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Novel Periodic Mesoporous Silicas: Synthesis, Structure and Properties

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Novel Periodic Mesoporous Silicas: Synthesis, Structure
and Properties

by

Krystyna Czechura

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ABSTRACT

Hybrid organic-inorganic mesoporous silicas represent an important class of materials with a wide variety of potential applications due to their physical robustness and the chemical diversity. This work involves incorporating organic groups into mesoporous materials for the purpose of adding a useful functionality, and their characterization to gain more knowledge regarding the formation of the silicate network at different levels.

A novel Gemini surfactant with a rigid organic spacer is synthesized and used to produce cubic MCM-48 silica mesophase by temperature induced phase transition. The transformation is studied under various pH and temperature conditions to understand the dynamics of the phase curvature change (Chapter 3). Further, to investigate the effect of high density of surface grafted amino groups, post-synthesis modification of grafted 3-halopropylsilane with amine is employed to generate long chain amines on the surface of pore-expanded MCM-41 silica (PE-MCM-41). The performance of such materials for CO₂ adsorption is discussed in relation to the structural differences caused by the choice of the synthetic method (Chapter 4). For the first time, a bridged photoresponsive arylorganosilane 1,4'-bis(triethoxysilyl)azobenzene is used as a precursor for the synthesis of pure azobenzene-bridged organosilica. Reversible photoisomerization of the azobenzene moieties integrated in mesoporous organosilica network is demonstrated indicating that the organosilica remains flexible enough to undergo such contractions under UV irradiation (Chapter 5). Lastly, periodic mesoporous organosilica is

synthesized using two silsesquioxane precursors containing bulky dimethylphenyl and a smaller ethylene spacer, and the 2D ^{29}Si - ^1H heteronuclear correlation technique is employed to specifically address the issue of structural homogeneity in the bifunctional PMO (Chapter 6).

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ABBREVIATIONS

a_0	lattice parameter
BET	Brunauer-Emmet-Teller
BJH	Barret-Joyner-Halenda
cmc	critical micelle concentration
CD	circular dichronism
CP	cross-polarization
CTAB	cetyltrimethylammonium bromide
d_{hkl}	interplanar spacing (with hkl Miller's indices)
IUPAC	International Union of Pure and Applied Chemistry
LC	liquid crystalline
MAS	magic angle spinning
MCM	Mobil Composition of Matter
MS	mass spectrum
NMR	nuclear magnetic resonance
NMP	N-methyl-2-pyrrolidone
P123	(polyethyleneoxide) ₂₀ -block-(polypropyleneoxide) ₈₀ -block-(polyethyleneoxide) ₂₀
PMO	periodic mesoporous organosilica
PMS	periodic mesoporous silica
rt	room temperature
SBA	Santa Barbara University
TEM	transmission electron microscopy
TEOS	tetraethylorthosilicate
TGA	thermogravimetric analysis
UV-vis	Ultraviolet-visible
V_p	pore volume
XRD	X-ray diffraction

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CHAPTER 1

Introduction

1.1. Ordered mesoporous silica materials

According to the IUPAC definition, pores in solid materials are divided in three groups based on their size. Micropores are less than 2 nm in diameter, whereas macropores are larger than 50 nm.[1] Pores with intermediate size from 2 to 50 nm are referred to as mesopores. Porous materials do not always belong exclusively to one category and may have a broad range of pore sizes. The expression nanopore is a loose designation of the pore with diameters in the nanometer range.

Applications of porous materials have been investigated in various fields for decades owing to their high surface area and large pore volume. Progress in the field of nanoporous materials has been often associated with the development of synthetic approaches to achieve more control over the chemical and physical properties of such materials. This includes their (i) porosity, i.e., pore size, pore volume, symmetry and connectivity, (ii) morphology and particle size, (iii) composition, (iv) crystallinity, (v) surface properties, e.g., hydrophobicity, hydrophilicity, redox, and (vi) stability, e.g., thermal, hydrothermal, mechanical. In early development, the property directed material design was achieved by synthesis of materials such as aerogels with large porosity and zeolites with defined pore structure. More recently, a process introducing a novel concept of material design was developed by Mobil scientists, leading to M41S type materials characterized by uniformly ordered mesopores.[2]

The preparation of periodic mesoporous silicas (PMS) involves a supramolecular assembly method in which surfactants mediate the condensation of silica precursors. Owing to their amphiphilic nature, at the critical micelle concentration (CMC1) the surfactant molecules organize spontaneously to form aggregates of colloidal dimensions, the micelles. The self-assembly of the surfactant molecules is seen as a compromise between (i) the tendency to minimize the water contact of hydrophobic groups and maximize their inter-organic interactions, (ii) the tendency for the polar parts to maintain contact with the aqueous environment, (iii) solvation energies that arise from the presence of water, alcohol and other organic molecules. Further increase in the surfactant concentration leads to coalescence of the spherical micelles to form cylindrical micelles (CMC2). Upon addition of the silica precursor, its spontaneous organization through interactions such as hydrogen bonding, Van der Waals forces, electrostatic forces, etc. takes place. Although, the formation pathway of these mesoporous structures is still not completely understood, two general mechanisms: liquid crystal templating (LCT) and cooperative formation mechanism, were accepted based on similarity of the mesostructure of lyotropic liquid crystal from surfactant assemblies and the structures of M41S materials.[3] The LCT mechanism employs CMC2 at which LC phase is formed prior to the addition of the silica source.[4] The cooperative assembly mechanism works below CMC2. It involves the LC mesophase as the template, however, it is believed to be formed after the addition of inorganic precursor.[5]

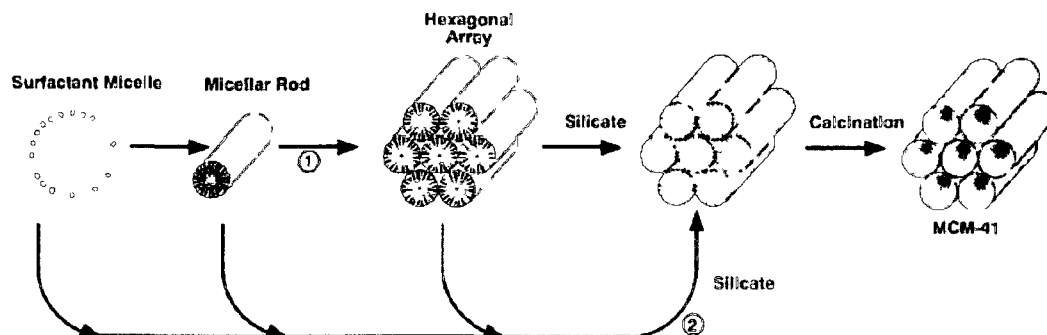
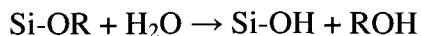


Figure 1.1. Possible mechanistic pathways for the formation of MCM-41: (1) liquid crystal phase and (2) cooperative assembly mechanisms.[3a]

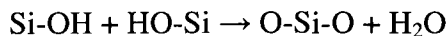
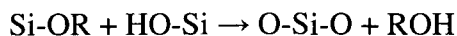
The formation of the surfactant-silica mesophase is based on the electrostatic charge-matching or electrically neutral pathways, as the inorganic precursor (I) and the surfactant (S) can be present as positive, negative or neutral species. The electrostatic interactions of type S^+I^- , $S I^+$ and $S^+X^-I^+$ are operative in the preparation of mesoporous silicas using ionic surfactants.[6] Related mechanisms designated as $(S^0H^+)(X I^0)$ and S^0I^0 were proposed to rationalize the formation of mesophases in the presence of non-ionic structure directing agents (SDA).[7]

When alkoxysilanes are used as the silica source, the polymerization of the precursor is a two step reaction, in which the alkoxide groups attached to the silicon atoms are hydrolyzed and subsequently condense to form siloxane bonds. When sodium silicate or fumed silica is used as the precursor, only condensation reaction needs to be considered.

Hydrolysis:



Condensation:



The hydrolysis and condensation rates depend on the pH of the solution. In acid catalyzed polymerization, condensation is the rate-limiting step in particle growth, while at higher pH, the rate of the polymerization is limited by the hydrolysis reaction, leading to the formation of larger condensed particles. Once the smaller units grow into a three dimensional network around the surfactant yielding a solid product, the surfactant can be extracted or calcined to give the final porous material.

Since the discovery of PMS extensive research has been conducted to gain increasing control over the final structure of these materials.[3] It was shown that the pore size can be tailored by a judicious choice of the preparation method and by using a suitable SDA. Various types of surfactants were used in the synthesis of PMS to meet the requirements of applications where specific pore diameters are needed, mainly to control selectivity and reactivity of the substrate. It was demonstrated that large pores ranging from 6 to 20 nm may be obtained in the presence of high molecular weight oligomers (triblock copolymers) while low molecular weight surfactants (alkylammonium ions) yield materials with smaller pores in range 2 to 4 nm. Control over the mesopore diameter is obtained using alkylammonium surfactants with different tail lengths. Use of different surfactants led to materials with other mesophases than MCM-41. The materials of particular interest are SBA-15 mesophase with large pores interconnected through smaller complementary pores

and high robustness owing to thick walls, and MCM-48 mesophase with three-dimensional array of hexagonal channels. SBA-15 was originally prepared in the presence of neutral Plutonic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) triblock co-polymer as the SDA,[8] whereas, MCM-48 was initially synthesized using an alkylammonium surfactant, and later, Gemini surfactants were introduced for the consistent preparation of this cubic mesophase.[9]

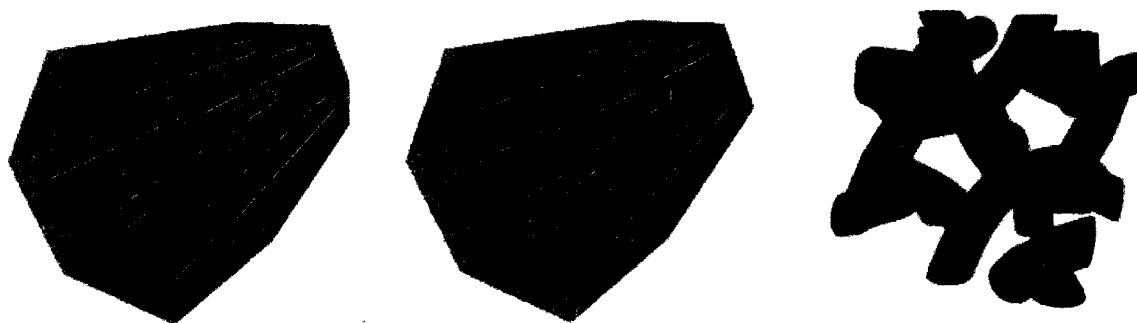


Figure 1.2. Representation of the pore arrangement of MCM-41, SBA-15 and MCM-48.[10]

To rationalize the structure of the mesophase obtained, the classical micellar packing parameter, that defines surfactant organization in amphiphilic LC arrays, was used:

$$g = V / a_0 l$$

where V is the total volume of the hydrophobic surfactant chain plus any co-solvent molecules,

a_0 is the effective hydrophilic headgroup size at the aqueous-micellar surface,

l is the kinetic surfactant tail length.

