendant groups (F-IM15-0.5s) with an inset for the azomethine group (N=C). Symbols; (+) – refers to hydrogen bonded O-H stretching bands from silanols and surface adsorbed water, (*) – refers to silica network Si-O-Si asymmetric stretching and (●) - represents a Si-OH band.
The presence of these bands confirms CH groups in imidazole ligand. The presence of imidazole groups in the pores of OMS-IM is more clearly evidenced by C=N stretch at 1650 cm\(^{-1}\) (see inset) [170].

4.4. CAGE-LIKE OMO CONTAINING UREIDOPROPYL AND BIFUNCTIONAL UREIDOPROPYL WITH MERCAPTOPROPYL PENDANT GROUPS

The amounts of incorporated organic pendant groups into SBA-16 and FDU-1 mesostructure with single ureidopropyl and bifunctional ureidopropyl and mercaptopropyl ligands were estimated on the basis of elemental analysis data (Table 12). The nitrogen and sulfur contents obtained for the resulting OMOs by elemental analysis represent around 50-85% of the values estimated on the basis of the initial molar composition of the synthesis gel mixture, indicating quite good incorporation efficiency.

Structural characterization of the extracted SBA-16 and FDU-1 organosilicas containing single ureidopropyl surface groups and two different pendant groups: ureidopropyl and mercaptopropyl was performed on the basis of the X-ray diffraction patterns shown in Figs. 40 and 41, respectively. The unit cell parameters for the samples studied are summarized in Table 13.

As can be seen from Figs. 40A and 41A, the diffraction profiles for the extracted SBA-16 organosilicas containing single and double groups exhibit one sharp reflection at \(2\theta \sim 0.8\) indexed as (110) and two minor reflections (200) and (211); these patterns resemble that for a purely siliceous SBA-16 (\(Im\text{3}m\) symmetry group) [47]. The XRD study shows that an increase in the concentration of groups slightly change the XRD
profiles, which is manifested by a reduction of the minor peak intensities suggesting a gradual deterioration of the mesostructural ordering. In all cases the major peaks showed a tendency to shift towards higher values of 20 angles suggesting a slight decrease in the unit cell (Table 13). As can be seen from Figs. 40B and 41B, the diffraction patterns for extracted functionalized FDU-1 materials exhibit a strong reflection and some less-resolved minor reflections. The XRD profiles for these samples were assigned according to the cubic \( Fm\bar{3}m \) symmetry group (body-centered-packing). The major and minor peaks show a tendency to decrease with increasing concentration of introduced organic groups in FDU-1. For instance, a high concentration of groups caused a significant reduction in the intensity of major and minor XRD peaks in comparison to those samples with small amounts. This change in the XRD profile suggests visible structure deterioration in the samples with higher concentrations of ligands.

Nitrogen adsorption-desorption isotherms measured at -196 °C for extracted SBA-16 (Panel A) and FDU-1 (Panel B) organosilicas containing different amounts of ureidopropyl and ureidopropyl-mercaptopropyl pendant groups are shown in Fig. 42 and 43, respectively. These isotherms were used to evaluate the following adsorption parameters: the BET specific surface area, single-point pore volume and mesopore cage diameter, which are listed in Table 13. Both SBA-16 (Panel A) and FDU-1 (Panel B) organosilicas with ureidopropyl and bifunctional samples with the smallest concentration of these groups exhibit type IV adsorption-desorption isotherms with sharp capillary/evaporation steps and pronounced H2 hysteresis loops.
Table 12. Molar composition in the synthesis gels used and the subsequent elemental analysis data for extracted cage-like SBA-16 and FDU-1 mesoporous organosilicas containing various concentrations of ureidopropyl (U) pendant groups and bifunctional ureidopropyl (U) and mercaptopropyl (SH) pendant groups (Figures 40-46).\(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthesis gel composition</th>
<th>Elemental analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(n_{\text{TEOS}}) [mmol]</td>
<td>(n_{\text{organosilane}}) [mmol]</td>
</tr>
<tr>
<td>S-U5-0.5s</td>
<td>19.15</td>
<td>1.01</td>
</tr>
<tr>
<td>S-U10-0.5s</td>
<td>18.14</td>
<td>2.02</td>
</tr>
<tr>
<td>S-U15-0.5s</td>
<td>17.14</td>
<td>3.02</td>
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<tr>
<td>F-U5-0.5s</td>
<td>9.46</td>
<td>0.50</td>
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<td>F-U10-0.5s</td>
<td>8.97</td>
<td>1.00</td>
</tr>
<tr>
<td>F-U15-0.5s</td>
<td>8.47</td>
<td>1.49</td>
</tr>
<tr>
<td>F-U20-0.5s</td>
<td>8.00</td>
<td>1.99</td>
</tr>
<tr>
<td>S-U5SH5-0.5s</td>
<td>18.14</td>
<td>1.01 - (1.01)</td>
</tr>
<tr>
<td>S-U5SH10-0.5s</td>
<td>17.14</td>
<td>1.01 - (2.02)</td>
</tr>
<tr>
<td>S-U5SH15-0.5s</td>
<td>16.13</td>
<td>1.01 - (3.02)</td>
</tr>
<tr>
<td>F-U5SH2.5-0.5s</td>
<td>9.21</td>
<td>0.5 - (0.25)</td>
</tr>
<tr>
<td>F-U5SH5-0.5s</td>
<td>8.96</td>
<td>0.5 - (0.5)</td>
</tr>
<tr>
<td>F-U5SH10-0.5s</td>
<td>8.47</td>
<td>0.5 - (1.0)</td>
</tr>
<tr>
<td>F-U5SH15-0.5s</td>
<td>7.97</td>
<td>0.5 - (1.5)</td>
</tr>
</tbody>
</table>

\(^a\) \(n_{\text{TEOS}}\), number of mmoles of TEOS; \(n_{\text{organosilane}}\), number of mmoles of ureidopropyltrimethoxysilane or 3-mercaptopropylsilane in brackets; %S and %N, sulfur and nitrogen weight percentages obtained from elemental analysis.
Figure 40. Powder X-ray diffraction (XRD) patterns for the extracted cage-like SBA-16 (A) and FDU-1 (B) mesoporous organosilicas containing various concentrations of ureidopropyl (U) pendant groups.
Figure 41. Powder X-ray diffraction (XRD) patterns for the extracted bifunctional SBA-16 (A) and FDU-1 (B) mesoporous organosilicas containing ureidopropyl (U) and various concentrations of mercaptopropyl (SH) pendant groups.
The condensation steps start at a relative pressure of about 0.6 and 0.7 for SBA-16 and FDU-1, whereas the evaporation steps end suddenly at about 0.45, which is typical for mesoporous materials containing cage-like pores and narrow PSDs (see PSDs in Figs. 44 and 45). The value of relative pressure at which capillary evaporation takes place can be used to evaluate the size of pore openings. However, for the samples studied the hysteresis loops close at the limiting pressure value for nitrogen at -196 °C, i.e., at relative pressure of about 0.45.

As can be seen from adsorption isotherms in Fig. 43 and PSDs in Fig. 45, an increase in the concentration of organic groups reduces the steepness of the evaporation steps for bifunctional organosilicas, which is not the case for single ureidopropyl containing SBA-16 materials. This example illustrates that the structural properties of cage-like materials are quite sensitive on the type of pendant groups as well as their concentration. For instance, an increase in the concentration of U-SH groups shifts the position of capillary condensation step towards lower values of relative pressure indicating a gradual reduction in the mesopore size (see PSDs in Figs. 44 and 45).

As can been seen from Figs. 42 B and 44B and, ureidopropyl-containing FDU-1 OMOs exhibit not only narrow PSDs but also uniform pore entrances, even for the sample with highest concentration of the surface ligand. This is not the case for bifunctional silicas (Figs. 45B), which possess narrow PSDs and uniform pore openings for the first two samples (F-U5SH2.5-0.5s and F-U5SH5-0.5s), whereas OMOs with higher ligand concentrations show non-uniform pore entrance sizes as evidenced by two-
step capillary evaporation. As can be seen from Table 13 the BET surface area and total pore volume gradually decrease with increasing amount of organic groups. Moreover, the pore size calculated according to the KJS method [243] shows the same trend and decreases slightly from 11.6 to 9.3 nm for the U organosilicas; however in the case of U-SH organosilicas this change is more substantial. It is worth to mention that PSDs shown in Figs. 44 and 45 were obtained by using the KJS method [243] calibrated on the basis of adsorption data for channel-like mesopores with diameter between 2 and 6.5 nm. Since this calibration was done using MCM-41 materials with cylindrical pores, this method leads to the underestimation of the diameter of cage-like mesopores by about 2 nm. Therefore, Table 13 lists also the pore diameters calculated using geometrical relation between the pore volumes and the unit cell derived for cubic $Im3m$ and $Fm3m$ symmetry groups [248].

Adsorption parameters such as the BET surface area and single-point pore volume for the organosilica samples decrease with increasing concentration of organic groups, except the S-U-5-0.5s sample, which possesses some residue of the template. As can be seen from PSDs in Figs. 44A and 45A, all functionalized silicas show larger volumes of complementary pores in relation to the volume of ordered pores, which can be calculated by subtracting the former from the total pore volume (see Table 13). It is interesting to notice that the relation between the volumes of complementary and ordered pores in FDU-1 is opposite; therefore for this material the volume of ordered mesopores is larger.
Figure 42. Nitrogen adsorption isotherms measured at -196 °C for the extracted cage-like SBA-16 (A) and FDU-1 (B) mesoporous organosilicas containing various concentrations of ureidopropyl (U) pendant groups. The isotherms for S-U5-0.5s and S-U10-0.5s were offset vertically by 165 and 90 cm³ STP g⁻¹, respectively.
Figure 43. Nitrogen adsorption isotherms measured at -196 °C for the extracted bifunctional cage-like SBA-16 (A) and FDU-1 (B) mesoporous organosilicas containing ureidopropyl (U) and various concentrations of mercaptopropyl (SH) pendant groups. The isotherm for S-U5SH5-0.5s was offset vertically by 50 cm$^3$ STP g$^{-1}$. 
**Figure 44.** Pore size distributions (PSDs) calculated according to the KJS method [243] for the extracted cage-like SBA-16 (A) and FDU-1 (B) mesoporous organosilicas containing various concentrations of ureidopropyl (U) pendant groups.
Figure 45. Pore size distributions calculated according to the KJS method [243] for extracted bifunctional cage-like SBA-16 (A) and FDU-1 (B) mesoporous organosilicas containing ureidopropyl (U) and various concentrations of mercaptopropyl (SH) pendant groups.
FTIR spectrum of ureidopropyl-mercaptopropyl FDU-1 sample is shown in Fig. 46. Similarly to OMO containing imidazole pendant group, the FTIR spectrum of bifunctional material exhibits similar sets of bands characteristic to siliceous structure. The vibration at 1650 cm\(^{-1}\) is attributed to the carbonyl (C=O) stretching band from \(-\text{NHCONH}_2\). The relatively low frequency for this carbonyl stretch is characteristic for an amidal type carbonyl. The stretching vibrations of NH\(_2\) in the 3380-3280 cm\(^{-1}\) region cannot be separately detected because of the overlap with a broad peak of hydrogen bonded OH stretching bands from silanols and surface adsorbed water. However an N-H bending absorbance is detected at 1550 cm\(^{-1}\) [168]. As regards to mercaptopropyl surface groups, the expected S-H stretching vibration at about 2500 cm\(^{-1}\) could not be detected. However, the presence of C-H vibrations and elemental analysis of sulfur (1.4 %) confirms mercaptopropyl groups on the pore walls of this mesoporous silica.