According to this model, different structures have different intrinsic curvature that depends on the value of packing parameter. As the hydrophilic headgroup size decreases relative to the total volume of the surfactant chain and the corresponding kinetic surfactant tail length, lamellar mesostructures ($g = 1$) are transformed to discontinuous cubic (Ia3d, $g = 1/2$ to $2/3$), hexagonal (P6m, $g = 1/3$ to $1/2$) and bicontinuous cubic (Pm3n, $g = 1/3$).[11,9]

The knowledge regarding the packing parameter was further used towards pore system engineering. Organic additives that dissolve in the surfactant tail region were used to change the curvature or the pore size. This process of pore expansion became one of the most effective ways to obtain mesoporous materials with large pore diameter, i.e. > 4 nm, and was achieved using 1,3,5-trimethylbenzene, triisomethylbenzene and alkanes.[12] The hydrothermal post-synthesis treatment of MCM-41 was discovered to also lead to enlargement of the pores.[13] It was later proven that the alkyltrimethyl ammonium ions partially decompose during the treatment, gradually generating a swelling agent, namely dimethylalkylamine causing increase in their size.[14] Finally, addition of long chain alkyl amines in a post-synthesis hydrothermal treatment of MCM-41 lead to enlargement of the pore size up to ca. 20 nm.[15] It was further reported, that during the hydrothermal treatment the stability of mesoporous silica can be improved remarkably by using salt effects.[16]

1.2. Framework modification

The range of compositions was further extended from pure silica by incorporation of various heteroatoms and by using other metal oxides or chalcogenides.[17,18] To introduce properties not attainable with purely inorganic PMSs, methods allowing functionalization of the internal surface of the host with an organic moiety via post-synthesis grafting or via one-pot co-condensation approach were developed.[19] In the post-synthesis grafting procedure, organic groups are incorporated by the reaction between uncondensed surface hydroxyl groups and an organosilane that bears a suitable functional group such as trialkoxysilane $X-Si-(OR)_3$ or trichlorosilane. This reaction yields surface grafted silane group $X-Si-[(OR)_n(O-surface)_{3-n}]$; $n = 0-2$ and an alcohol or hydrochloric acid. The drawbacks of the post-synthesis grafting strategy are that it is limited by the reactivity of the surface hydroxyl groups, their density and distribution. In addition, introduction of organic groups by post-synthesis grafting often leads to inhomogeneous distribution of the organic groups, as a consequence of diffusion limitations during the surface reaction, and therefore grafting often takes place at the pore openings. Moreover, anchored molecules often occupy a substantial part of the channel volume which can lead to pore blocking.[20]

The modification of the surface by the one-pot co-condensation method offers several advantages such as short preparation time, avoidance of pore blocking, greater amount of functional groups and their homogeneous distribution on the surface. However, in the material modified this way, the organic units become a direct part of the mesoporous framework and therefore extend less into the pores consequently becoming less accessible. The produced materials also display less defined pore size distribution, moreover, above

trialkoxysilane loading of around 25% the order is lost and the mesostructure collapses. Further, the organic precursors have to be selected in consideration of experimental conditions, such as solvent extraction, so it is not converted to another group by a side reaction.

Up to date, numerous types of organically modified mesoporous silicas have been prepared and used in a wide range of applications including catalysis, sensing, optoelectronics, separation and adsorption. Considerable attention has been focused on tailoring the chemical composition of surface modified silica, while aminopropyl have been the most widely used functionality for various applications including base-catalyzed reactions and CO₂ adsorption.

1.3. Periodic Mesoporous Organosilicas

In an effort to overcome the limitations of silica functionalization, the concept of organic surface modification of periodic mesoporous silica was expanded in 1999, by introducing organosiloxane precursors $[(RO)_3Si-R-Si(OR)_3]$; R = organic spacer] as the network forming species.[21-23] The transfer of the concept of the structure-directed synthesis of pure silica mesophases to the bis-silylated organosilica precursors gave rise to a new generation of nanoporous materials with high loadings of framework organic species termed periodic mesoporous organosilicas (PMOs) in which the organic bridges are integral components of the silica network.

Insertion of organic spacers into sol-gel silicate networks was reported prior to the discovery of PMOs. Slower condensation kinetics of hybrid precursors compared to their

inorganic counterparts was observed using NMR, suggesting that the silanol groups are too isolated to quickly react with the matrix.[24] Possibly due to these inherent differences between silica and organosilica precursors and low yields obtained during the organosilsesquioxane synthesis, the idea of combining templating synthetic approach and organosilsesquioxane polymerization was realized much later. PMOs opened up a broad range of research opportunities. The “soft” organic component is capable of modifying the chemical properties of the resulting materials and therefore greatly expanding their applications.

1.3.1. Literature review

Here, we summarize the recent developments in the synthesis of pure periodic mesoporous organosilica materials and their applications. Materials synthesized with the aid of inorganic silica source will be beyond the scope of this review.

1.3.1.1. Discovery of PMOs

The early reports on PMO focused on materials containing aromatic and aliphatic bridging groups. The first PMO materials reported by three independent research groups were comparable to purely inorganic materials, they had high surface areas of up to 1200 m²/g and narrow pore size distributions. Inagaki et al.[21] successfully prepared highly ordered mesoporous ethane-bridged PMO templated by alkyltrimethylammonium chloride surfactant. XRD pattern, TEM data and calculated unit cell parameter values were

representative of 2D or 3D hexagonal mesophase, depending on the synthesis temperature and the alkyl chain length of the surfactant. SEM analysis of the morphology of the materials showed the formation of hexagonal rods in 2D hexagonal sample and spherical particles in 3D hexagonal sample. The specific surface areas were 750 and 1170 m²/g, with pore diameters of 3.1 and 2.7 nm for the 2D and 3D hexagonal materials, respectively. The lack of Q-species in ²⁹Si NMR spectra was strong evidence that the Si-C bond was stable under the synthesis conditions.

Stein et al.[22] prepared organosilica in the presence of cetyltrimethylammonium bromide (CTABr) using ethane- and ethylene-bridged siloxane precursors. The obtained materials had surface areas of approximately 1200 m²/g and narrow pore size distributions. TEM measurements, however, indicated the presence of worm-like pore architecture. Further experiments showed that the high organic group content of periodic mesoporous organosilica leads to superior materials properties such as increased stability and hydrophobicity concurrent with the ability to adsorb organic compounds. Also, to demonstrate the accessibility of the organic linkers, ethylene-bridged PMO was reacted with bromine gas. The ¹³C CP NMR measurements confirmed the presence of brominated carbons that constituted around 29% of the total carbon content. Ozin et al.[23] showed that prolonged treatment of the ethylene organosilica with bromine in refluxing dichloromethane ultimately affords complete halogenation reaction. However, only 10% of these bonds reacted with bromine due to the competing hydrogenation process with the solvent or moisture. Sayari et al.[25] demonstrated that elimination of moisture during the reaction with gaseous bromine increases the conversion to 51%. The remaining fraction of the framework ethylene double bonds buried within the pore walls was not accessible to

bromine. In fact, despite the chemical similarity of framework bridging groups and grafted groups, in material containing ethylene moieties bonded in two different ways, terminal groups can selectively undergo chemical modification.[26]

Ozin et al. also studied co-condensation of 1,2-bis(triethoxysilyl)ethylene with TEOS using CTABr as the structure directing agent. Using TEM and nitrogen adsorption analysis, increased order of the materials with higher TEOS content was observed. ^{29}Si NMR analysis showed that the removal of the surfactant increases the intensity of T^2 peaks relative to T^3 [$\text{RSi}(\text{OSi})_n(\text{OH})_{3-n}$; $n = 1-3$], indicating a decrease of electron density of surface silanols.[27]

1.3.1.2. Further development of PMOs

Molecular-scale order

The early work on organosilicas, researchers focused on synthesis of materials containing methane,[21] ethane,[21,22] and ethylene bridges[21-23] due to the commercial availability of the precursors and ease of the material synthesis. In 2002, Inagaki et al.[28] extended the library of such materials by introducing benzene-bridged PMO. The distinctive feature of the material was not only its novel organic moiety, but also the molecular-scale order observed, that gave rise to a series of sharp, intense and equidistant XRD signals. These diffraction peaks with lattice spacing of 7.6 Å represent the O...O distance in the precursor. TEM images of the material supported this finding, as lattice fringes with matching spacing were observed. This indicated that the organic spacers are stacked in a lamellar structure within the pore walls. Corresponding lattice spacing of 5.6 Å was observed in mesoporous ethylene. Other organosilicas with crystal-like wall structure

containing aromatic groups were reported by Inagaki (1,4-phenyl[29], biphenyl[30], naphthylene[31]), Sayari (divinybenzene[32], azobenzene[33]) and Fröba (divinylstilbene, divinylazobenene[34]).