The TG patterns and the corresponding differential TG (DTG) profiles for SBA-16 organosilicas with ureidopropyl and ureidopropyl-mercaptopropyl pendant groups recorded under nitrogen atmosphere are displayed in Figs. 47 and 48, respectively. The TG study shows that the extraction of the block copolymer F127 template from cage-like SBA-16 organosilicas with acidified ethanol solution was incomplete. This is especially visible on the DTG curve for the first sample (S-U5-0.5s) in the series of organosilicas containing ureidopropyl groups when compared with the corresponding DTG curve for the template-containing S-U5-0.5s-p sample (see Fig. 47B). As can be seen from this figure the thermogravimetric event at \(-400\) °C for the extracted S-U5-0.5s sample, which is related to the decomposition of the F127 template, is still quite visible; it is possible
that this sample has smaller pore openings. For the remaining ureidopropyl samples the extraction process was much better. However, it should be noted that the removal of polymeric templates from cage-like mesostructures is more difficult than in the case of channel-like mesostructures, especially when the cage openings in the former structures are small and the attached surface groups are relatively large.

In summary, two cubic cage-like mesoporous organosilicas, SBA-16 (Im3m) and FDU-1 (Fm3m), with different concentrations of imidazole, ureidopropyl and bifunctional ureidopropyl and mercaptopropyl pendant groups were synthesized by co-condensation of tetraethoxy orthosilicate and appropriate organosilane precursors, in the presence of poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethyleneoxide) (EO_{106}PO_{70}EO_{106}) and poly(ethylene oxide)-block-poly(butylene oxide)-block-poly(ethylene oxide) (EO_{39}BO_{47}EO_{39}) triblock copolymers, respectively, under low acidic conditions and with addition of sodium chloride. The polymeric templates used were removed via extraction with acidified ethanolic solution. The amount of incorporated pendant groups gradually increased with increasing concentration organosilane precursors in the synthesis gel. This incorporation was slightly better for FDU-1, which has larger mesopores and mesopore entrances than those in SBA-16. The interplanar d-spacing, total pore volume, pore diameter and specific surface area tended to systematically decrease with increasing loadings of organic ligands. This work reveals that an enlargement of pore openings in the cage-like organosilicas studied can be achieved by controlling time of their hydrothermal treatment.
Table 13. Adsorption and structural parameters determined from nitrogen adsorption isotherms measured at -196 °C and powder X-ray diffraction (XRD) for the extracted cage-like SBA-16 and FDU-1 mesoporous organosilicas containing various concentrations of ureidopropyl (U) pendant groups and bifunctional ureidopropyl (U) and mercaptopropyl (SH) pendant groups (Figures 40-46).a

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ [m$^2$ g$^{-1}$]</th>
<th>$V_c$ [cm$^3$ g$^{-1}$]</th>
<th>$V_t$ [cm$^3$ g$^{-1}$]</th>
<th>$w_{KJS}$ [nm]</th>
<th>$w_d$ [nm]</th>
<th>$a$ [nm]</th>
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<tbody>
<tr>
<td>S-U5-0.5s</td>
<td>494</td>
<td>0.18</td>
<td>0.32</td>
<td>6.5</td>
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<td>14.8</td>
</tr>
<tr>
<td>S-U10-0.5s</td>
<td>613</td>
<td>0.23</td>
<td>0.41</td>
<td>6.8</td>
<td>8.4</td>
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<tr>
<td>S-U15-0.5s</td>
<td>553</td>
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<td>0.38</td>
<td>6.7</td>
<td>8.5</td>
<td>14.7</td>
</tr>
<tr>
<td>F-U5-0.5s</td>
<td>890</td>
<td>0.23</td>
<td>1.07</td>
<td>11.6</td>
<td>14.3</td>
<td>22.5</td>
</tr>
<tr>
<td>F-U10-0.5s</td>
<td>658</td>
<td>0.16</td>
<td>0.82</td>
<td>11.2</td>
<td>12.9</td>
<td>20.8</td>
</tr>
<tr>
<td>F-U15-0.5s</td>
<td>505</td>
<td>0.13</td>
<td>0.62</td>
<td>10.8</td>
<td>12.9</td>
<td>21.8</td>
</tr>
<tr>
<td>F-U20-0.5s</td>
<td>437</td>
<td>0.10</td>
<td>0.51</td>
<td>9.3</td>
<td>12.3</td>
<td>21.3</td>
</tr>
<tr>
<td>S-U5SH5-0.5s</td>
<td>360</td>
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<td>0.24</td>
<td>5.7</td>
<td>7.2</td>
<td>14.3</td>
</tr>
<tr>
<td>S-U5SH10-0.5s</td>
<td>357</td>
<td>0.09</td>
<td>0.20</td>
<td>4.7</td>
<td>7.0</td>
<td>13.2</td>
</tr>
<tr>
<td>S-U5SH15-0.5s</td>
<td>225</td>
<td>0.07</td>
<td>0.14</td>
<td>3.6</td>
<td>6.1</td>
<td>13.0</td>
</tr>
<tr>
<td>F-U5SH2.5-0.5s</td>
<td>668</td>
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<td>0.80</td>
<td>10.9</td>
<td>11.5</td>
<td>18.7</td>
</tr>
<tr>
<td>F-U5SH5-0.5s</td>
<td>521</td>
<td>0.15</td>
<td>0.53</td>
<td>9.0</td>
<td>9.7</td>
<td>17.3</td>
</tr>
<tr>
<td>F-U5SH10-0.5s</td>
<td>658</td>
<td>0.20</td>
<td>0.62</td>
<td>8.20</td>
<td>9.7</td>
<td>17.1</td>
</tr>
<tr>
<td>F-U5SH15-0.5s</td>
<td>302</td>
<td>0.09</td>
<td>0.27</td>
<td>6.5</td>
<td>7.9</td>
<td>16.4</td>
</tr>
</tbody>
</table>

a $S_{BET}$, BET specific surface area; $V_c$, volume of complementary pores calculated from PSD by integration between 0 and 4 nm; $V_t$, single-point pore volume; $w_{KJS}$, mesopore cage diameter calculated by the KJS method [243]; $w_d$, pore width calculated on the basis of unit cell parameter and pore volumes according to the relations derived for the cubic $Im3m$ (Equation 13) and $Fm3m$ (Equation 11) structure [248] for SBA-16 and FDU-1 materials, respectively; $a$, unit cell parameter calculated on the basis of the first reflection of SAXS pattern.
Figure 46. Infrared spectra of the extracted bifunctional cage-like mesoporous organosilica containing ureidopropyl (U) and mercaptopropyl (SH) pendant groups, whereas the insets present the enlargement of spectra in the carbonyl (C=O) stretching and CH bending regions between 1400 and 1800 cm⁻¹. Symbols; (+) – refers to hydrogen bonded O-H stretching bands from silanols and surface adsorbed water, (*) – refers to silica network Si-O-Si asymmetric stretching and (●) - represents a Si-OH band.
Figure 47. High-resolution thermogravimetric (TG) profiles (A) and the corresponding DTG profiles (B) recorded in flowing nitrogen for cage-like SBA-16 mesoporous organosilicas containing various concentrations of ureidopropyl (U) pendant groups.
Figure 48. High-resolution thermogravimetric (TG) profiles (A) and the corresponding DTG profiles (B) recorded in flowing nitrogen for bifunctional cage-like SBA-16 mesoporous organosilicas containing ureidopropyl (U) and mercaptopropyl (SH) pendant groups.
V. ORDERED SILICEOUS MESOSTRUCTURES WITH ORGANIC BRIDGING GROUPS*

An introduction of heterocyclic bridging groups into cubic SBA-16 and FDU-1 mesostructures represents a major challenge due to the large bulky size of the moiety and complex 3D network of spherical cage-like pores. Therefore, the aim of this work was to improve the synthesis of periodic mesoporous organosilicas containing bulky bridging groups in the framework. Moreover, the template removal is a challenging task because of the presence of bridging groups and high curvature of these mesostructures. Thus, the latter issue will be discussed. The periodic mesoporous isocyanurate-organosilicas were carefully investigated by SAXS, argon and nitrogen adsorption, FTIR, high resolution TG and elemental analysis.

5.1. EXPERIMENTAL

Synthesis of FDU-1 organosilica with bulky isocyanurate bridging groups

A large mesopore isocyanurate-containing FDU-1 organosilica was prepared in aqueous solution using poly(ethylene oxide)-block-poly(butylene oxide)-block-poly(ethylene oxide) triblock copolymer B50-6600 (EO\textsubscript{39}BO\textsubscript{47}EO\textsubscript{39}) as a structure-directing agent at 0.5M and 2M HCl acidic conditions after a slight modification of the

This Chapter is based on the following publications:

procedure reported by Yu et al. [74]. In a typical synthesis, 2 g of B50-6600 was dissolved in 120 ml of 0.5 M or 2M HCl. After addition of TEOS, the resulting slurry was prehydrolyzed (15 minutes), and then slowly tris[3-(trimethoxysilyl)propyl] isocyanurate (ICS) was added to the solution (see experimental details given in subsequent chapter). The resulting mixture was stirred at room temperature for 6 h and then transferred into a polypropylene bottle and hydrothermally treated at 100 °C under static conditions for another 6 h. The solid product was collected by filtration and dried. The template from as-made samples was removed by extraction (20 ml concentrated H$_2$SO$_4$ and 100 ml EtOH) followed by heat treatment in flowing nitrogen at 360 °C with a 3 °/min heating rate for 4 h or in flowing air at temperatures within 200-300 °C. The isocyanurate-containing silicas are designated as F-ICSx-eTy, where x, e, T and y refer to the extracted (e) sample number (a, b, c) with the specified ICS molar ratio, temperature of heat treatment and type of flowing gas (A for air and N for nitrogen), respectively. The c symbol refers to calcination. The lack of e symbol refers to as-synthesized sample. Therefore, F-ICSb-ec200A denotes a partially extracted sample containing the ICS molar ratio of 0.077 and further thermally treated at 200 °C in air.

**Synthesis of SBA-16 organosilica with bulky isocyanurate bridging groups**

The synthesis of SBA-16-type OMOs with ICS bridging groups (Scheme 11) was analogous as in ref. [217]; 2 g of polymer F127 and 7.05 g NaCl were dissolved in 20 ml of 2M HCl and of 60 ml DW to form a clear F127-NaCl-HCl-DW mixture. The specified amount of TEOS and ICS were added to the polymer-containing solution under vigorous stirring to synthesize samples (see experimental details given in subsequent chapter).
Scheme 11. Schematic illustration of the SBA-16-type PMO with large heterocyclic isocyanurate bridging groups. White triangles represent tris[3-(trimethoxysilyl)propyl] isocyanurate bridging groups incorporated into the silica framework.
The mixture was further stirred for 20 h at 40 °C and subjected for a hydrothermal treatment for 24 h at 100 °C. The product was filtered, washed with DW and dried at 70 °C in the oven. The template-containing samples were extracted twice with 20 ml of H$_2$SO$_4$ and 100 ml of 95 % EtOH at 70 °C followed by calcination at 315 °C in nitrogen to remove the remaining polymer. Also, these samples were calcined at 550 °C in air for 4 h to fully remove organics. The isocyanurate-containing SBA-16 samples are denoted as S-ICSx-eTy, where x refers to the samples having the specific mole fraction of ICS; e refers to the extracted samples, T denotes the temperature of heat treatment, y refers to flowing nitrogen (N) or air (A). Samples S-ICSd-p and S-ICSf-p are designated to the polymer-containing ICS OMOs. The lack of e symbol refers to the samples subjected to the calcination only without prior extraction. In general, all isocyanurate-containing samples are referred as ICS-OMOs.