1,3-benzene-bridged organosilica with molecularly ordered pore walls was prepared by Inagaki's group to demonstrate that the interlayer spacing is not confined only to the molecular geometry. Although, its structure is unlike that of 1,4-substituted benzene, the moieties present in the framework order themselves in such a way, to display the interlayer distance equal to the 1,4 system. Indeed, the results of molecular simulations revealed that bond angles and distances are different for each system.[35]

The periodicity observed for a particular system also depends on the synthesis conditions. It was demonstrated that if the PMO material does not fully condense, the hydroxyl groups formed may stabilize the structure via interlayer hydrogen bonding. As a result the organosilica layers would substantially elongate and the resulting interlayer distance observed would be about 2.5 Å larger than in conventional crystalline PMO. However, the influence of the hydrogen bonding on the average lattice spacing varies with the degree of silicate condensation. Benzene-silica with large amount of Si T¹ and T² species (low degree of condensation), showed structural periodicity of 10.1 Å.[36] In contrast, phenylene-bridged silica with mostly T² and T³ species, was reported to have a peak at $d = 9.3$ Å in addition to peaks indicating molecular-scale periodicity of 7.6 Å.[37]

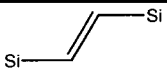
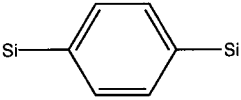
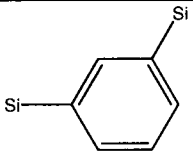
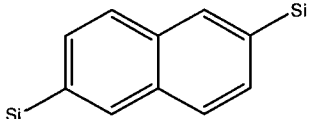
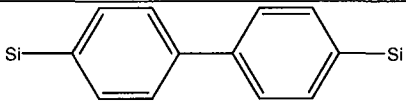
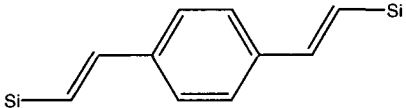
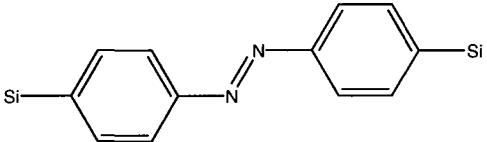
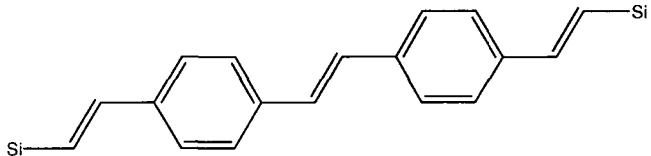
In a different case,[38] phenylene-silica material with lamellar structure was obtained. The XRD pattern of the organosilica sample displayed periodicity of 4.2 Å, associated with the stacking of phenylene moieties due to π - π interactions. While there was no report on a PMO material displaying π - π and interlayer periodicity simultaneously, it is exclusively PMOs

with aromatic groups that exhibit long range molecular order. Therefore, although π -stacking may be in one with interlayer hydrogen bonding the driving force for the organization of organosilicas, it is believed to be weakened during the polymerization as an expense of energy optimization. In fact, conformations obtained by computer simulation and energy minimization display random orientation of the aromatic groups in materials that exhibit interlayer periodicity.[39,40]

Inagaki et al.[37] showed, it is also possible to derive crystal-like PMO from allylorganosilane precursor, which in some cases may be more chemically accessible. Here, mesoporous order and molecular scale organization of the material was found to depend on the amount of base in the synthesis mixture. To obtain stable and well organized crystalline material, the synthesis temperature had to be close to 90° to allow for sufficient condensation. Similar materials obtained via co-condensation with TEOS displayed relatively broad XRD peaks at higher angles, indicating poor crystallinity. However, as expected, higher surface areas were observed for these materials prepared by addition of inorganic precursor to organosilsesquioxane, at the expense of molecular-scale periodicity.

It was shown that if the synthesis conditions are chosen carefully, the molecular order can also occur in PMO materials prepared under acidic conditions. Interestingly, phenylene-silica prepared by Sayari et al.[41] in the presence of acid revealed no higher order X-ray diffraction peaks, however some fine lattice fringes were observed in TEM images of this material, indicating partial molecular ordering in the walls. The observed ordering of the bridged molecules was not at right angles with respect to the pore channels, as in materials prepared in basic conditions, but at an angle of about 57°.

Table 1.1. Periodicities observed in PMO materials.

PMO structure	Observed periodicity; Å
	5.6
	7.6 (10.1 ^a , 9.3 ^a , 4.2 ^b)
	7.6
	4.49 - 4.70
	11.6
	11.9
	(16.6 ^a)
	18

^a periodicities observed in materials with low degree of polymerization i.e. interlayer hydrogen bonding

^b periodicity in a material displaying parallel stacking of organic moieties

Inagaki et al.[42] demonstrated that treatment of PMO materials prepared under acidic conditions, with alkaline solution improves the periodicity within the pore wall. The increased crystallinity of the treated samples is believed to be induced by more complete hydrolysis of the precursor molecules and therefore by increased hydrophobicity of the silyl

groups. Sayari et al.[32] pointed out that material prepared in the absence of surfactant, but under the same basic conditions as conventional PMO, will display molecular order without the occurrence of a periodic pore system. Similarly to organosilica prepared with sol-gel method,[24,43] the divinylbenzene-silica material prepared exhibited high surface area of 202 m²/g and a broad distribution of small mesopores.

Precursor preparation

During early stages of research on PMOs, several reports dealt with novel preparation methods of organosilica precursors. Initial preparations usually employed Grignard or BuLi reagents to obtain organoalkoxysilane from bromo-substituted precursors and TEOS, in yields of 11-55%. To obtain organosilica precursors in higher yields and purity, synthetic routes that used catalysts were explored. Rhodium(I) was found to be an effective catalyst for silylation of a wide range of aryl halides.[44,45] Replacing the leaving group of bromo-precursor with iodine, gave significantly higher yields. In the case of aryl bromides, increase in reactivity is observed upon treatment with equal amount of tetra-*n*-butylammonium iodide. Palladium(0) catalyst/ligand system has been developed that allows for the silane to be added via Heck reaction between vinyltriethoxysilane and aryl halide. Although, the newly formed double bonds of the organic unit make the precursor bulkier and more difficult to handle, they offer new opportunities for chemical modifications.[32] Coupling reaction of triethoxysilane with aryl iodines in the presence of palladium catalyst was also successfully employed for the preparation of organosilica precursors.[33]

Incorporation of organic functionalities in the framework can be thought of as a replacement of oxygen atoms in some of SiOSi linkages by organic groups. Such organic

moieties can bind more than two silyl groups, therefore creating more possibilities in obtaining materials with desired functionality. Due to slower kinetics of decomposition, it is expected that these materials would exhibit improved stability. For instance, Ozin et al.[46] synthesized 1,3,5-benzene silica bonded via three Si-C linkages within the network. Indeed, enhanced thermal stability was observed due to the larger number of bonds required to be cleaved compared to PMOs with two-point attachment. Moreover, higher amount of silyl groups can aid to decrease of hydrophobicity of molecules with bulky organic spacer, to allow for their use as PMO precursors. Ozin et al.[47] have found that C₆₀ can be functionalized with multiple 3-aminopropyltriethoxysilane groups and subsequently used as PMO precursor. Material derived from such precursor lacked long range order, however dilution with TEOS allowed for a preparation of organized material with up to 91 %vol of C₆₀. Osmium tetroxide reacted with remaining double bonds of C₆₀ was used as a label, to show uniform distribution of the fullerenes in the network using energy dispersive X-ray fluorescence.

Silsesquioxanes typically have just one organic group bound to each silicon atom, although more than one oxygen atom can be replaced with an organic group. Such cyclic precursor with Si/R ratio of one was prepared by Ozin group.[48] The material derived from it had a surface area of 1706 m²/g and pore diameter of 2.5 nm. ²⁹Si NMR signals observed at -17 and -25 ppm were attributed to D² and D¹ sites [(CH₂)₂Si(SiO)_n(OH)_{2-n}; n = 0-2]. Dendrisilicas were also prepared using similar analogy.[49] Vinyl groups interconnected with silicon atoms and terminated with chloro groups to form various cores were used as basic units. Further, a second-generation dendimer was synthesized by replacing the chloro groups by vinyl groups and subsequent hydrosilylation. These precursors, terminated with

trialkoxo silyl groups, lead to well organized materials with surface areas up to 1102 m²/g.

²⁹Si NMR spectra, in addition to peaks attributed to T species, showed 3.5 ppm signal due to SiC₄.

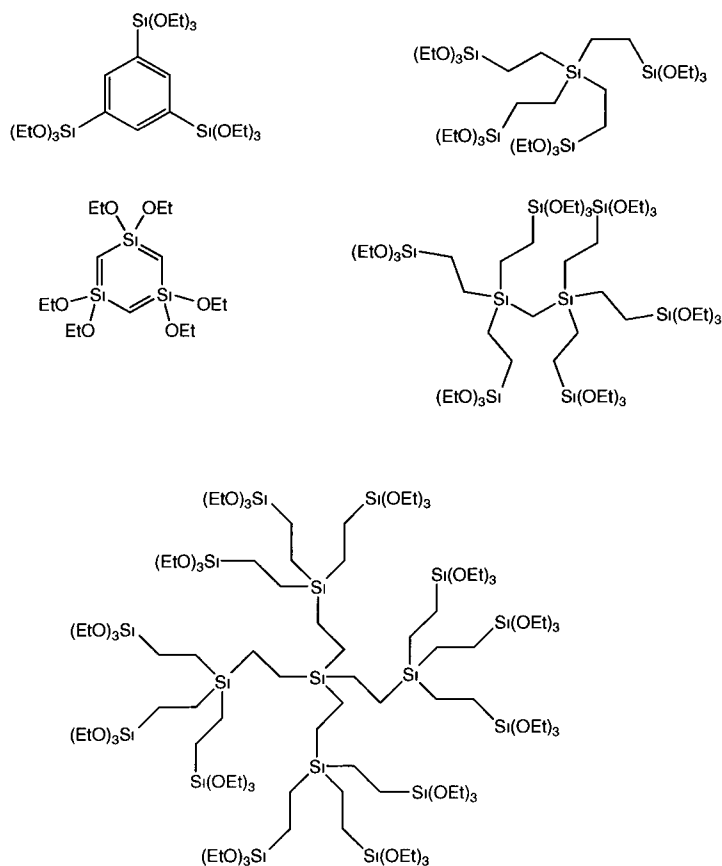


Figure 1.3. Examples of organosilica precursors with different connectivity.

Modification of ethene silsesquioxane

With few exception, attempt to incorporate bulky functional groups into the framework resulted in disorganized PMO materials. However, accessibility of organic moieties in the pore walls of organosilicas provides opportunities for further functionalization by chemical transformation of simple PMO. Recently, Kondo et al.[50] modified ethene-silica to introduce sulfonated phenylene groups into the material. The organic groups were transformed through Diels-Alder reaction with benzocyclobutene, followed by sulfonation with concentrated H_2SO_4 . Total number of introduced groups was quantified by titration to be 1.44 mmol/g, indicating that around 19% of the ethylene groups were accessible to reactant molecules. NMR studies confirmed the absence of Si-C bond cleavage and the presence of Ph-SO₃H groups. Matching nitrogen adsorption isotherms of the samples prior and after chemical modification indicated the preservation of the original mesoscopic structure. The activity of Ph-SO₃H functionalized silica for acetate formation, Beckmann and pinacol rearrangements was remarkably higher than that of other heterogeneous catalysts and comparable to that for concentrated H_2SO_4 . The high activity of the material in acid-catalyzed reactions was attributed to the high density of the active sites and their ease of access by the reactant molecules inside the mesopores.

Polarz et al.[51] demonstrated that PMO building blocks can be modified prior to the material assembly. First, bis(trimethoxysilyl)ethene was enantioselectively hydroborated in the presence of rhodium(I) chiral catalyst. Subsequent addition of organic peroxide in methanol afforded oxidation of B-C bond. The reaction mixture was directly used in ordered organosilica preparation in the presence of cationic surfactant. The surface area and the pore size of the obtained chiral material were 1093 m²/g and 2.86 nm.