**Synthesis of bifunctional SBA-16 organosilica with isocyanurate and ethane bridging groups**

The preparation of bifunctional PMOs containing isocyanurate and ethane bridging groups was performed analogously to the procedure reported by Qiu et al [217] (Schemes 12 and 13). In a typical synthesis, 10.5 ml of DW, 4.5 ml of 2M HCl was mixed with 0.75 g of polymer F127 and 1.764 g of NaCl and stirred at 40 °C for 2h to form a clear solution. A specified volume of BTESE was transferred to a solution containing 12.5 ml of DW and 30 ml of 2M HCl at 40 °C. The P123-DW-HCl-NaCl solution was then slowly added to the BTESE-DW-HCl mixture under vigorous stirring.
Scheme 12. Chart illustrating the synthesis procedure for cage-like mesoporous SBA-16 organosilica containing ethane and isocyanurate bridging groups.
Scheme 13. Schematic illustration of the cage-like OMO with bulky heterocyclic bridging groups (left image) and bifunctional PMO containing isocyanurate and ethane bridging groups (right image). Dark triangles and black squares represent isocyanurate and ethane bridging groups incorporated into the silica framework, respectively.
and then after 15 minutes ICS was pipetted to achieve the desired molar composition of both silanes. After further stirring for 20 h at 40°C, the resulting slurry was subsequently heated at 100°C for 24 h. The product was filtered, washed with DW, and dried in the oven at 80 °C and extracted. The extracted ethane-isocyanurate PMOs with various loadings of isocyanurate groups (see experimental details given in subsequent chapter) are designated as S-E-e, S-EICSa-e, S-EICSb-e and SEICSc-e (where E and EICS refer to ethane and ethane-isocyanurate PMOs with different concentrations of ICS denoted a, b, c; e - refers to the extracted samples), whereas extracted and heated materials at 315 °C in nitrogen are denoted as S-E-ec315N, S-EICSa-ec315N, S-EICSb-ec315N and S-EICSc-ec315N. S-E-p, S-EICSa-p, S-EICSb-p and S-EICSc-p denote the polymer-containing ethane-isocyanurate-containing PMOs. In contrast to ICS-OMOs, all ethane-isocyanurate-containing PMOs are referred as E-ICS-PMOs.

5.2. CAGE-LIKE FDU-1 PMO CONTAINING BULKY HETEROCYCLIC ISOCYANURATE BRIDGING GROUPS

Effect of calcination on the FDU-1 PMO structure

Fig. 49 illustrates the powder X-ray diffraction profiles of the extracted (F-ICSb-ec200A, F-ICSb-ec250A) and as-synthesized (F-ICSb-c200A, F-ICSb-c250A, F-ICSb-c300A) isocyanurate-containing FDU-1 organosilicas with 0.077 molar ratio of ICS (ICS/ICS+TEOS), which were calcined between 200 and 300 °C in flowing air. As can be seen from the Fig. 49, each XRD pattern shows one major (110) peak and two minor peaks, which were assigned as (220) and (321). The patterns are analogous to the pure
Figure 49. Powder X-ray diffraction (XRD) for the extracted and as-synthesized cage-like FDU-1 mesoporous organosilicas containing heterocyclic isocyanurate bridging groups (0.077 molar ratio) calcined in flowing air between 200-300 °C.
Figure 50. Argon adsorption-desorption isotherms measured at – 196 °C for the extracted and as-synthesized cage-like FDU-1 mesoporous organosilicas containing heterocyclic isocyanurate bridging groups (0.077 molar ratio) subjected to calcination in flowing air between 200-300 °C. The isotherms for F-ICSb-c250A, F-ICSb-c300A, F-ICSb-ec200A and F-ICSb-ec250A were offset by 120, 280, 520 and 720 cm³ STP g⁻¹.
Figure 51. Pore size distributions (PSDs) calculated according to the KJS method [243] for the extracted and as-synthesized cage-like FDU-1 mesoporous organosilicas containing heterocyclic isocyanurate bridging groups (F-ICSb) calcined in flowing air between 200-300 °C. The PSDs for F-ICSb-c250A, F-ICSb-c300A, F-ICSb-ec200A and F-ICSb-ec250A were offset by 0.05, 0.11, 0.18, 0.24 cm$^3$ g$^{-1}$ nm$^{-1}$. 
siliceous SBA-16 [47], indicating that the ICS-silica possesses a body-centered cubic structure \((Im3m)\). Usually pure siliceous materials synthesized without addition of ICS at these conditions possess a face-centered cubic \((Fm3m)\) structure [75]. Therefore, it is believed that the ICS molecule induces smaller curvature because of its bulky size. It is noteworthy that the ICS has three propyl chains connecting three silicon atoms with isocyanurate heterocyclic ring. The unit cell values calculated for the (110) diffraction are summarized in Table 14. The diffraction peaks are gradually shifted toward larger 2\(\theta\) angles due to the structural shrinkage of unit cell induced at high temperatures. Nevertheless, the XRD patterns are similar to each other regardless of calcination temperature. Therefore, it can be concluded that the crystallographic ordering of mesopores is retained under heat treatment.

The preservation of structural ordering during calcination was further confirmed by argon measurements. Ar adsorption-desorption isotherms (Fig. 50) show type IV adsorption isotherms with well-defined hysteresis loops characteristic for mesoporous solids with narrow constrictions [75]. Analysis of Ar isotherms is summarized in Table 14. The data indicate that the calcination of extracted and as-synthesized samples in air in the range of 200 - 300 °C lead to small changes in the adsorption properties due to freed space after decomposition of the template. Therefore, the BET surface area and pore volume progressively increased with increasing temperature, whereas the pore size was slowly decreasing because of the pore structure shrinkage (see PSDs shown in Fig. 51).
Table 14. Structural parameters determined from nitrogen adsorption isotherms measured at -196 °C, small angle X-ray scattering (SAXS) and high-resolution thermogravimetric analysis (TG) for the cage-like SBA-16 mesoporous organosilicas with heterocyclic isocyanurate bridging groups (Figures 47-57).a

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}}) [m(^2) g(^{-1})]</th>
<th>(V_c) [cm(^3) g(^{-1})]</th>
<th>(V_t) [cm(^3) g(^{-1})]</th>
<th>(w_{\text{KJS}}) [nm]</th>
<th>(w_d) [nm]</th>
<th>(a) [nm]</th>
</tr>
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<tbody>
<tr>
<td>F-ICSa-e</td>
<td>413</td>
<td>0.11</td>
<td>0.43</td>
<td>9.6</td>
<td>13.8</td>
<td>14.16</td>
</tr>
<tr>
<td>F-ICSa-ec360N</td>
<td>632</td>
<td>0.20</td>
<td>0.58</td>
<td>9.3</td>
<td>13.3</td>
<td>13.53</td>
</tr>
<tr>
<td>F-ICSb-c200A</td>
<td>440</td>
<td>0.13</td>
<td>0.41</td>
<td>9.1</td>
<td>10.9</td>
<td>11.61</td>
</tr>
<tr>
<td>F-ICSb-c250A</td>
<td>600</td>
<td>0.20</td>
<td>0.52</td>
<td>9.0</td>
<td>10.7</td>
<td>11.35</td>
</tr>
<tr>
<td>F-ICSb-c300A</td>
<td>703</td>
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<td>0.57</td>
<td>8.9</td>
<td>10.4</td>
<td>11.04</td>
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<td>F-ICSb-e</td>
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<td>10.5</td>
<td>14.16</td>
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<td>0.53</td>
<td>9.0</td>
<td>10.9</td>
<td>11.30</td>
</tr>
<tr>
<td>F-ICSb-ec360N</td>
<td>677</td>
<td>0.23</td>
<td>0.58</td>
<td>9.1</td>
<td>12.8</td>
<td>13.38</td>
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<tr>
<td>F-ICSc-e</td>
<td>291</td>
<td>0.08</td>
<td>0.34</td>
<td>10.5</td>
<td>14.3</td>
<td>15.20</td>
</tr>
<tr>
<td>F-ICSc-e360N</td>
<td>434</td>
<td>0.13</td>
<td>0.45</td>
<td>9.8</td>
<td>13.8</td>
<td>14.30</td>
</tr>
</tbody>
</table>

\(S_{\text{BET}}\), BET specific surface area; \(V_c\), volume of micropores calculated from PSD, including the volume of interconnecting pores, if the latter are of diameter below about 4 nm; \(V_t\), single-point pore volume; \(w_{\text{KJS}}\), mesopore diameter calculated by the KJS method [243]; \(a\), unit cell parameter calculated from the first observed characteristic Bragg’s reflection.
Figure 52. Thermogravimetric weight change (TG) profiles (A) and the corresponding differential thermogravimetric (DTG) patterns (B) measured in flowing nitrogen for the cage-like FDU-1 mesoporous organosilicas containing heterocyclic isocyanurate bridging groups (0.077 molar ratio): as-synthesized (F-ICSb-p), as-synthesized calcined at 250 °C in air (F-ICSb-c250A), extracted (F-ICSb-e), extracted calcined at 250 °C in air (F-ICSb-ec250A).
The overall shape of Ar isotherms remained unchanged with steep capillary condensation/evaporation steps, suggesting that the quality of materials was not altered during the calcination process.

The presence of isocyanurate groups after additional calcination in air at different temperatures was monitored by the TG (A) and DTG (B) measurements, as shown in Fig. 52. As can be seen, the TG and DTG of the as-synthesized material (F-ICSb-p) depict a slight weight loss below 100 °C due to the evaporation of adsorbed water and other solvents. This peak is followed by another event occurring at 360 °C with a major weight loss that is related to the thermodesorption and decomposition of polymeric surfactant. The third peak centered at around 480 °C corresponds to the weight loss of isocyanurate bridging groups. The TG and DTG profiles of the extracted sample (F-ICSb-e) show only a partially reduced peak of the remaining template suggesting that the extraction was insufficient for effective removal of the polymer from cage-like materials.

Also, an additional calcination in air in the range of 200 and 300 °C of both as-synthesized and extracted samples was insufficient because it induced not only the template removal but also the decomposition of ICS. Therefore, the data indicate that the thermal treatment in air of either extracted or as-made materials in not a suitable method to efficiently liberate the spherical pores of the material from polymer.

The results of elemental analysis provide evidence that the ICS groups are partially removed during calcination in air. Table 15 summarizes the nitrogen contents of ICS-containing samples calcined in air.
Effect of thermal treatment on the FDU-1 PMO

Shown in Fig. 53 are the SAXS patterns for the extracted F-ICSa-e, F-ICSb-e, F-ICSc-e samples and for the extracted samples followed by thermal treatment at 360 °C in flowing nitrogen (F-ICSa-e360N, F-ICSb-e360N, F-ICSc-e360N). The SAXS patterns of F-ICSa-e and F-ICSb-e feature three peaks indexed as (110), (220) and (321) of a cubic \(Im\bar{3}m\) structure. These results indicate that F-ICSa-e and F-ICSb-e possess highly ordered structure. As can be further seen, the SAXS patterns gradually change from those having three peaks to those with two reflections as the loading of the ICS groups increased, indicating a gradual decrease in the structural ordering. As can be noticed, the SAXS patterns of F-ICSa-e360N, F-ICSb-e360N and F-ICSc-e360N follow a similar trend to that observed for the extracted materials. However, their peak positions are slightly offset to larger angles due to the structure contraction. It is noteworthy that it is quite difficult to prepare highly ordered mesoporous ICS-silica with high isocyanurate loadings because ICS is a large molecule. Argon adsorption isotherms and the corresponding pore size distributions (PSDs) for the ICS-containing organosilicas are shown in Figs. 54 and 55, respectively. As can be seen from Fig. 54, all samples exhibit type IV isotherms with pronounced hysteresis loops. In contrast to the samples further treated in the oven (F-ICSa-e360N, F-ICSb-e360N and F-ICSc-e360N), the amount adsorbed on the extracted samples (F-ICSa-e, F-ICSb-e, F-ICSc-e) is much lower indicating that only some fraction of the template was removed from the porous structure during extraction, whereas for the samples heated in nitrogen the pores were emptied from the residual template. All samples display steep capillary condensation steps on the adsorption branches, which are
Table 15. Molar fraction of ICS in the synthesis gel composition and subsequent elemental analysis data for cage-like FDU-1 mesoporous organosilicas with isocyanurate bridging groups (Figures 47-57).^a

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthesis gel composition</th>
<th>Elemental analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$X_{ICS}$</td>
<td>$n_{total}$ [mmol]</td>
</tr>
<tr>
<td>F-ICSa-e</td>
<td>0.036</td>
<td>37.19</td>
</tr>
<tr>
<td>F-ICSa-ec360N</td>
<td>0.036</td>
<td>37.19</td>
</tr>
<tr>
<td>F-ICSb-c200A</td>
<td>0.077</td>
<td>34.54</td>
</tr>
<tr>
<td>F-ICSb-c250A</td>
<td>0.077</td>
<td>34.54</td>
</tr>
<tr>
<td>F-ICSb-c300A</td>
<td>0.077</td>
<td>34.54</td>
</tr>
<tr>
<td>F-ICSb-e</td>
<td>0.077</td>
<td>34.54</td>
</tr>
<tr>
<td>F-ICSb-ec200A</td>
<td>0.077</td>
<td>34.54</td>
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<tr>
<td>F-ICSb-ec250A</td>
<td>0.077</td>
<td>34.54</td>
</tr>
<tr>
<td>F-ICSb-ec360N</td>
<td>0.077</td>
<td>34.54</td>
</tr>
<tr>
<td>F-ICSc-e</td>
<td>0.125</td>
<td>31.88</td>
</tr>
<tr>
<td>F-ICSc-e360N</td>
<td>0.125</td>
<td>31.88</td>
</tr>
</tbody>
</table>

^a $X_{ICS}$, mole fraction of ICS in the synthesis gel mixture; $n_{total}$, total number of mmoles of tris[3-(trimethoxysilyl)propyl]isocyanurate (ICS); %N*; nitrogen percentage predicted on the basis of the synthesis gel mixture; %N; nitrogen percentage obtained from elemental analysis; C$_{ICS}$, surface concentration of isocyanurate bridging groups calculated on the basis of %N obtained from elemental analysis.
**Figure 53.** Small angle X-ray scattering (SAXS) (A, B) and X-ray diffraction (XRD) (C) patterns for the cage-like FDU-1 mesoporous organosilicas containing three different isocyanurate molar ratios: extracted (F-ICSa-e, F-ICSb-e, F-ICSc-e, solid line) as well as extracted and heat treated samples at 360 °C in nitrogen (F-ICSa-ec360N, F-ICSb-ec360N, F-ICSc-ec360N, dashed line).
Figure 54. Argon adsorption-desorption isotherms (A, B, C) measured at – 196 °C for the cage-like FDU-1 mesoporous organosilicas containing three different isocyanurate molar ratios: extracted (F-ICSa-e, F-ICSb-e, F-ICSc-e) as well as extracted and heat treated samples at 360 °C in nitrogen (F-ICSa-ec360N, F-ICSb-ec360N, F-ICSc-ec360N).
Figure 55. Pore size distributions (PSDs) (A, B, C) calculated according to the KJS method [243] for the cage-like FDU-1 mesoporous organosilicas containing three different isocyanurate molar ratios: extracted (F-ICSa-e, F-ICSb-e, F-ICSc-e) as well as extracted and heat treated samples at 360 °C in nitrogen (F-ICSa-ec360N, F-ICSb-ec360N, F-ICSc-ec360N).
associated with narrow PSDs (see Fig. 55). However, desorption branches exhibited
tendency to broaden the capillary evaporation as the amount of ICS in the synthesis gel
increased (see Fig. 54), suggesting irregularity in the pore openings (F-ICS-e, F-ICS-
e360N). The sharp peaks on PSDs show the pore width about 10 nm, which are slightly
shifted for the samples after heating treatment. The BET specific surface area and pore
volume for all samples dramatically increased after thermal treatment (see Table 14).

A quantitative determination of ICS bridging groups in the mesostructure of the
as-synthesized, extracted and extracted - heated (at 360 °C in flowing nitrogen) samples
was carried out by recording the TG in nitrogen (as shown in Fig. 56). As can be seen
from Fig. 56 and 57, the TG and DTG curves for F-ICSa-p, F-ICSb-p and F-ICS-c-p show
two peaks centered at 360 °C and 480 °C with significant weight losses corresponding to
the degradation of the template and the ICS loadings, respectively. A gradual increase of
the isocyanurate groups inside the framework structure is evidenced by a progressively
growing ICS peak. This peak is the most prominent for the sample with the highest
concentration of ICS (F-ICSc-p). Similarly to Fig. 52, the extracted samples (F-ICSa-e,
F-ICSb-e, F-ICS-c-e) show only a slightly lower weight loss (TG) and thus less intensive
DTG peak indicating a partial removal of the template. Since the peak of polymer
appears at 360 °C, whereas the peak of ICS occurs at 480 °C, an additional heat treatment
at 360 °C in nitrogen permitted a complete removal of the remaining polymer without
decomposition of the functional groups. This can be clearly observed from the TG and
DTG patterns of the extracted samples followed by heat treatment in nitrogen at 360 °C
(F-ICSa-e360N, F-ICSb-e360N and F-ICS-c-e360N). Their TG and DTG data indicate a
complete disappearance of the strong peak at 360 °C and show an unchanged peak at 480 °C. In addition, these results point out high thermal stability of isocyanurate-containing materials.

Nitrogen contents in the isocyanurate-silicas were analyzed by elemental analysis; the results are listed in Table 15. In general, about 50-70% of the ICS organosilane was combined with TEOS to form the framework. The relatively small values of the incorporated ICS can be associated to experimental error due to the stickiness of this organosilane to the pipette. Therefore, not all ICS was transferred to the reaction vessel quantitatively. In addition, it is likely that condensation rate of ICS is significantly slower than that of TEOS, thus not all ICS is able to condensate to form the structure.

The FTIR spectra of isocyanurate-containing mesostructures further confirm a successful incorporation of ICS. Figs. 58 and 59 illustrate the FTIR spectra of the extracted, extracted-heated in nitrogen and as-synthesized silicas with three different ICS molar ratios. The characteristic symmetric and asymmetric stretching vibrations of -Si-O-Si- around 790 and 1110 cm\(^{-1}\) attributed to the formation of a condensed silica network are present. Also, a non-condensed silica -SiOH is present, which is manifested by a small peak around 950 cm\(^{-1}\) corresponding to the asymmetric stretching vibrations. A shoulder appears in the range of 3200 to 3500 cm\(^{-1}\) due to the hydrogen-bonded OH stretching vibrations originated from surface OH groups and molecularly adsorbed water. An evidence of gradual incorporation of ICS groups in the framework is apparent on the IR spectra by the presence of strong vibrations of carbonyl groups at 1680 cm\(^{-1}\) that increases with increasing ICS molar ratio in the synthesis gel mixture.
Figure 56. Thermogravimetric weight change (TG) profiles (A, B, C) measured in flowing nitrogen for the cage-like FDU-1 mesoporous organosilicas containing three different isocyanurate concentrations: extracted (F-ICSa-e, F-ICSb-e, F-ICSc-e), as-synthesized (F-ICSa-p, F-ICSb-p, F-ICSc-p) as well as extracted and heat treated at 360 °C in nitrogen (F-ICSa-ec360N, F-ICSb-ec360N, F-ICSc-ec360N).
Figure 57. The differential thermogravimetric (DTG) patterns (A, B, C) measured in flowing nitrogen for the cage-like FDU-1 mesoporous organosilicas containing three different isocyanurate concentrations: extracted (F-ICSa-e, F-ICSb-e, F-ICSc-e), as-synthesized (F-ICSa-p, F-ICSb-p, F-ICSc-p) as well as extracted and heat treated at 360 °C in nitrogen (F-ICSa-ec360N, F-ICSb-ec360N, F-ICSc-ec360N).
Figure 58. Infrared spectra of cage-like FDU-1 organosilicas containing heterocyclic isocyanurate bridging groups. Panel A shows a comparison of three spectra for one sample with 0.036 molar ratio of ICS: as-synthesized (F-ICSa-p), extracted (F-ICSa-e) and extracted followed by heat treatment at 360 °C in flowing nitrogen (F-ICSa-ec360N).  
1 - Corresponds to hydrogen bonded OH stretching bands from silanols and surface adsorbed water; 2 - to CH stretching vibrations in the 2900 cm\(^{-1}\) region; 3 - carbonyl (C=O) stretching at 1680 cm\(^{-1}\); 4 - CH bending modes around 1450 cm\(^{-1}\), 5 – C-O stretching around 1300 cm\(^{-1}\) and 6 - to silica network Si-O-Si asymmetric stretching as well as 7 - Si-OH band.
Figure 59. Infrared spectra of cage-like FDU-1 organosilicas containing heterocyclic isocyanurate bridging groups. Panel A and B represent spectra for extracted (F-ICSb-e, F-ICSb-ec360N) and extracted-heated (at 360 °C in flowing nitrogen) (F-ICSb-ec360N, F-ICSb-ec360N) samples with 0.077 (A) and 0.125 (B) ICS molar ratios, respectively. For indexes 1-7 see Figure 56.
In addition, the asymmetric and symmetric stretching and bending vibrations of alkyl (CH) groups are present at 2900 cm\(^{-1}\) and 1450 cm\(^{-1}\), respectively that correspond to propyl chains attached to the ICS ring and to ethyl and butyl blocks from the copolymer template. As can be seen from Fig. 58, the IR spectrum of as-made sample (F-ICSa-p) features intensive peaks of alkyl C-H stretching vibrations at 2900 cm\(^{-1}\) and less intensive C-O stretchings at 1300 cm\(^{-1}\), which decreased only slightly after extraction. However, an additional thermal treatment resulted in a significant decrease of C-H vibrations and a complete disappearance of C-O stretchings bands. The heated samples show all typical other vibrations characteristic for isocyanurate groups, indicating that ICS remained intact after heating procedure. Therefore, these results are in good agreement with the TG and EA experiments.