Phenyl and biphenyl derivatives

Synthesis of phenylene PMOs substituted with different functionalities was accomplished by Ozin.[52] These novel PMOs were proposed to lead to a wide range of derivatives with various properties via simple chemical transformations. Toluene-, p-xylene- and 1,4-dimethoxybenzene-bridged organosilica precursors were afforded via Grignard reaction in 32 - 44% yield. X-ray diffraction patterns of the new materials, showed sharp low angle peaks. In addition to the template extraction, water removal significantly improved the organization of the material, apparent in the significant increase of the diffraction intensity. Improved organization of the material was less striking in the case of electron-rich dimethoxybenzene-silica. Also, ^{29}Si NMR displayed relatively larger amount of uncondensed sites with increasing bulkiness of the side groups, from toluene to dimethoxybenzene-silica. Increasing spatial demand of the bridging groups was also manifested in the increase of the wall thickness from 19 to 25 Å.

Alternative approach to the fabrication of functionalized phenylene organosilica derivatives is modification of framework moieties of benzene-bridged PMO. Using this approach, amination of phenylene bridges was performed by Inagaki et al.[53] via two-step reaction with mixed acid solutions of $\text{HNO}_3/\text{H}_2\text{SO}_4$ and SnCl_2/HCl at 27 °C for 3 days each. Successful modification of the materials with amine groups was confirmed by Fourier transform infrared and NMR measurements. The mesostructure of the material produced was retained and the surface area was found to decrease only by 8% despite the severe synthesis conditions. The furnished organosilica efficiently catalyzed Knoevenagel condensation reaction at 60 °C in toluene, yielding quantitative amount of 1,1-

dicyanophenylethylene after 3 h. The results suggested high robustness of the catalyst for recycled use.

Modification of 1,2-ethyltriethoxysilane PMO monomer was also applied to develop “all-in-one” organosilica precursor.[54] Organosilsesquioxane with template covalently bound to the organic linker was synthesized by hydroboration reaction of the double bond followed by substitution of alkyl chain. This precursor underwent self-organization and hydrolysis in the presence of acid. Cleavage of the C-B template-monomer bond by aminolysis gave mesoporous organosilica with amine functionalized channel walls. Surface area of 974 m²/g and pore diameter of 3.9 nm ensured accessibility of the amine groups. Cu(II)-binding experiment revealed high availability of the amine groups that allowed to bind 27 mol% of copper with respect to the amine content.

Chemical modification of PMOs with simple bridging moieties may be limited by the reactivity of the intermediate under conditions that are not destructive to the PMO framework. Polarz et al.[55] was able to synthesize 1,3-bis(trialkoxysilyl)-5-bromobenzene PMO precursor that was then used to synthesize a small library of phenyl PMO derivatives by either modifying the organic linker prior or after the hydrolysis in presence of a structure directing agent. It was found that when the chemical transformation is done at the level of PMO precursor, the choice of the alkoxide group is crucial. Larger alkoxide groups such as tert-butoxy and iso-propoxy offer higher stability during the treatment, leading to higher yield. However, precursors containing tert-butoxy groups, display slow condensation kinetics leading to unsuccessful PMO material preparation. On the other hand, only materials with wormhole-like mesostructure could be obtained from isopropoxysilyl

derivatives, as isopropyl alcohol obstructs the structure-directing action of the template due to its excellent solvent properties.

Multifunctional PMOs

Elaboration of PMOs by incorporating multiple functional bridging groups allows to further expand the range of PMO applications by finely tailoring the properties of the resulting materials through variation of the content of the two functionalities. One way to generate PMOs with different functionalities is to use multiple organosiloxane precursors. However, differences in hydrolysis and condensation rates of the precursors may lead to phase separation or inhomogeneous products, therefore, often organic precursors with comparable chemical reactivity are used. Preparation of material composed of two precursors with different hydrolysis and condensation kinetics is more challenging, since the synthesis procedure has to be carefully designed to avoid large decrease in mesostructural order and surface area. Often, different hydrolysis and condensation efficiencies may result in monomers incorporation into the final material with different ratio than in the synthesis gel.

The first report on bifunctional organosilica dealt with co-condensation of ethylene and phenylene-bridged silanes in the presence on Brij79 surfactant.[56] ^{13}C and ^{29}Si CP MAS NMR spectra of the copolymers indicated the presence of both functionalities with higher relative phenylene monomer contribution to the formation of the final material. Up to three distinct organic groups were incorporated into this type of materials by Jaroniec's group.[57] ^{29}Si NMR spectra of the bifunctional and trifunctional organosilica products were simulated, deconvoluted and integrated. The obtained values represented relative

composition of Tⁿ species of each moiety in the material. The degree of hydrolysis of the silane monomer was found to depend not only on the nature of the organic bridge but also on the ratio of the monomer relative to the other precursors. Overall, hydrolysis of ethane-bridged silane was more complete than that of phenylene and thiophene containing silane.

Organosilica precursors with small bridging groups could also be used in place of tetraethoxysilane to be able to incorporate larger bulky precursors into the framework. The examples include chiral trans-(1R,2R)-bis-ureido-cyclohexane and R-(+)-Binol silica co-condensed with ethane silica.[58,59] Increasing the amount of bulky precursor to above 10%, however, often leads to disorganization of the pore structure, because of the higher steric demand of the linker, producing samples with wormlike motif or microporous structure.

Laser Raman spectroscopy was performed by on materials containing thiophene and phenylene organic linkers to determine their chemical composition.[62] Due to the loss of symmetry around the bridges in the solid material, influenced by the surrounding environment, complex spectra were obtained. Peaks corresponding to vibrational modes characteristic only of the given moiety were selected and the peak areas calculated. Linear relationship was confirmed between the peak area of the aromatic units in PMOs and the molar ratio of the corresponding precursors in the reaction mixture. Since, the vibrational spectroscopy is not a reliable method for monitoring the integrity of the Si-C bond, calibration using solid-state NMR was necessary.

Sayari and Yang studied bifunctional organosilica materials synthesized using different molar ratios of phenyl- and biphenyl-bridged precursors.[60] Various characterization methods such as TEM, SEM, EDX and nitrogen adsorption failed to

discriminate between the formation of a single phase with both spacers randomly distributed or some level of segregation. However, two distinct series of molecular-scale periodicities of phenyl- and biphenyl-bridged PMOs were observed by X-ray diffraction. This indicated that phase separation or phase segregation occurred even in organized materials.

Although, the structure and composition of bifunctional PMOs have been extensively characterized by various methods, only limited information as to whether one or more phases occur when multiple precursors are used is available. Khimyak et al.[61] synthesized bifunctional periodic mesoporous organosilica with ethane and ethene bridging groups and used NMR as the main characterization tool. ^1H - ^{13}C CP MAS NMR kinetic experiments enabled only to identify organic group with different mobility. Groups with faster cross-polarization kinetics were associated with organic moieties residing at the wall interface. ^1H - ^{29}Si NMR kinetic curves were analyzed to observe differences between the relaxation times of monofunctional and bifunctional PMO T sites [$\text{CSi}(\text{OSi})_n\text{OH}_{3-n}$, $n = 1-3$], and suggested their unique level of organization. Only ^1H - ^{29}Si HETCOR experiments provided an unambiguous answer concerning the spatial proximity of the two organic moieties.[62] The homogeneity of the samples prepared for the study was controlled by the prehydrolysis conditions. Separate prehydrolysis as opposed to joint prehydrolysis led to domain formation within the material. The presence of cross-peaks in HETCOR spectra correlating ^1H resonance of one bridging group to the silicon sites of the other linking moiety indicated that the two functionalities were more homogeneously distributed throughout the framework of jointly prehydrolyzed samples.

1.3.1.3. Advanced PMOs

Both mesoporous organic and inorganic frameworks are highly regarded for a large range of possible applications; however, advances in the preparation of mesoporous inorganic silica materials have far outpaced their organic counterparts. Recently, a number of mesoporous organosilica materials have been reported with the aim of increasing their potentiality with respect to applications.

Chiral PMOs for chromatography and catalysis

The increasing demand for enantiomerically pure compounds has prompted the design and synthesis of chiral organosilicas. Initial attempts dealt mostly with diaminecyclohexane and Binol derivatives towards the synthesis of PMOs. The synthesis of these materials was achieved only in combination with a large fraction of inorganic silica source to stabilize the network. In addition to the challenges encountered during the incorporation of these bulky functional groups into the framework, it was difficult to avoid the racemization of the chiral centre due to harsh synthetic conditions.[63]

Polarz and Kuschel reported synthesis of organosilicas from chiral precursors, however, the chiral character of the obtained materials was not investigated.[51,54] Determination of enantiomeric purity in PMO was achieved for the first time by Inagaki et al.,[63] by eluting organic groups with HF treatment and subsequent stereospecific oxidation of silicon-carbon bonds to yield the corresponding alcohols (Tamao oxidation). The enantiopurity of 95% was reported for the phenylethane-bridged chiral organosilica prepared in acidic conditions, and matched that of the precursor used. Nitrogen adsorption isotherm of

the material revealed the presence of uniform micropores and a high surface area of 1180 m²/g. The same chiral precursor was mixed with phenyl-bridged silane to obtain bifunctional material in basic medium. Loss of the optical activity of the mixed material was ascribed to the severe synthesis conditions.

Chiral organosilica derived from a precursor with rigid benzylic ether bridge attached to silicon atoms was synthesized by Fröba et al.[64] The precursor was obtained by a four-step reaction starting from 1,4-dibromobenzene. Use of chiral ruthenium catalyst in an asymmetric hydrogenation reaction afforded the product in good enantiomeric excess of 88%. Surfactant assisted assembly yielded material with surface area of 820 m²/g and average pore diameter of 2.3 nm. To measure the chirality of the organic constituent a non-destructive method was chosen; the optical activity measurement was adapted for solid-state samples. The measurements on suspended solids are complicated by light-scattering which changes the rotation-magnitude. To allow for the measurement to be valid, the phenomena of particle scattering needed to be concealed since it is not a manifestation of optical activity. This can be done by matching the refractive index of the suspending media and finely-powdered crystals. Therefore, the sample was suspended in a carefully chosen non-chiral solvent (1:1 ethanol/chloroform) for the measurements. As expected, the rotation angle was found to be directly proportional to the concentration of PMO. The measured optical activity of the precursor of -200° dm⁻¹ at 633 nm, and -275° dm⁻¹ for the corresponding PMO product, confirmed the presence of the chiral units.