5.3. CAGE-LIKE SBA-16 PMO CONTAINING BULKY HETEROCYCLIC ISOCYANURATE BRIDGING GROUPS

The symmetry group of the extracted PMOs was determined by small angle X-ray scattering data (SAXS), which is shown in Fig. 60, whereas the unit cell parameters are listed in Table 16. For instance, the S-ICSf-e sample synthesized with the largest amount of ICS exhibits a strong peak at 2\(q\) of about 0.74 attributed to the (110) reflection and three minor well-resolved peaks at 2\(q\) of about 1.05, 1.29, and 1.96 attributed to the (200), (211), and (310) reflections, respectively. This assignment is consistent with the cubic \(Im\overline{3}m\) symmetry. As can be seen from Fig. 60, an increase in the percentage of ICS in PMO led to a pronounced change in the SAXS profiles, indicating that the structural order in the PMOs studied is dependent to a certain degree on the amount of introduced
ICS. The minor peak intensities attributed to the second and third reflections increased upon increasing the molar ratio of the bridging groups, which may suggest some improvement of the mesophase order. This finding indicates that upon addition of a small amount of large bridging groups (low concentration of ICS) some disruption in the formation of ordered mesostructure may occur, because the aforementioned amount of these groups may not be sufficient to ensure their uniform distribution in the entire framework. Also, at high concentrations of ICS, the structure deterioration may be observed because of geometrical constrictions to accommodate a high amount of ICS groups in the framework. Thus, the SAXS data suggest that there is an optimal concentration range of large bridging groups to form highly ordered mesostructures. For the SBA-16-ICS system and experimental conditions studied, the best samples were obtained for the mole fractions of ICS between 0.07 and 0.12.

Shown in Figs. 61 and 62 is a comparison of nitrogen adsorption-desorption isotherms measured at -196 °C and the corresponding pore size distributions (PSDs) for a series of the PMOs studied. All isotherms are type IV with sharp capillary condensation/evaporation steps and a pronounced hysteresis loop starting at a relative pressure of about 0.7 and abruptly ending at 0.45. This is typical for good-quality cage-like structures with narrow pore size distributions (see Fig. 62) and uniform pore openings.

As can be seen from Fig. 61, a gradual incorporation of ICS progressively shifts the capillary condensation step toward lower relative pressures, which reflects a decrease in the mesopore diameter [Table 16; see the pore diameter values evaluated according to
the KJS (Kruk, Jaroniec, Sayari) method [243] applicable for cylindrical mesopores as well as those estimated on the basis of SAXS and pore volume data.

It should be mentioned that the pore diameters estimated on the basis of SAXS and pore volume data for the cubic \textit{Im3m} symmetry are greater by about 2-3 nm than those obtained with the KJS method [76]. For the sample with the highest concentration of ICS (S-ICSf-e), the isotherm features a smaller uptake volume of adsorbate that indicates a decrease in the volume of primary mesopores. This can be expected because of the geometrical constrictions associated with accommodation of a high amount of large isocyanurate bridging groups into the mesopore walls.

**Effect of thermal treatment on the SBA-16 PMO structure**

The structure of two series of heat-treated isocyanurate-containing OMOs was determined using small angle X-ray scattering (SAXS) data shown in Figs. 63A and 63B. The unit cell values are summarized in Table 16. As can be seen from Figs. 63A and 63B, the SAXS curves for the extracted isocyanurate-containing OMOs (S-ICSd-e and S-ICSf-e) feature one major narrow peak at the scattering vector (q) of \( \approx 0.52 \) and four minor peaks indexed as (110), (200), (211) (310) and (321) according to the body-centered cubic \textit{Im3m} symmetry analogous to SBA-16 reported earlier by Sakamoto et al. [47]. An additional calcination of partially extracted and as-made samples at 315 °C in flowing nitrogen (S-ICSd-ec315N and S-ICSf-ec315N) and air (S-ICSd-c315A and S-ICSf-c315A) did not lead to any significant deterioration of the SAXS patterns. The unit cell parameter (Table 16) showed a tendency to decrease with increasing calcination
Table 16. Structural parameters determined from nitrogen adsorption isotherms measured at -196 °C, small angle X-ray scattering (SAXS) and high-resolution thermogravimetric analysis (TG) for the cage-like SBA-16 mesoporous organosilicas with heterocyclic isocyanurate bridging groups (Figures 58-66). a

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) [m² g⁻¹]</th>
<th>( V_c ) [cm³ g⁻¹]</th>
<th>( V_t ) [cm³ g⁻¹]</th>
<th>( w_{\text{KJS}} ) [nm]</th>
<th>( a ) [nm]</th>
<th>TG wt. loss [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-ICSa-e</td>
<td>712</td>
<td>0.27</td>
<td>0.49</td>
<td>7.44</td>
<td>16.74</td>
<td>20.07</td>
</tr>
<tr>
<td>S-ICSa-ec315N</td>
<td>777</td>
<td>0.29</td>
<td>0.49</td>
<td>7.04</td>
<td>16.01</td>
<td>14.63</td>
</tr>
<tr>
<td>S-ICSb-e</td>
<td>748</td>
<td>0.29</td>
<td>0.49</td>
<td>7.23</td>
<td>16.53</td>
<td>21.74</td>
</tr>
<tr>
<td>S-ICSb-ec315N</td>
<td>761</td>
<td>0.29</td>
<td>0.48</td>
<td>7.05</td>
<td>15.40</td>
<td>15.91</td>
</tr>
<tr>
<td>S-ICSc-e</td>
<td>870</td>
<td>0.33</td>
<td>0.59</td>
<td>7.24</td>
<td>16.63</td>
<td>21.91</td>
</tr>
<tr>
<td>S-ICSc-ec315N</td>
<td>886</td>
<td>0.33</td>
<td>0.57</td>
<td>6.89</td>
<td>16.65</td>
<td>17.97</td>
</tr>
<tr>
<td>S-ICSd-e</td>
<td>881</td>
<td>0.33</td>
<td>0.56</td>
<td>7.20</td>
<td>17.24</td>
<td>24.11</td>
</tr>
<tr>
<td>S-ICSd-ec315N</td>
<td>891</td>
<td>0.34</td>
<td>0.53</td>
<td>7.06</td>
<td>16.17</td>
<td>18.82</td>
</tr>
<tr>
<td>S-ICSd-c315A</td>
<td>734</td>
<td>0.25</td>
<td>0.42</td>
<td>6.2</td>
<td>7.8</td>
<td>15.00</td>
</tr>
<tr>
<td>S-ICSd-ec550A</td>
<td>714</td>
<td>0.24</td>
<td>0.47</td>
<td>5.4</td>
<td>8.7</td>
<td>14.20</td>
</tr>
<tr>
<td>S-ICSe-e</td>
<td>840</td>
<td>0.32</td>
<td>0.53</td>
<td>7.41</td>
<td>17.80</td>
<td>26.46</td>
</tr>
<tr>
<td>S-ICSe-ec315N</td>
<td>776</td>
<td>0.29</td>
<td>0.49</td>
<td>7.04</td>
<td>17.25</td>
<td>22.37</td>
</tr>
<tr>
<td>S-ICSf-e</td>
<td>736</td>
<td>0.29</td>
<td>0.44</td>
<td>6.58</td>
<td>16.82</td>
<td>28.83</td>
</tr>
<tr>
<td>S-ICSf-ec315N</td>
<td>785</td>
<td>0.29</td>
<td>0.45</td>
<td>6.37</td>
<td>15.66</td>
<td>23.96</td>
</tr>
<tr>
<td>S-ICSf-c315A</td>
<td>600</td>
<td>0.19</td>
<td>0.32</td>
<td>5.6</td>
<td>6.9</td>
<td>14.90</td>
</tr>
<tr>
<td>S-ICSf-ec550A</td>
<td>462</td>
<td>0.16</td>
<td>0.27</td>
<td>6.2</td>
<td>6.4</td>
<td>13.20</td>
</tr>
</tbody>
</table>

a \( S_{\text{BET}} \), BET specific surface area; \( V_c \), volume of micropores calculated from PSD, including the volume of interconnecting pores, if the latter are of diameter below about 4 nm; \( V_t \), single-point pore volume; \( w_{\text{KJS}} \), mesopore diameter calculated by the KJS method [243]; \( a \), unit cell parameter calculated from the first observed characteristic Bragg’s reflection; TG, weight loss recorded in flowing nitrogen in the range of 100 and 800 °C.
Figure 60. Small angle X-ray scattering (SAXS) patterns for the extracted cage-like SBA-16 mesoporous organosilicas containing various concentrations of isocyanurate bridging groups.
Figure 61. Nitrogen adsorption-desorption isotherms measured at -196 °C for the extracted cage-like SBA-16 mesoporous organosilicas containing various concentrations of isocyanurate bridging groups. The isotherms for S-ICSb-e, S-ICSc-e, S-ICSc-e, S-ICSe-e and S-ICSf-e were offset vertically by 120, 205, 309, 471, and 600 cm$^3$ STP g$^{-1}$. 
Figure 62. Pore size distributions (PSDs) calculated according to the KJS method [243] for the extracted cage-like SBA-16 mesoporous organosilicas containing various concentrations of isocyanurate bridging groups.
Figure 63. Small angle X-ray scattering (SAXS) patterns for the cage-like SBA-16 mesoporous organosilicas containing heterocyclic isocyanurate bridging groups with 0.077 (A) and 0.125 (B) molar ratios: extracted (S-ICSd-e and S-ICSf-e), extracted and heated at 315 °C in nitrogen (S-ICSd-ec315N and S-ICSf-ec315N) and extracted and calcined at 550 °C in air (S-ICSd-ec550A and S-ICSd-ec550A) and calcined nanocomposite at 315 °C in air (S-ICSa-c315A). The insets in Panel A and B show enlargement of minor peaks for S-ICSd-e and S-ICSf-e samples.
temperature and reached the smallest value for the sample calcined at 550 °C (S ICSd-ec550A), which is attributed to a substantial structural shrinkage, in this case caused also by the degradation of bridging groups. It is noteworthy that the structure was preserved even after a complete removal of isocyanurate bridging rings, which was confirmed by the SAXS profiles shown in Figs. 63A and 63B and nitrogen adsorption isotherms.

Adsorption isotherms were measured at -196 °C for a series of the extracted and calcined ICS-OMSs with two different isocyanurate mole fractions; 0.08 (S-ICSd) and 0.12 (S-ICSf), see Figs. 64A and 64B, respectively. Adsorption parameters such as the specific surface area, total pore volume, volume of complementary pores and pore diameter are summarized in Table 16. The nitrogen adsorption isotherms were also used to evaluate the Kruk-Jaroniec-Sayari (KJS) pore size distributions (PSDs) displayed in Fig. 65A and 65B, respectively. As can be seen from Figs. 65A and 65B, PSDs are typical for the SBA-16 materials [24, 25] exhibiting two narrow peaks; the first intense peak in the range below 4 nm and the second in the range of 4-10 nm. These peaks are associated with the presence of small complementary pores and primary ordered mesopores, respectively. Since the triblock copolymer F127 contains 106 hydrophilic polyethylene oxide (PEO) moieties and 70 polypropylene oxide (PPO) hydrophobic groups, the resulting cage-like mesoporous materials usually exhibit a higher ratio of micropores in contrast to primary mesopores due to the penetration of PEO blocks into the silica walls as well as due to the presence of apertures. Since KJS method [243] was based on the BHJ algorithm elaborated for cylindrical pores [244], the spherical pore diameters are underestimated by about 2-3 nm. Therefore, the primary mesopore
diameters were also calculated using equation 13, which was derived for the \textit{Im3m} symmetry group, and relates the unit cell parameter obtained from the SAXS/XRD data with the volume of primary pores and total pore volume estimated from nitrogen adsorption isotherms [246].

The extracted ICS-OMSs samples (S-ICSd-e and S-ICSf-e) exhibit type IV isotherms with steep capillary condensation/evaporation steps and apparent hysteresis loops that are characteristic for high quality cage-like materials with uniform pore entrances. As can be seen from Figs. 64A and 64B, there is only a small difference between adsorption isotherms for the extracted (S-ICSd-e and S-ICSf-e) and extracted-calcined (S-ICSd-ec315N and S-ICSf-ec-315N) ICS-OMOs because of the structural shrinkage due to the sample calcination at 315 °C. As can be noticed from Table 16, the extracted-calcined S-ICSd-ec315N and S-ICSf-ec315N materials exhibited a slight increase in the specific surface area by 10 and 49 m² g⁻¹ and a small decrease in the KJS pore widths (w) by 0.1 and 0.2 nm, respectively.

On the contrary, nitrogen adsorption isotherms for the calcined as-synthesized samples (S-ICSd-p and S-ICSf-p) at 315 °C in flowing air (S-ICSd-c315A and S-ICSf-c315A) show a slight broadening and a shift of the capillary condensation steps to the lower values of relative pressure. This indicates a reduction in the pore diameters, which is also visible on the PSD curves shown in Fig. 65A and 65B, where maxima of the primary pores are shifted to the smaller pore sizes; 6.2 nm and 5.6 nm for S-ICSd-c315A and S-ICSf-c315A, respectively. In comparison to the extracted S-ICSd-e and S-ICSf-e samples (Table 16), the specific surface areas for S-ICSd-c315A and S-ICSf-c315A were
reduced by 147 and 136 m²·g⁻¹, the volume of complementary pores changed by ~0.08 and 0.1 cm³·g⁻¹, whereas the total pore volume decreased by 0.14 and 0.12 cm³·g⁻¹, respectively.

In order to determine the stability of isocyanurate-silica mesostructures, the extracted samples (S-ICSd-e and S-ICSf-e) were subjected to the calcination at 550 °C in air to completely remove the organic moieties. The nitrogen adsorption isotherms for S-ICSd-ec550A and S-ICSf-ec550A still exhibit a typical type IV shape with hysteresis loop characteristic for mesoporous materials, suggesting that even after total degradation of isocyanurate bridging groups in the framework the mesoporous structure did not lose its ordering. As can be seen from Table 16, the specific surface area was reduced by 167 and 274 m²·g⁻¹, the volumes of complementary pores changed by about 0.09 and 0.13 cm³·g⁻¹, whereas the total pore volumes decreased by 0.09 and 0.17 cm³·g⁻¹ for ICSd-ec550A and S-ICSf-ec550A, respectively.

Removal of the polymeric template (Pluronic F127) from ICS-PMOs was also monitored by high-resolution thermogravimetry (TG) and elemental analysis (Table 17). The TG curves recorded in flowing nitrogen are shown in Figs. 66A and 67A, whereas the corresponding differential (DTG) curves are shown in Figs. 66B and 67B for S-ICSd and S-ICSf materials, respectively. The weight loss values and the ICS coverage densities are listed in Table 16. As can be seen from Figs. 66A and 67A, the TG profiles of the as-made material (S-ICSd-p and S-ICSf-p) represent two major decomposition steps; the first step occurs within 300-400 °C and the second step between 400-650 °C, which are more clearly illustrated using the weight loss derivative as shown in Figs. 66B and 67B.
Table 17. Molar fraction of ICS in the synthesis gel and subsequent elemental analysis data for cage-like SBA-16 mesoporous organosilicas with isocyanurate bridging groups (Figures 58-66).^a

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthesis gel composition</th>
<th>Elemental analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$X_{ICS}$</td>
<td>$n_{total}$ [mmol]</td>
</tr>
<tr>
<td>S-ICSa-e</td>
<td>0.017</td>
<td>39</td>
</tr>
<tr>
<td>S-ICSa-ec315N</td>
<td>0.017</td>
<td>39</td>
</tr>
<tr>
<td>S-ICSb-e</td>
<td>0.036</td>
<td>37.6</td>
</tr>
<tr>
<td>S-ICSb-ec315N</td>
<td>0.036</td>
<td>37.6</td>
</tr>
<tr>
<td>S-ICSc-e</td>
<td>0.056</td>
<td>36.3</td>
</tr>
<tr>
<td>S-ICSc-ec315N</td>
<td>0.056</td>
<td>36.3</td>
</tr>
<tr>
<td>S-ICSd-e</td>
<td>0.077</td>
<td>34.9</td>
</tr>
<tr>
<td>S-ICSd-ec315N</td>
<td>0.077</td>
<td>34.9</td>
</tr>
<tr>
<td>S-ICSd-c315A</td>
<td>0.077</td>
<td>34.9</td>
</tr>
<tr>
<td>S-ICSd-ec550A</td>
<td>0.077</td>
<td>34.9</td>
</tr>
<tr>
<td>S-ICSf-e</td>
<td>0.100</td>
<td>336</td>
</tr>
<tr>
<td>S-ICSf-ec315N</td>
<td>0.100</td>
<td>33.6</td>
</tr>
<tr>
<td>S-ICSf-c315A</td>
<td>0.125</td>
<td>32.2</td>
</tr>
<tr>
<td>S-ICSf-ec550A</td>
<td>0.125</td>
<td>32.2</td>
</tr>
<tr>
<td>S-ICSf-c315A</td>
<td>0.125</td>
<td>32.2</td>
</tr>
<tr>
<td>S-ICSf-ec550A</td>
<td>0.125</td>
<td>32.2</td>
</tr>
</tbody>
</table>

^a $X_{ICS}$, mole fraction of ICS in the synthesis gel mixture; $n_{total}$, total number of mmoles of tris[3-(trimethoxysilyl)propyl]isocyanurate (ICS); %N*; nitrogen percentage predicted on the basis of the synthesis gel mixture; %N; nitrogen percentage obtained from elemental analysis; $C_{ICS}$, surface concentration of isocyanurate bridging groups calculated on the basis of %N obtained from elemental analysis.
Figure 64. Nitrogen adsorption isotherms measured at –196 °C for the cage-like mesoporous organosilicas containing 0.077 (A) and 0.125 (B) molar ratios of ICS. The isotherms in Panel A for S-ICSd-c315A, S-ICSd-ec315N, S-ICSd-e were offset by 80, 95, 180 cm$^3$ STP g$^{-1}$, whereas isotherm in Panel B for S-ICSf-e was offset by 100 cm$^3$ STP g$^{-1}$, respectively.
Figure 65. Pore size distributions (PSDs) calculated according to the KJS method [243] for the cage-like mesoporous organosilicas containing 0.077 (A) and 0.125 (B) molar ratios of ICS. The PSDs in Panel A for S-ICSd-c315A, S-ICSd-ec315N, S-ICSd-e were offset by 0.09, 0.15, 0.23 cm$^3$ g$^{-1}$ nm$^{-1}$, whereas PSDs in panel B for S-ICSf-c315A, S-ICSf-ec315N, S-ICSf-e were offset by 0.08, 0.13 and 0.21 cm$^3$ g$^{-1}$ nm$^{-1}$, respectively.
The DTG curves display two distinct peaks located at around 375 °C and 480 °C, which are attributed to the thermodesorption/degradation of triblock copolymer (F127) template and the decomposition of isocyanurate bridging groups, respectively.

The TG weight losses for as-synthesized materials with various loadings of the ICS groups (S-ICSd-p and S-ICSf-p) were 41.85 % and 46.23 %, whereas after partial removal of a polymer template due to extraction (S-ICSd-e and S-ICSf-e) these losses were reduced to 24.1 and 28.8%, respectively (see Table 16). In contrast, the ICS contents evaluated on the basis of nitrogen percentages obtained by elemental analysis for S-ICSd-e and S-ICSf-e were 0.76 and 1.08 mmol/g, respectively. In addition, after heating in nitrogen at 315 °C, the weight losses were further reduced to 18.8 % and 24 %, which correspond to the ICS contents of 0.67 and 0.97 mmol/g, respectively. This suggests that the extraction removed only a part of the polymeric template and additional calcination at 315 °C in nitrogen removed the remaining polymer. As can be seen from Figs. 66B and 67B, there are still small peaks for the extracted samples (S-ICSd-e and S-ICSf-e) arising from the residual amount of template, whereas these peaks are not present for the samples after additional heating at 315 °C in nitrogen (S-ICSd-ec315N and S-ICSf-ec315N) indicating a complete removal of Pluronic F127 without elimination of the isocyanurate groups.

In contrast, the samples calcined in air without prior extraction (S-ICSd-c315A and S-ICSf-c315A) exhibited the TG weight losses of 12.6 and 14.1 % as well as the ICS contents of 0.33 and 0.44 mmol/g, which reflect a dramatic reduction of about 57 and 59 % of the ICS groups, respectively. This indicates that a direct calcination of as-
synthesized materials removes not only the polymer template but also a major part of isocyanurate functionality. This can be seen from the DTG curve (Fig. 66B), which is broad and significantly less-intensive compared to the DTG curve of the S-ICSd-ec315N sample. An additional calcination in flowing nitrogen of the extracted cage-like PMOs was possible because the aforementioned thermogravimetric events are well separated.

Calcination of the extracted samples at 550 °C in air caused not only a complete removal of the F127 polymer template as reflected by the lack of characteristic peak at 375 °C on the DTG pattern but also a major decomposition of the ICS groups (Fig. 66B). Elemental analysis indicated the reduction of nitrogen contents to 0.14 and 0.22 mmol/g attributed to the removal of about 82 and 80 % of ICS from the Ia-e550A and Ib-e550A mesostructures, respectively.

It is noteworthy that under neutral atmosphere (e.g., nitrogen) thermal desorption of the polymeric template occurred between 300 °C and 400 °C for the system studied, whereas the maximum rate of ICS decomposition was at much higher temperature (~480°C) because of its covalent bonding in the framework. This is not the case for the thermal treatment of the polymer-containing samples in air, where both thermal events overlap due to the oxidative degradation of the polymeric template and ICS groups. Therefore, the extracted samples were thermally treated in nitrogen in order to completely remove the polymeric template.

The proposed procedure of the template removal (i.e., extraction and controlled heating in nitrogen) can be used for cage-like mesoporous organosilicas with other
Figure 66. Thermogravimetric weight change (TG) profiles (A) measured in flowing nitrogen and the corresponding differential DTG curves (B) for the cage-like mesoporous organosilicas containing 0.077 molar ratio of ICS: as-synthesized (S-ICSd-p), extracted (S-ICSd-e), extracted and heated at 315 °C in nitrogen (S-ICSd-ec315N) and extracted and calcined at 550 °C in air (S-ICSd-ec550A) and calcined nanocomposite at 315 °C in air (S-ICSd-c315A).
Figure 67. Thermogravimetric weight change (TG) profiles (A) measured in flowing nitrogen and the corresponding differential DTG curves (B) for the cage-like mesoporous organosilicas containing 0.125 molar ratio of ICS: as-synthesized (S-ICSf-p), extracted (S-ICSf-e), extracted and heated at 315 °C in nitrogen (S-ICSf-ec315N) and extracted and calcined at 550 °C in air (S-ICSf-ec550A) and calcined nanocomposite at 315 °C in air (S-ICSf-c315A).
organic groups, which decompose in nitrogen at temperatures much higher than that of the template removal.