Many reports dealt with incorporation of diaminocyclohexane into the silica by various methods such as grafting or co-condensation with TEOS. However, pure monofunctional PMO was not afforded to date. Li et al.[58] successfully synthesized

bifunctional organosilica consisting of chiral *trans*-(1R,2R)-bis(propylureido)cyclohexane and ethane bridged silica framework. The molar ratio of the two precursors was adjusted to control the morphology, as a result a sample with uniform particle size of 6-9 μm and smooth surface texture was obtained. In order to ensure good performance of the material as a chiral stationary phase in high performance liquid chromatography (HPLC), the N,N-dimethyldecylamine was used as a pore expander to enlarge pore size from 1.7 to 10 nm, and the surface silanol groups were capped with trimethylethoxysilane. The final material obtained using 30% of the chiral precursor showed a good surface area of 597 m^2/g and a pore volume of 0.66 cm^3/g . The chromatographic separation of R/S-1,1'-bi-2-naphthol enantiomers was studied by HPLC, using a column packed with the material. High permeability due to the morphology and high ligand loading of 0.93 mmol/g enabled fast separation at high flow, thanks to low back pressure. Efficient resolution was achieved at flow rates as high as 2.5 ml/min. Baseline separation in this case was R_s 1.58 and the retention times 1.0 and 1.7 min.

In addition to chromatography, organosilicas with chiral bridges are also suitable as ligands for performing asymmetric catalysis. A chiral R-(+)-Binol-organosilica material was synthesized for preparing optically active products by addition of diethylzinc to benzaldehyde.[59] (R)-2,20-Dimethoxy-6,60-di-[(2-trimethoxysilyl)-ethenyl]-1,10-binaphthyl was used as precursor and co-condensed with 1,2-bis(trimethoxysilyl)ethane in the presence of P123 surfactant. The obtained materials contained 10 to 100% of R-(+)-Binol-bridged precursor; however, only the TEM images of the sample with a chiral silane fraction of 10% showed well ordered hexagonal mesostructure. Addition of larger amount of precursor led to worm-like pore arrangement, whereas, material with exclusively R-(+)-

Binol moieties was found to be amorphous. Treatment with BBr_3 to deprotect hydroxyl groups followed by reaction with $\text{Ti}(\text{O}^i\text{Pr})_4$ furnished the complex. Although successful incorporation of the chiral groups was proven by NMR and IR, some Si-C bond cleavage was observed. To ensure that the chiral character of the bridging group was maintained, circular dichroism (CD) spectroscopy was employed. The negative Cotton effect measured for the organosilica dissolved in 1M NaOH indicated that the chiral character was maintained during the material synthesis. The novel catalyst synthesized using 40% of R-(+)-Binol containing precursor could catalyze asymmetric addition of diethylzinc to aldehyde with high yield of 99% after 24 h. The material gave moderate selectivity of 39.7%, which was lower than that of corresponding homogenous catalyst (94%), possibly due to the steric constraints imposed on the catalyst by the surrounding framework.

Crudden et al.[65] presented a new organization mechanism in PMO. Mesoporous material composed mainly of biphenyl silica was doped with low concentration of a precursor with chiral bridge to induce chirality in the framework. This chiral amplification by cooperative interaction was possible due to the high rotational barrier of 40 kcal/mol around the biphenyl C-C bond. The dopant chosen for transmitting chirality was 4,4'-bis-(triethoxysilyl)-6,6'-dimethyl-2,2'-dimethylester-1,1'-biphenyl. It was prepared from 2-nitro-3-methylbenzoic acid by an eight-step reaction with overall yield of 26%. Materials containing 15, 30 or 100% of the M or P biphenylester enantiomers showed strong CD signals. However, PMO derived from 15% of the chiral precursor and TEOS did not display the characteristic CD signal, indicating that the intermolecular interaction is crucial in transmitting absorption wavelengths observed in CD spectra. This observation proved that the two different monomers indeed interact with each other to create homochiral domains

within the framework. Reorganization of the material and loss of the CD signal upon hydrothermal treatment further supports this phenomenon.

Photosensitive PMOs

Obtaining PMOs that are responsive to external stimuli in a controlled manner was long desired. The first example of such material was presented by Lu et al.[66] The synthesized PMO containing a diacetylene bridge revealed intense chromatic switch from blue to red in response to external stimuli, in this case being temperature. The precursor was synthesized by reacting 12-docosadiyndioic acid with two stoichiometric equivalents of isocyanatopropyltriethoxysilane. Synthesis of the corresponding PMO followed by surfactant removal gave a material with organic units forming highly ordered molecular close packing, which ensured the consequent topo-polymerization of the diacetylene units. Diacetylene is known to undergo a blue-to-red adsorption band shift upon increase in temperature, due to an increase in the HOMO-LUMO spacing of the delocalized p electrons. The colorimetric changes can be easily perceived by UV-absorption spectroscopy and are defined as the percentage of blue-to-red transition. The colorimetric response was measured to be 14% at 103 °C and decreased to 0.2% at 20 °C, over 15 thermal cycles, illustrating the exceptional reversibility of the material. The rigidity of the silica network enhanced the thermal stability of the material, therefore increasing the onset temperature at which the diacetylene units disorder and become irresponsive.

Although other materials with conjugated organic molecules and potential optical properties have been prepared, their potential applications were investigated only recently.

These compounds with organic conjugated systems display luminescent properties and have potential for optoelectronic applications.

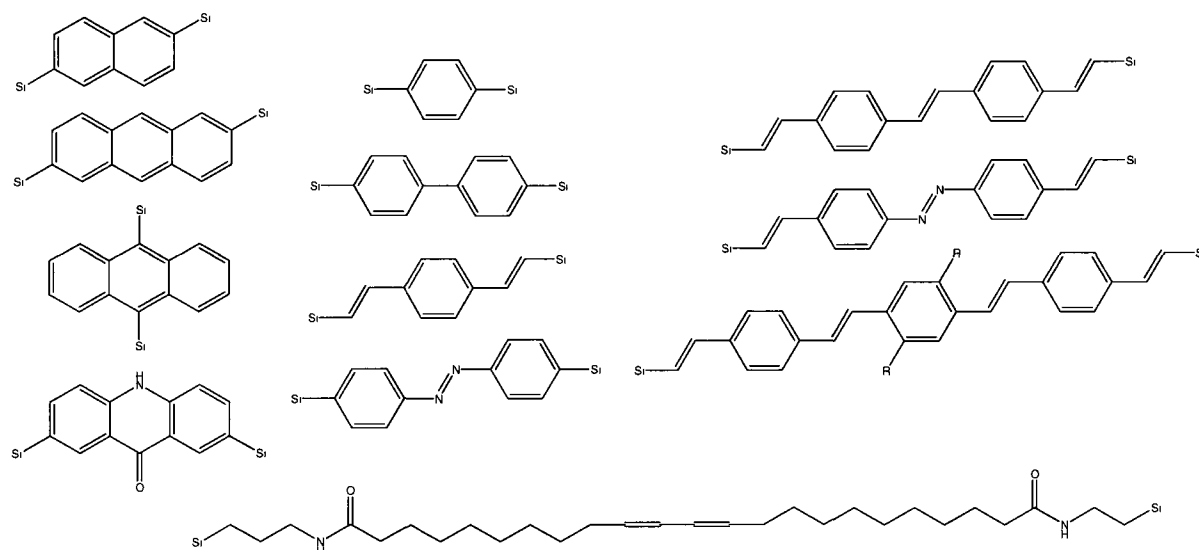


Figure 1.4. Schematic structures of organic-bridges of PMOs displaying luminescent properties.

Sayari et al.[32] first reported the synthesis of PMO with fully conjugated 10 π -electron system. Fröba et al.[34] further increased the number of π -electrons in PMO bridge to 18 electron system by introducing 4,4'-divinylstilbene and 4,4'-divinylazobenzene bridged organosilica precursors. Due to high hydrophobicity of these precursors the obtained materials had a poor or no periodicity. XRD of divinylstilbene-bridged organosilica revealed a broad reflection in the small-angle region indicative of a poor order. Indeed, TEM micrograph showed worm-like mesoporous structure. The BET surface area and pore size of this material were measured to be 620 m²/g and 5.4 nm respectively. The XRD of the corresponding divinylazobenzene organosilica did not display periodic organization. Some

worm-like porosity was apparent in the TEM image and the nitrogen physisorption measurement indicated the presence of large pores with diameter of 8.1 nm and a surface area of 240 m²/g. Although, control over the organization of these materials was hard to achieve, materials with absorption in the visible light region were obtained. The UV spectra displayed absorbance bands up to 412 and 530 nm for 4,4'-divinylstilbene organosilica and 4,4'-divinylazobenzene, respectively.

A rigid PMO precursor containing azobenzene bridge was synthesized by Sayari et al.[33] with the hope of obtaining good control over the PMO organization. The resulting material displayed pore diameter of 3.9 nm and a specific surface area of 384 m²/g, however, only samples with PMO content below 20% showed hexagonal arrangement of mesopores in TEM micrographs. For the first time, however, pure mesoporous organosilica was shown to respond to light in a controlled manner. Reversible *trans*-to-*cis* isomerization of the azobenzene moieties integrated in the framework was induced using UV irradiation. The UV absorption spectra of the organosilica sample displayed two bands at 325 and 450 nm, attributed to the *trans* and *cis* isomers, extending into the green part of the spectrum giving the sample orange colour. Exposure of the sample to 8 W of UV-A for 30 min gave a strong response. The initial *trans* population was restored after 1 day under ambient conditions.

It is known that different π -conjugation patterns and substituents have a dramatic effect on electronic properties of oligo(phenylenevinylene) (OPV) containing materials, causing apparent differences in their absorption and emission spectra. To obtain materials with such a range of properties, Inagaki et al.[68] synthesized a series of OPV based PMO films with various alkoxy lateral substituents, each derivative having a characteristic

emission spectrum. Again, no mesostructure was observed in the films prepared from pure PMO precursors, however, better organization of the materials was achieved with addition of 50 or 66% of TEOS. Blue shift of adsorption maximum wavelength and a red shift of emission wavelength upon polymerization of the unsubstituted precursor suggested stacking of the organic chromophores in the PMO material. The aggregation of OPV moieties was suppressed by the introduction of the bulky substituents. Because excimer formation is dependent on molecular interactions, difference in fluorescence behavior was observed. Longer fluorescence lifetimes were recorded for PMO derived from sterically demanding precursors. Moreover, less pronounced intermolecular fluorescence quenching resulted in higher fluorescence yields.

Further, various aromatic-bridged PMOs were explored by Inagaki et al. in order to correlate the optical properties with composition and structure of these materials and contribute towards their optimization.[31] Novel 2,6-naphthylene-bridged organosilica was prepared to examine the effect of the rotational motion on the fluorescence spectra. Adjusting the synthetic conditions afforded amorphous materials with meso-scale periodicity under acidic condition and mesoporous organosilica with molecular-scale periodicity in the presence of base using the same surfactant C₁₈TMACl. Fluorescence spectra of the precursor and the corresponding organosilica materials were compared at RT and -196 °C, in order to determine the strength of the intermolecular interactions which, in large part, determine the optical behavior. Moreover, to be able to assess the influence of the rigidity of naphthylene-bridged PMO on the fluorescence behavior, it was compared to biphenyl organosilica. The emission spectrum of the cooled amorphous naphthalene silica showed slightly blue shifted broad band indicative of excimer formation. Fluorescence spectrum of the corresponding

crystalline sample at -196 °C displayed a monomer-like band with partially resolved vibronic structures and increased intensity when compared to the room temperature measurement. Indeed, conformations obtained by computer simulation display random orientation of organic linkers in the crystal-like framework, but aggregated bridging species are present in amorphous naphthylene silica. In contrast, both spectra of the amorphous and the crystal-like biphenyl organosilica suggested interaction between the bridging groups in the excited state. The excimer formation was attributed to the rotation of the bridging group.

Inagaki et al.[69] also studied the optical properties of organosilica films prepared from precursors containing organic chromophores including 9,10-anthracene. Mesoporous structures were obtained with no molecular scale order. The positions of the absorption bands remained close to those of the corresponding precursors, indicating negligible interaction between the bridging groups in the ground state. On the other hand, fluorescence spectra significantly red-shifted and broadened, indicating the occurrence of a strong interaction of the organic moieties in the excited state. The excimer formation led to reduced quantum yields of the organosilica films with the exception of the biphenyl-bridge containing PMO. Biphenyl silica displayed quantum yield of 0.45 compared to 0.35 of its precursor. This behavior is an example of aggregation induced fluorescence enhancement, reported for the first time in PMOs.

With the aim of further exploring the effect of structure on the optical properties of PMO, 2,6-anthrylene and 9,10-anthrylene-bridged organosilica films were prepared.[70,71] Absorbance spectra of the products were found to be slightly broadened and red-shifted, indicative of weak interactions among organic groups in the framework. 2,6-anthrylene PMO powder sample was also prepared and analyzed. Stronger acidity of the synthesis

mixture led to higher degree of condensation and therefore to the presence of stronger intermolecular interactions, which manifested in substantially broadened and red-shifted absorption bands. The broader fluorescence spectrum and lower quantum yield of the powder 2,6-anthrylene silica, as compared to the corresponding PMO film, supported the evidence that the organic groups are packed more densely in the material. As a consequence of the restriction in the rotational motion, due to the silicon substitution position and limited interaction of the bridging groups, the quantum yield of 2,6-anthrylene-bridged PMO of 0.13 was more pronounced than that of 9,10-anthrylene silica (0.07).

Recently, preparation of material consisting of an energy donor and acceptor incorporated into the framework and the surfactant micelles, respectively, was reported.[72] PMO films were prepared using biphenyl-bridged precursor using P123 as a structure directing agent, and simultaneously doped with coumarin 1 dye. Adsorption spectrum of the novel organosilica revealed two bands attributed to the distinct organic moieties in the material. The luminescence spectra and fluorescence quantum yield measurements showed that the energy transfer from the coumarin 1 to the biphenyl bridge occurs in the material. The fluorescence spectrum obtained showed two peaks due to the biphenyl and coumarin 1 emission. With increase in the dye concentration, the biphenyl peak weakened as the coumarin 1 emission increased, indicating energy transfer from biphenyl. To confirm this behavior, the total luminescence quantum yield was measured and showed that the yield undoubtedly depends on the dye concentration. Quantitative studies of the energy transfer in the PMO film showed that the transfer efficiency is close to 100%, therefore greatly enhances the luminescence from the chromophores in the mesochannels.

1.4. Objectives

This work is a contribution toward the synthesis and characterization of periodic mesoporous materials. In addition to an original synthesis of the three-dimensional MCM-48 using a Gemini surfactant with rigid spacer (Chapter 3), two chapters are devoted to surface (Chapter 4) and framework (Chapter 5) modification. In Chapter 4 post-synthesis modification of grafted 3-halopropylsilane with pentaamine is employed to generate long chains containing multiple amine groups on the surface of pore-expanded MCM-41 silica. The performance of such materials for CO₂ adsorption is discussed in relation to the structural differences caused by the choice of the synthesis method. Chapter 5 describes the synthesis of novel azobenzene organosilica and the reversible photoisomerization of the azobenzene moieties integrated in the mesoporous organosilica framework. Chapter 6 combines synthesis of PMOs using two different precursors and advanced NMR characterization.

Note that the experimental part associated with each chapter is reported in the last section.

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CHAPTER 2

Instrumentation and Analysis

2.1. Introduction

Many analytical methods are often employed to characterize the structure and organization of the periodic mesoporous materials. The most important include: XRD, nitrogen adsorption, TEM and SEM. In addition to these techniques, other tools are required when examining the molecular composition of the mesoporous silica materials, especially those containing organic functionalities. In order to gain more information concerning the chemical nature of the materials, NMR and TGA are often employed.

2.2. Powder X-ray diffraction (XRD)

The phenomenon of diffraction occurs when the dimension of the diffracting objects is comparable to the wavelength of radiation and when there exists ordered structure in the material. A reflection is observed when the angle of incidence (θ) satisfies the Bragg law:

$$n\lambda = 2d \sin \theta$$

where λ is the wavelength of the beam, typically 1.541 Å (K α radiation from Cu),

d_{hkl} is the reflecting lattice plane (with hkl Miller indices).

Since the porous structure in ordered mesoporous materials is as regular as the structure of crystalline materials, powder XRD can be used to probe their porosity. In a typical XRD pattern, a high intensity peak is apparent at around $2\theta = 2^\circ$, and is accompanied by low intensity peaks in the $3 - 9^\circ$ range. The peaks at the lower and higher diffraction angles create a pattern representative of a given point-group symmetry.

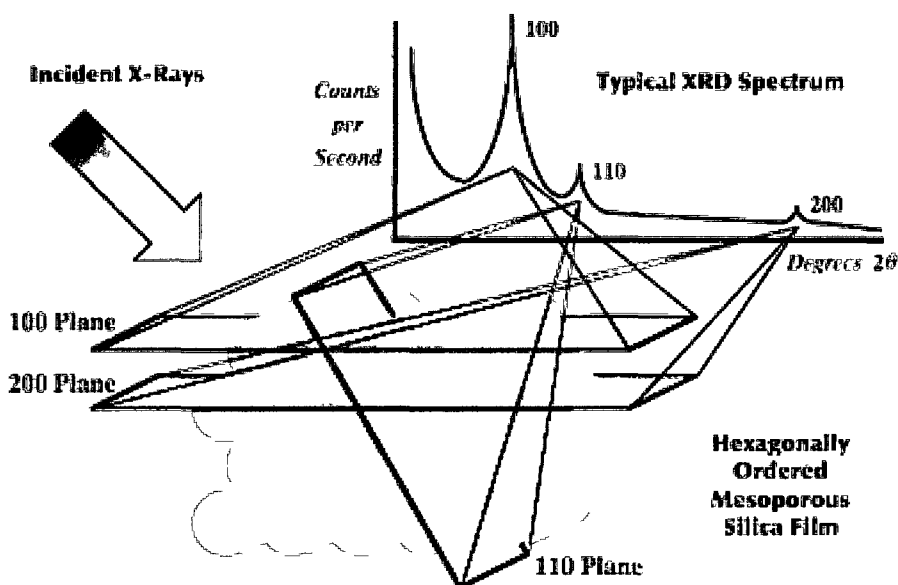


Figure 2.1. Schematic of XRD spectrum of MCM-41.[1]

The d-spacing ratio of each peak to the first maximum peak can be used to determine the symmetry of the pore structures. Subsequently, the Miller indices can be assigned and the unit cell dimension (pore centre to centre) can be calculated from the position of the peaks. Typically, d-spacing ratio of 0.58 implies the indexation of (100), (110) and (200) diffraction peaks for 2D hexagonal space group (P6m). The d-spacing ratio of 0.87 is

representative of discontinuous cubic (Ia3d) symmetry and the first two diffraction peaks can be indexed as (211) and (220).[2]

After removal of the template by calcination, a better-resolved XRD pattern is observed with a little shrinking of the cell parameter due to capillary tension, and further condensation.[3]

2.3. Nitrogen Adsorption Porosimetry

Due to its non-destructive nature, gas adsorption became one of the most powerful techniques for investigating mesoporosity of voids in solid materials. Adsorption can be either physical or chemical in nature. The physical adsorption is most suitable for surface area, pore size and pore volume determination, as indicated by the following:

- (i) Physisorption is driven by van der Waals' forces. Low heats of adsorption (no chemical bonding) exclude the occurrence of disruptive structural changes. Moreover, equilibrium is achieved rapidly, since no activation energy is required.
- (ii) First a monolayer is formed on the inner surface. Since the adsorbed molecules are not restricted to specific sites, the area of the entire surface can be covered. Knowledge of the amount of gas involved in a single monolayer allows the calculation of surface area.
- (iii) As the pressure is increased further, all pores are filled up through capillary condensation, enabling pore size and pore volume calculation.
- (iv) Physically adsorbed gases can be readily removed from the solid surface by reducing pressure, enabling both the adsorption and the desorption to be studied.

The amount of gas required to form monolayer and to subsequently fill pores in various sizes is measured as a function of the equilibrium (relative) gas pressure at known temperature, usually the boiling point of the analysis gas. Such a plot, referred to as adsorption isotherm, covers the gas pressure from vacuum to saturation. The term desorption denotes the reverse process.

2.3.1. Surface area

The Langmuir equation is one of the earliest and most widely used equations describing a relationship between the pressure of a gas in equilibrium with a flat surface and the volume of gas adsorbed. One of the assumptions in deriving the equation is that as a mononuclear layer of the adsorbed gas forms, the repulsion from the adsorbed molecules hinders the formation of subsequent layers. Brunauer, Emmett and Teller (BET) extended the Langmuir's theory to a multilayer theory allowing for some adsorbate molecules to adsorb upon other molecules.[4] This theory, capable of describing adsorption at high pressure, is given by the following equation:

$$P/V_a(P_0-P) = 1/V_m C + [(c-1)/V_m C]P/P_0$$

where V_a is the volume of gas adsorbed at equilibrium pressure, P

P is the saturated vapour pressure of the adsorbate,

C is the isothermal constant,

V_m is the volume of gas to achieve monolayer.