The introduction of isocyanurate bridging groups into the SBA-16 mesostructures and its preservation during the thermal removal of triblock copolymer was monitored by FT-IR spectroscopy in the range of 4000 and 550 cm\(^{-1}\). Fig. 68 shows a comparison of the IR spectra for two materials containing the same loadings of isocyanurate rings; extracted (S-ICSd-e) and extracted-heated sample at 315 °C in nitrogen (S-ICSd-ec315N). As can be seen, the IR spectrum for the S-ICSd-e material exhibits a very broad shoulder between 3200 and 3500 cm\(^{-1}\) that is associated with hydrogen-bonded OH stretching vibrations originating from surface hydroxyl groups and adsorbed water. In addition, the spectrum shows two typical bands of asymmetric and symmetric stretching vibrations at 1110 cm\(^{-1}\) and 790 cm\(^{-1}\), which are attributed to the formation of siloxane bond, i.e., condensed silica network (-Si-O-Si-). The asymmetric stretching vibrations of non-condensed silica (-SiOH) are present at 950 cm\(^{-1}\). Small bands at around 2900 cm\(^{-1}\) are related to alkyl stretching vibrations originating from the remaining residue of the polymeric template and isocyanurate groups, whereas the band at 1450 cm\(^{-1}\) is characteristic of bending vibrations of alkyl (CH) bond. The presence of ICS incorporated to the silica framework can be further confirmed by the presence of carbonyl (C=O) stretching vibrations at 1680 cm\(^{-1}\). The IR spectrum of the extracted-heated sample (S-ICSd-ec315N) exhibits all characteristic peaks for the extracted isocyanurate-containing mesoporous silica (S-ICSd-e). However, these peaks are less intense especially in the region of 3200 and 3500 cm\(^{-1}\) due to the thermodesorption of
Figure 68. A comparison of infrared spectra of the cage-like mesoporous organosilicas containing identical concentration of ICS; extracted (S-ICSa-e) as well as extracted and heated samples at 315 °C in flowing nitrogen (S-ICSa-ec315N). 1 - corresponds to hydrogen bonded OH stretching bands from silanols and surface adsorbed water; 2 - CH stretching vibrations in the 2900 cm$^{-1}$ region; 3 - carbonyl (C=O) stretching at 1680 cm$^{-1}$; 4 - CH bending modes around 1450 cm$^{-1}$, 5 - silica network Si-O-Si asymmetric stretching as well as 6 - an Si-OH band.
molecularly adsorbed water. This finding suggests that ICS remained intact after polymer removal during calcination at 315 °C in nitrogen.

5.4. CAGE-LIKE SBA-16 BIFUNCTIONAL PMO CONTAINING BULKY HETEROCYCLIC ISOCYANURATE AND ALIPHATIC ETHANE BRIDGING GROUPS

Effect of thermal treatment on the bifunctional SBA-16 PMO structure

The structures of extracted as well as extracted and calcined ICS-E-PMOs materials were investigated using XRD as shown in Figs. 69A and 69B, respectively. The unit cell parameters obtained for the first Bragg’s reflection are listed in Table 18. The XRD patterns for PMOs containing only ethane bridging groups (S-E-e and S-E-e315N) show one intensive reflection and three minor reflections indexed as (110), (200), (211) and (321) assigned to the $Im3m$ symmetry similar to ICS-OMOs. It is noteworthy that Qiu et al. [217] assigned the structure of the ethane-bridge PMO as face-centered cubic ($Fm3m$); however Qiu and co-workers carried out the synthesis in the presence of potassium chloride (KCl) and herein sodium chloride was used. As reported already by others [71, 81, 268, 269], various inorganic salts can induce formation of different structures. For instance, Fan et al. [71] showed that the use of KCl in the presence of the F127 template led to the development of high-purity $Fm3m$ phase, which is relatively difficult to synthesize. In contrast, the use of NaI facilitates the formation of $Ia3d$ phase [81]. In general, inorganic salts can be used to control the morphology and adsorption properties such as the micropore volume, the volume of primary pores, pore size and
surface area. Nonetheless, based on the peak positions for the S-E-e and S-E-ec315N samples, it was very difficult to assign the symmetry group as \textit{Fm\textit{3}m}. Introduction of isocyanurate rings into ethane-silica samples (extracted S-EICSa-e, S-EICSb-e and extracted-heated S-EICSa-ec315N, S-EICSb-ec315N) led to a gradual disappearance of (200) and (211) peaks, however the structure was not changed; thus the peaks for bifunctional E-ICS-PMOs were also assigned according to the \textit{Im\textit{3}m} symmetry group. As regards to the samples with the highest ICS concentration (S-EICSc-e and S-EICSc-ec315N) only a broad shoulder was observed suggesting high structural deterioration.

A comparison of nitrogen adsorption isotherms measured at -196 °C for extracted as well as extracted-calcined samples is shown in Figs. 70A and 70B, respectively, whereas the corresponding adsorption parameters are listed in Table 17. The pure ethane-silica samples (S-E-e and S-E-ec315N) exhibited a type IV isotherm with pronounced hysteresis loop and quite apparent capillary condensation/evaporation steps, which indicates the formation of high quality cage-like mesoporous materials.

Introduction of the ICS rings into the ethane-silica structure led to a slight change in the isotherm shape indicating the similarity of both mesoporous structures. However, as can be seen from Table 18 for the extracted-calcined samples, a gradual addition of ICS influenced the BET specific surface area and the volume of complementary pores, which decreased progressively from 1012 to 462 m$^2$g$^{-1}$ and from 0.42 to 0.12 cm$^3$g$^{-1}$, respectively. It is noteworthy that at high relative pressures close to unity, the shape of nitrogen adsorption isotherms for bifunctional ICS-E materials, especially for the S-EICSc-e sample, exhibited a significant tailing. This behaviour can be attributed to
Figure 69. Powder X-ray diffraction (XRD) patterns for the extracted (A) and extracted followed by heat treatment in nitrogen at 315 °C (B) bifunctional cage-like mesoporous organosilicas containing various concentrations of isocyanurate and ethane bridging groups.
Figure 70. Nitrogen adsorption isotherms measured at –196 °C for the extracted (A) and extracted followed by heat treatment in nitrogen at 315 °C (B) bifunctional cage-like mesoporous organosilicas containing various concentrations of isocyanurate and ethane bridging groups. The isotherm on Panel A for S-EICSa-e was offset by 40 cm$^3$ STP g$^{-1}$, whereas isotherms on Panel B for E1a-e315N and E-e315N were offset by 50 and 100 cm$^3$ STP g$^{-1}$, respectively.
**Figure 71.** Pore size distributions (PSDs) calculated according to the KJS method [243] for the extracted (A) and extracted followed by heat treatment in nitrogen at 315 °C (B) bifunctional cage-like mesoporous organosilicas containing various concentrations of isocyanurate and ethane bridging groups. The PSDs on Panel A for S-E-e, S-EICSa-e and S-EICSb-e were offset by 50 and 100 cc STP g⁻¹, whereas the PSDs on Panel B for S-EICSb-ec315N, S-EICSa-ec315N and S-E-ec315N were offset by 0.06, 0.17 and 0.24 cm³ g⁻¹ nm⁻¹, respectively.
increase of the textural porosity. Unlike pendant groups, which are attached to the pore surface, isocyanurate bridging groups are in the framework. Since the bridging groups are embedded in the framework, a gradually increased concentration does not necessarily alter the pore diameter (see Figs. 71A and 71B). Thus, the pore sizes of the E-ICS materials are similar and the estimated pore diameters are between 4.9 and 6.5 nm.

Fig. 72 displays four panels for the ethane PMO samples with progressively increasing concentration of isocyanurate bridging groups, whereas Fig. 73 represents the corresponding DTG curves. Thermogravimetric weight losses recorded under nitrogen are listed in Table 19. Each panel shows patterns for composite (S-E-p, S-EICSa-p, S-EIsb-p, S-EICSc-p), extracted (S-E-e, S-EICSa-e, S-EICSb-e, S-EICSc-e) as well as extracted and heated E-ICS-PMO samples at 315 °C in flowing nitrogen (S-E-ec315N, S-EICSa-ec315N, S-EICSb-ec315N, S-EICSc-ec315N). As can be seen from Figs. 72 and 73, the as-synthesized composites exhibit two events; one pronounced peak between 200 and 450 °C attributed to the decomposition of the F127 template and the second peak between 450 and 650 °C related to the degradation of both ethane and isocyanurate bridging groups, respectively. The peak related to the F127 template disappeared partially after extraction, however additional heating at 315 °C in nitrogen led to its total disappearance. The preservation of isocyanurate-ethane bridging groups during heating in nitrogen is confirmed by the second event, which still appears on the TG profile suggesting a complete removal of the polymer without destruction of the organics. These results are in agreement with isocyanurate-silica samples discussed earlier.
Fig. 74 shows a comparison of the IR spectra for the solvent-extracted SBA-16 PMO samples containing ethane bridging groups with two different loadings of isocyanurate rings. These spectra display similar sets of vibrations as those for ICS-PMOs shown in Fig. 68, related to the formation of non-condensed and condensed silica networks (550-1200 cm\(^{-1}\) region) as well as to the hydrogen-bonded OH stretching vibrations originating from silanol and surface adsorbed water (2900-3500 cm\(^{-1}\) region). In comparison to ICS-OMOs, these E-ICS-PMOs contain less water, which is manifested by a relatively low-intensity band from the hydrogen bonded stretching vibrations suggesting much more hydrophobic nature of these bifunctional materials due to the presence of ethane groups in the framework. In addition to the stretching and bending vibrations of CH bond in the 2900 cm\(^{-1}\) region and at about 1450 cm\(^{-1}\) as well as carbonyl stretching vibrations at 1680 cm\(^{-1}\), there are also two other bands present at 1260 cm\(^{-1}\) and 700 cm\(^{-1}\). These new modes are attributed to the Si-C bond. The presence of the Si-C peaks provides an evidence of ethane attachment and the lack of bond cleavage that could occur during extraction. Based on the elemental analysis data shown in Table 19, the nitrogen contents increase gradually for the extracted samples with increasing concentration of bridging groups indicating a successful incorporation of the ICS.

This study shows that mesoporous organosilicas with bulky isocyanurate bridging groups were successfully synthesized by employing B50-6600 (FDU-1) and F127 (SBA-16) triblock copolymer templates, isocyanurate precursor and TEOS or ethane-containing silane in the case of PMOs. Gas adsorption analysis and small angle X-ray scattering demonstrated that both structures exhibited 3D cubic \(Im\overline{3}m\) network of large cage-like
Table 18. Structural parameters determined from nitrogen adsorption isotherms measured at -196 °C, small angle X-ray scattering (SAXS) and high-resolution thermogravimetric analysis (TG) for bifunctional cage-like SBA-16 mesoporous organosilicas with heterocyclic isocyanurate and aliphatic ethane bridging groups (Figures 67-72).\textsuperscript{a}

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ [m$^2$ g$^{-1}$]</th>
<th>$V_c$ [cm$^3$ g$^{-1}$]</th>
<th>$V_t$ [cm$^3$ g$^{-1}$]</th>
<th>$w_{\text{KJS}}$ [nm]</th>
<th>$w_d$ [nm]</th>
<th>$a$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-E-e</td>
<td>1008</td>
<td>0.43</td>
<td>0.68</td>
<td>5.9</td>
<td>8.3</td>
<td>15.8</td>
</tr>
<tr>
<td>S-E-ec315N</td>
<td>1012</td>
<td>0.43</td>
<td>0.71</td>
<td>5.8</td>
<td>7.5</td>
<td>14.0</td>
</tr>
<tr>
<td>S-EICSa-e</td>
<td>912</td>
<td>0.38</td>
<td>0.75</td>
<td>6.1</td>
<td>8.5</td>
<td>16.1</td>
</tr>
<tr>
<td>S-EICSa-ec315N</td>
<td>868</td>
<td>0.37</td>
<td>0.77</td>
<td>5.6</td>
<td>7.5</td>
<td>13.9</td>
</tr>
<tr>
<td>S-EICSb-e</td>
<td>826</td>
<td>0.33</td>
<td>0.63</td>
<td>6.5</td>
<td>9.1</td>
<td>17.3</td>
</tr>
<tr>
<td>S-EICSb-ec315N</td>
<td>829</td>
<td>0.33</td>
<td>0.63</td>
<td>6.4</td>
<td>8.2</td>
<td>15.6</td>
</tr>
<tr>
<td>S-EICSb-e</td>
<td>531</td>
<td>0.15</td>
<td>1.15</td>
<td>5.6</td>
<td>7.8</td>
<td>14.8</td>
</tr>
<tr>
<td>S-EICSb-ec315N</td>
<td>462</td>
<td>0.12</td>
<td>0.8</td>
<td>4.9</td>
<td>6.7</td>
<td>13.1</td>
</tr>
</tbody>
</table>