By plotting $P/V_a(P_0-P)$ vs. P/P_0 and determining V_m from the slope of the resultant straight line typically in the partial pressure range of 0.05 to 0.35, the specific surface area can then be determined by:

$$S_{BET} = V_m N \sigma_0 / m V_a$$

where N is Avogadro's number,

σ_0 is the area occupied by one molecule of gas ($16.2 \text{ \AA}^2$ for nitrogen),

m is the mass sample in grams.

2.3.2. Pore size and total volume

In the calculation of pore size from nitrogen adsorption isotherms, Kelvin equation is used to relate the size of the pores to the pressure at which capillary condensation for the gas occurs within it.

$$\ln(P/P_0) = -(2\gamma V \cos\theta / rRT)$$

where P is the equilibrium vapour pressure within a pore with radius r ,

P_0 is the vapour pressure over a flat surface at the same temperature,

γ and V are the surface tension and the molar volume of the liquid,

θ is the contact angle with which the liquid meets the pore wall.

The model developed by Barret, Joyner and Halenda (BJH), based on the Kelvin equation assuming an open ended cylindrical pore model, and corrected for multilayer adsorption, is the most widely used method for calculations of pore size distributions over the mesopore range.[5] However, there are systematic discrepancies between the geometrically defined

pore size distributions and those obtained from classical BJH isotherm. The differences are attributed to the underestimation of pore size by Kelvin equation, particularly in the smaller pore size range. Therefore, Kruk-Jaroniec-Sayari (KJS) proposed a method that corrects and calibrates the classical BJH equation and extends its applicability to the range of small mesopores (2 - 6.5 nm) for MCM-41 type materials.[6]

From the pore size distribution, the average pore size can be calculated. For MCM-41 type materials, the difference between the unit cell parameter (obtained from XRD measurements) and the pore size gives the wall thickness of the mesoporous channels. Whereas, the total pore volume of any material is calculated from the adsorption isotherm by multiplying the volume of nitrogen adsorbed at a relative pressure as close as possible to 1, with the conversion factor 0.00156 that converts the volume of nitrogen at standard temperature and pressure to liquid.

2.3.3. Types of isotherms

The adsorption isotherms are classified by IUPAC into 6 types.[7] In this classification, type I shows adsorption isotherms on microporous solids, for which the adsorption is limited to, at most, few molecular layers. Type II isotherm is representative of non-porous or macroporous solids. It displays an inflection point that indicates the stage at which monolayer coverage is complete and multilayer adsorption begins to occur. Type III isotherm is convex to the P/P_0 axis and is not common. This type is typical for vapor adsorption. Types IV and V feature a hysteresis loop (ie. desorption occurs at lower pressure than adsorption in similar sized pores), which is associated with occurrence of capillary

condensation. For solids owing mesoporosity, isotherm type IV is typically obtained. A rare case is isotherm type VI, which represents stepwise multilayer adsorption on a uniform, non-porous surface.

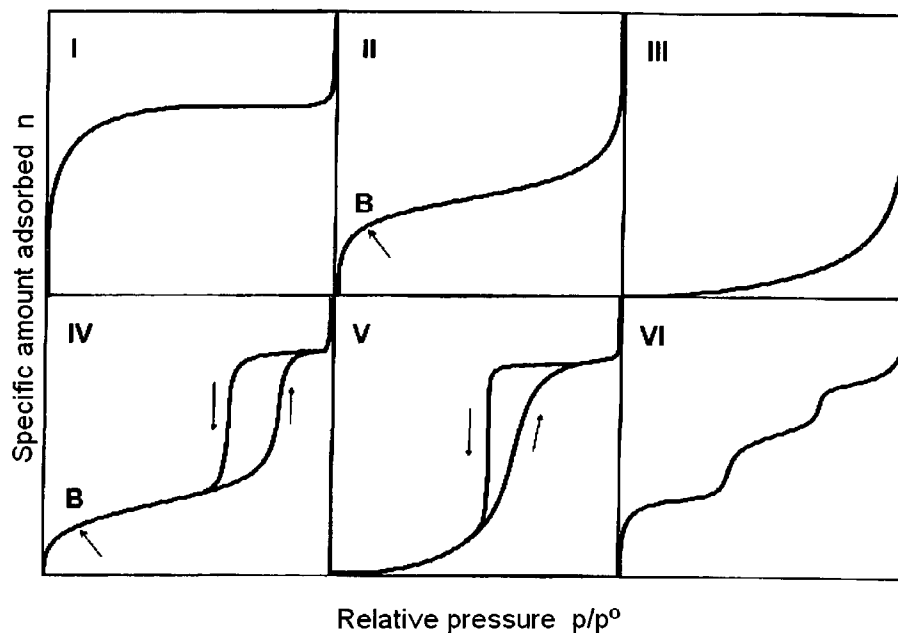


Figure 2.2. The IUPAC classification for adsorption isotherms.[8]

2.4. Solid state nuclear magnetic resonance (NMR)

2.4.1. ^{29}Si NMR

^{29}Si NMR is a valuable tool for monitoring the polymerization reaction of alkoxy silanes and for analyzing the chemical environment of silicon atoms in the resulting materials. For silica consisting of inorganic SiO_2 network, Q^n notation is used to represent

species with n number of condensed units. Therefore, Q^4 stands for silicon species with no hydroxyl groups that typically lie around -120 ppm relative to TMS. For every hydroxyl bond condensed to form siloxane bond, a signal shift upfield of approximately 10 ppm occurs.

The exchange of one Si-O bond with Si-C bond results in a significant difference in chemical shift of about 40 ppm. Such silicon species of organosilane are designated T^n , where n ranges from 0 to 3. If two carbon atoms are attached to silicon atom D species are formed with shifts as low as -14 ppm.[9]

2.4.2. Cross Polarization (CP) and Magic-Angle Spinning (MAS) NMR

Solid state NMR is generally not able to discriminate between silicon atoms that bear unhydrolyzed alkoxy groups and those that have hydroxyl groups, resulting in broader lines. Line broadening increases further with the degree of condensation, reflecting the diversity of the possible chemical environments. In order to obtain high-resolution carbon and silicon spectra and improve the signal-to-noise ratio in solid-state NMR various techniques are employed. Magic-angle spinning (MAS) technique averages the chemical shift-anisotropy and dipolar interactions that cause line broadening. Further, cross polarization technique is used in order to enhance signal intensity of nuclei such as silicon or carbon with low γ gyromagnetic ratio. In this case, the polarization is enhanced via polarization transfer by dipolar coupling with higher abundance nuclei such as protons. Unfortunately, the CP trends tend to underestimate groups that do not have protons in their proximity and therefore cannot be used to obtain truly quantitative results.

2.4.3. ^{13}C NMR

Although ^{13}C NMR is not quantitative, it can be used to give an indication whether the surfactant was removed successfully and of a presence of unhydrolyzed ethoxy groups. Solid state ^{13}C NMR is also often employed for the determination of structural integrity of organosilica materials. Although, ^{29}Si NMR would reveal instability of Si-C bond by presence of Q sites with the signals at -90 to -120 ppm, in case of materials prepared from a mixture of organic and inorganic precursors, carbon NMR is the only means of analyzing the stability of the materials during the process of synthesis and surfactant removal. In this case, lack of additional carbon peaks is the evidence of the structural integrity.

2.5. Transmission electron microscopy (TEM)

The XRD often gives insufficient reflection peaks to confirm existence of a given silica phase, therefore, TEM became widely used technique for structural determination of these materials. TEM images of mesoporous silica show projected structure information along the direction of incidence. The pore size can be directly calculated from an image if the micrograph is taken viewing down the channels. Otherwise, the apparent pore centre to centre distance can be used to calculate the unit cell parameter.[10]

High-resolution TEM of organosilica samples may also provide direct evidence of the molecular order within the pore walls. Lattice fringes observed along the channel axes, with a uniform spacing, indicate ordered packing of the hydrolyzed precursor molecules.[11]

2.6. Thermogravimetric analysis (TGA)

Thermogravimetry is a technique which allows the change in the sample mass to be analyzed while the sample is subjected to temperature alterations. The specimen contained in a crucible is suspended from an electronic microbalance enabling simultaneous recordings of mass and temperature to be made.

TGA can be useful in studies of surface modified silica and organosilica materials. The analysis provides information about temperature range of decomposition and the content of the organic functionalities. The weight loss observed in the lower temperature range is primarily due to the condensation of the remaining ethoxy and hydroxyl groups. The organic functionalities readily decompose at the elevated temperatures. Only SiO_2 remains inert though the range of the decomposition temperature from the original composition of the surface grafted silica (SiO_2 and $[\text{O}_2\text{Si-R}]$) or the organosilica ($[\text{O}_{2/3}\text{Si}]_2\text{-R}$) frameworks. The amount of organic functionalities in the material calculated from this assumption can be used to determine the stability of Si-C bond during the synthesis of PMO material or the grafting efficiency of a given procedure.

Sorption capacity of materials, such as propylamine modified silicas, can be also determined with aid of TGA by measuring the weight uptake of the sample when exposed to analyte gas. The TGA weight curves provide information on adsorption capacity, equilibration time, effect of temperature on the adsorption and desorption kinetics, and the recyclability of the material of interest.

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CHAPTER 3

Synthesis of MCM-48 Silica Using Gemini Surfactant with a Rigid Spacer

Abstract: Gemini surfactant (*p*-phenylenedimethylene)bis(*n*-hexadecyldimethylammonium) dibromide (abbreviated C₁₆-DMB-C₁₆; with DMB = para-CH₂-C₆H₄-CH₂-) with a rigid spacer was found to produce cubic MCM-48 silica mesophase by temperature induced phase transition. The synthesis involved two steps; a precipitation stage at room temperature for a period of time t_1 , followed by an ageing step at higher temperature for a period of time t_2 . The synthesis was optimized for particular combinations of t_1 and t_2 periods. The transformation was studied under various pH and temperature conditions. Although it was observed that ethanol partitioning induced, at least partially, the formation of cubic structure, the transformation was shown to be also influenced by the degree of silicate polymerization. The MCM-48 silica prepared under optimized conditions exhibited a type IV nitrogen adsorption isotherm, a BET surface area of 1164 m²/g and a narrow pore size distribution with a maximum at 2.5 nm.