\textsuperscript{a} $S_{\text{BET}}$, BET specific surface area; $V_c$, volume of micropores calculated from PSD, including the volume of interconnecting pores, if the latter are of diameter below about 4 nm; $V_t$, single-point pore volume; $w_{\text{KJS}}$, mesopore diameter calculated by the KJS method [243]; $a$, unit cell parameter calculated from the first observed characteristic Bragg’s reflection; TG, weight loss recorded in flowing nitrogen in the range of 100 and 800 °C.
Table 19. Molar fraction of ICS in the synthesis gel and subsequent elemental analysis data for bifunctional cage-like SBA-16 mesoporous organosilicas with heterocyclic isocyanurate and aliphatic ethane bridging groups (Figures 67-72).a

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthesis gel composition</th>
<th>Elemental analysis</th>
<th>TG wt. loss [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XICS</td>
<td>n_{total} [mmol]</td>
<td>% N*</td>
</tr>
<tr>
<td>S-E-e</td>
<td>0</td>
<td>8.04</td>
<td>0</td>
</tr>
<tr>
<td>S-E-ec315N</td>
<td>0</td>
<td>8.04</td>
<td>0</td>
</tr>
<tr>
<td>S-EICSa-e</td>
<td>0.03</td>
<td>7.90</td>
<td>1.47</td>
</tr>
<tr>
<td>S-EICSa-ec315N</td>
<td>0.03</td>
<td>7.90</td>
<td>1.47</td>
</tr>
<tr>
<td>S-EICSB-e</td>
<td>0.10</td>
<td>7.63</td>
<td>2.74</td>
</tr>
<tr>
<td>S-EICSB-ec315N</td>
<td>0.10</td>
<td>7.63</td>
<td>2.74</td>
</tr>
<tr>
<td>S-EICSc-e</td>
<td>0.22</td>
<td>7.24</td>
<td>4.82</td>
</tr>
<tr>
<td>S-EICSc-ec315N</td>
<td>0.22</td>
<td>7.24</td>
<td>4.82</td>
</tr>
</tbody>
</table>

a X_{ICS}, mole fraction of ICS in the synthesis gel mixture; n_{total}, total number of mmole of tris[3-(trimethoxysilyl)propyl]isocyanurate (ICS) and 1,2-bis(triethoxysilyl)ethane (BTESE); % N*; nitrogen percentage predicted on the basis of the synthesis gel mixture; %N; nitrogen percentage obtained from elemental analysis; C_{ICS}, surface concentration of isocyanurate bridging groups calculated on the basis of %N obtained from elemental analysis.
Figure 72. Thermogravimetric weight change (TG) profiles (A-D) measured in flowing nitrogen for bifunctional PMOs containing ethane and gradually increasing concentrations of isocyanurate: as-synthesized (S-E-p, EICSa-p, EICSb-p, EICSc-p), extracted (S-E-e, S-EICSa-e, S-EICSb-e, S-EICSc-e) and extracted-heated samples at 315 °C in nitrogen (S-E-ec315N, S-EICSa-ec315N, S-EICSb-ec315N, S-EICSc-ec315N).
Figure 73. The differential thermogravimetric (DTG) patterns (A-D) measured in flowing nitrogen for bifunctional PMOs containing ethane and gradually increasing concentrations of isocyanurate: as-synthesized (S-E-p, EICSa-p, EICSb-p, EICSc-p), extracted (S-E-e, S-EICSa-e, S-EICSb-e, S-EICSc-e) and extracted-heated samples at 315 °C in nitrogen (S-E-ec315N, S-EICSa-ec315N, S-EICSb-ec315N, S-EICSc-ec315N).
Figure 74. A comparison of infrared spectra of the extracted mesoporous ethanesilicas with two different concentrations of isocyanurate. 1 - corresponds to hydrogen bonded OH stretching bands from silanols and surface adsorbed water, 2 - CH stretching vibrations in the 2900 cm\(^{-1}\) region; 3 - carbonyl (C=O) stretching at 1680 cm\(^{-1}\); 4 - CH bending modes around 1450 cm\(^{-1}\), 5 - silica network Si-O-Si asymmetric stretching as well as 6 - an Si-OH band.
pores with high surface area up to 1000 m$^2$g$^{-1}$, large open pore diameter (4.9-7.4 nm), large pore volume up to 1.15 cm$^3$g$^{-1}$, and the ICS loading of about 1 mmolg$^{-1}$. Taking advantage of temperature-controlled calcination, the templates were successfully removed making these mesostructures accessible for different molecules. FTIR, elemental analysis and high resolution TG analysis employed for the characterization of these materials revealed that the bulky ICS groups are intact in the framework after heat treatment at 315 ºC and 360 ºC in flowing nitrogen for SBA-16 and FDU-1 PMOs, respectively.
VI. CONCLUSIONS

This doctoral dissertation was focused on the study of ordered mesoporous materials such as FDU-1 and SBA-16 with cubic $Fm\bar{3}m$ and $Im\bar{3}m$ structures, respectively. The specific topics studied include: (i) improvement of the synthesis conditions of ordered cage-like siliceous mesostructures by optimization of the self-assembly time, the polymer/silica ratio, the amount of added inorganic salt, the amount of added polymer and pH as well as the development for the removal of polymeric template (ii) fabrication of ordered siliceous mesostructures with various organic pendant ligands and (iii) development of ordered siliceous mesostructures with bulky heterocyclic bridging groups.

It is shown that the optimization of the first step of the synthesis of the cage-like FDU-1 OMS, at room temperature can be shortened to six hours of the original 24 hours without diminishing the quality of these materials. The optimal triblock copolymer/silica ratio for these materials was found to be 135:1. The materials synthesized below or above this ratio exhibited less ordered structure and less uniform pore openings. When a double amount of the triblock copolymer was used at low acid concentration in the presence of sodium chloride (NaCl/template ratio of 2.5:1) the FDU-1 materials with larger volume of mesopores and narrow pore size distribution were obtained.

A two-step template removal method that combines initial treatment of as-made silica in acidified ethanolic solution (extraction) followed by calcination at much lower temperature (usually below 350 °C) was shown to be an effective way to completely
remove the block copolymer. The aforementioned temperature-controlled calcination was essential for improvement of structural properties of cubic (Im3m) cage-like SBA-16 mesostructures with increased surface area from 941 to 1187 m² g⁻¹, pore volume from 0.60 to 0.84 cm³ g⁻¹ and pore size from 7.02 to 8.56 nm.

The co-condensation method was used to incorporate a variety of multifunctional organic pendant groups into the pore walls of cage-like structures. It was shown that the vinyl-containing OMOs synthesized from triethoxyvinylsilane (TEVS) and tetraethyl orthosilicate (TEOS) in the presence of B50-6600 triblock copolymer as a structure directing agent under acidic conditions exhibited cubic Fm3m structure with cage-like pores at low loadings of TEVS. At higher concentrations of TEVS (>20%), a disordered structure was formed with broad PSDs and non-uniform pore openings. In the event of mercaptopropyl-containing OMOs synthesized using TEOS and 3-mercaptopropyltrimethoxysilane (MPTMS), less-defined structures were formed under the same conditions.

Nevertheless, the use of improved conditions reported in chapter 3 gave highly ordered mesoporous materials with high loadings of vinyl and mercaptopropyl surface groups when lower acid concentration (0.5M), NaCl and a double amount of triblock copolymer B50-6600 were used. At low molar percentage of vinyl groups (15%), a cubic Fm3m structure was formed analogous to FDU-1. For OMOs with 20% of vinyl groups the structure changed from cubic Fm3m to hexagonal p6mm. In the case of mercaptopropyl groups, all loadings of MPTMS resulted in the formation of the p6mm structure. It was shown that the structural change was induced by addition of functional
reagents (TEVS and MPTMS). Other parameters such as addition of NaCl, an increased amount of the polymer template and lower acid concentration only improved the quality of the resulting organosilicas by narrowing PSD and increasing the uniformity of pore entrances.

When single imidazole, single ureidopropyl and ureidopropyl along with mercaptopropyl pendant groups were incorporated into both cubic cage-like SBA-16 and FDU-1 mesostructures using N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (imidazole), ureidopropyltrimethoxysilane (ureidopropyl) and 3-mercaptopropyltrimethoxysilane (MPTMS) precursors and TEOS in the presence of F127 and B50-6600 templates, better structural properties were attained for larger-pore FDU-1 silica. It was shown that an increase in the imidazole, ureidopropyl and ureidopropyl-mercaptopropyl concentration led to a decrease in the interplanar spacing, BET specific surface area, pore volume and pore diameter. The incorporation of various surface ligands into SBA-16 and FDU-1 mesostructures was relatively successful as confirmed by FTIR, TG and elemental analysis. Both functionalized mesoporous cage-like organosilicas showed long-range crystallographic ordering that was gradually reduced with increasing concentration of the introduced functionality. In contrast to the FDU-1 organosilicas, the SBA-16 organosilicas with similar contents of organic pendant groups tended to have lower volume of mesopores, smaller pore size and lower surface area.

This study shows that the incorporation of imidazole, ureidopropyl and bifunctional ureidopropyl-mercaptopropyl groups (with higher contents than 20%) into cage-like mesostructures is more difficult than in the case of smaller ligands such as vinyl
and mercaptopropyl groups, for which incorporation can be performed up to 40% without significant diminishment of the structural and adsorption properties. Therefore, for larger pendant groups studied no transformation from cubic to hexagonal was observed as in the case of small groups.

Finally, mesoporous isocyanurate-containing organosilicas were prepared under acidic conditions by co-condensation of tris[3-(trimethoxysilyl)propyl]isocyanurate (ICS) and TEOS as well as ICS and 1,2-bis(triethoxysilyl)ethane (BTESE) in the presence of B50-6600 and F127 polymeric templates. Ordered large-pore isocyanurate-containing organosilicas with body-centered cubic \( Im3m \) structures were successfully synthesized. The extraction turned out to be insufficient to completely remove the polymeric template. Therefore, an additional heating of extracted samples was performed to free the pores from residual polymer. However, the calcination in air between 200 and 300 °C of both extracted and as-synthesized organosilicas led to the removal of the polymer as well as to a partial decomposition of the ICS bridging groups. In contrast, the thermal treatment of the extracted organosilicas in flowing nitrogen at 360 °C and 315 °C for FDU-1 and SBA-16 PMOs, respectively, was effective for the removal of the remaining template without degradation of organic group. The resulting materials exhibited relatively high loadings of bulky isocyanurate rings, high surface area and large pore volume. Furthermore, the complete removal of large heterocyclic bridges via their thermal degradation in air at 550 °C caused a visible shrinkage of the mesostructure but its ordered nature was retained.
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