3.1. Introduction

The synthesis of periodic nanoporous materials templated by surfactant supramolecular assemblies has attracted considerable interest in recent years. Much attention has been focused on the 2D hexagonal mesophase (MCM-41) due to its wide stability domain, thus the ease of synthesis. However, cubic phases such as MCM-48, SBA-1, SBA-16, FDU-1 and KIT-6 with 3D pore systems are more compelling candidates as adsorbents

or catalyst supports. By use of MCM-48, potential pore blockage can be avoided due to its highly interwoven pore structure.[1]

Introduction of Gemini surfactants for the consistent preparation of MCM-48 cubic mesophase by Huo et al.[2] and further development of a post-synthesis treatment improving the pore size distribution and order greatly facilitated the synthesis of MCM-48.[3] Since then, the emphasis has been placed on optimizing the chain and spacer length of the surfactant and the duration of hydrothermal treatment during the synthesis.[3, 4] Alami et al. noticed that variations of the size of the spacer group bring about changes of the surface area occupied by the surfactant headgroup at the interface.[5] The area initially increases then decreases as the length of the alkyl spacer groups increases. Formation of good quality MCM-48 was reported to occur in the presence of Gemini surfactants with spacers having 2, 10, 12 carbon atoms and long alkyl tails with 12, 16, 18, 22 carbon atoms. As the length of the surfactant tail increases, the spontaneous curvature remains nearly the same, although significant deviations are observed as the carbon number becomes larger than 20 and the chain coils. By adjusting synthetic parameters, surfactants with long chains can be used to produce materials with larger pores.[2, 3, 4, 6]

Although, cubic MCM-48 was shown to be successfully produced at room temperature using Gemini surfactant, the synthesis was tedious and had low yield.[2] Therefore some workers focused on the restructuring of surfactant-silicate mesophases to synthesize MCM-48 through a phase transformation process.[2, 6, 7, 8] The transformation was performed by initially generating MCM-41 mesophase, followed by heating at higher temperature to induce the structural change. In situ X-ray diffraction was utilized by Landry et al. to illustrate the change of mesophase and show that it proceeded in an epitaxial manner

without dissolution of the original MCM-41 phase.[9] It has been claimed that the gradual release of ethanol from the synthesis gel during the hydrolysis of TEOS drives the transformation by altering the surfactant packing parameter $g = V/a_0l$, where V is the total volume of the surfactant chain plus any cosolvent molecules, a_0 is the effective area of the headgroup and l is the kinetic surfactant chain length.[8] The g value, hence MCM-48 formation, however depends on other parameters besides the presence of organic additives. The first approach for the control of the silica mesophase structure in the presence of chain surfactants was through adjustment of the molar ratio of surfactant and silica.[10] MCM-48 type materials were usually prepared by using high surfactant to silica ratios.[11] At lower ratios, extended aging periods are required to produce well organized material,[2] while Gemini surfactants with very low critical micelle concentration are an exception. Siliceous MCM-48 was also shown to be formed under high pH conditions and at elevated temperature. Another parameter shown to play an important, but not yet fully understood role is the silica polymerization rate.

In this study, the importance of synthetic parameters, such as precipitation time or base to surfactant molar ratio, was investigated for the synthesis of MCM-48 silica using for the first time a Gemini surfactant with a bulky rigid spacer, i.e. C16-DMB-C16, as template.

3.2. Results and Discussion

The XRD patterns of the material obtained after $t_1 = 0.5$ or 1 h and $t_2 = 2$ or 3 days (Figure 1 samples (d), (b)) are consistent with the occurrence of Ia3d symmetry and show intense (211) and (220) diffraction peaks. A more diffuse pattern observed in the 3-4° region

can be attributed to 400, 420, 332 and 431 reflections. The ratio between the d spacing of the peaks assigned as (211) and (220) is 0.87 which is consistent with cubic MCM-48 mesophase.[13] The lattice parameter calculated from this pattern reflects a structural periodicity with a unit cell of 40 Å.

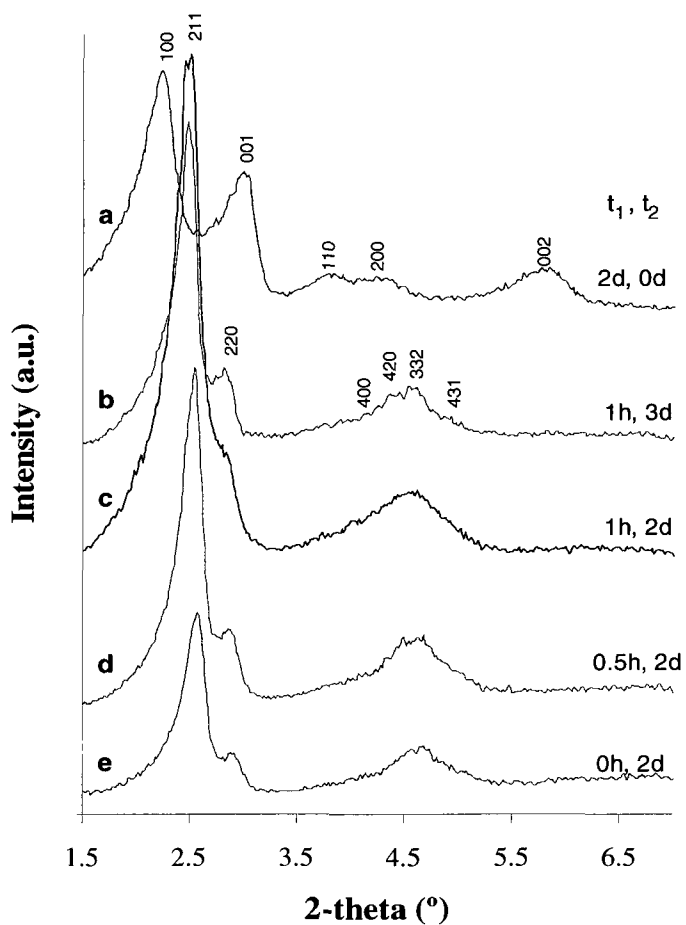


Figure 3.1. X-ray diffraction patterns of solid materials prepared after various reaction times (t_1, t_2) as indicated.

The TEM images confirm that the structure of the materials prepared is consistent with cubic MCM-48 mesophase. The images (Figure 2) of the sample viewed down the [100] and [110] zone axes of a cubic unit cell are consistent with literature data.[14] Along the [100] direction the image shows a square pore network arrangement consistent with the occurrence of a cubic mesophase and along the [110] direction the electron density variation in projection in different regions creates the channel like appearance.

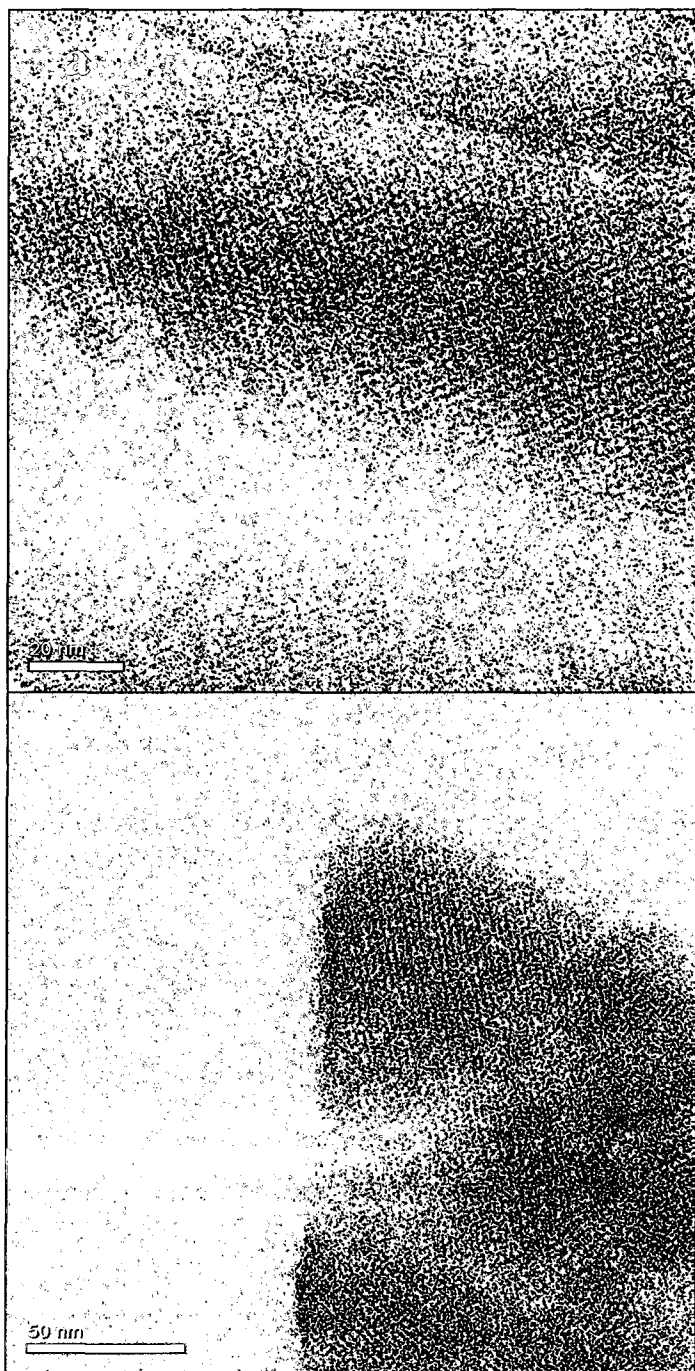


Figure 3.2. TEM of mesoporous silica prepared from starting mixture 1 TEOS:0.064 C₁₆-DMB-C₁₆:0.74 NaOH:185 H₂O ($t_1 = 0.5$ h, $t_2 = 2$ d) recorded along the (a) [100] and (b) [110] directions (scale bars 20 and 50 nm respectively).

The MCM-48 formation through solid mesophase transformation is possible given that the time of room temperature precipitation (t_1) is relatively short and the degree of condensation of the silica is still low enough that by further changing the synthesis conditions, e.g., increase the temperature, it would be possible to transform the composite materials from one mesophase to another. The XRD patterns displayed in Figure 1 show that the material prepared at room temperature, i.e. $t_1 = 2$ days; $t_2 = 0$, consists of a mixture of hexagonal (H) and lamellar (L) mesophases. Ageing this mixture at 100 °C, gave rise to a single cubic MCM-48 (C) mesophase. It has been suggested in the literature that the transition from H to L is a reversible process whereas the transition into the cubic phase is more thermodynamically favorable and less reversible.[9] Consistent with this statement, the current work showed that the L phase appears when $t_2 = 0$ and as t_2 increases the, L phase vanishes. Decrease in the amount of L phase was also observed as t_1 increased from 0.5 h to 2 days, at $t_2 = 0$.

In surfactant systems, the addition of salt screens the electrostatic repulsive forces between neighboring polar headgroups, thus changing the spontaneous curvature. The addition of NaOH in microemulsion systems with ionic surfactants is therefore a means to control the mesophase and thus its concentration is often employed as an experimental control parameter. Pena et al.[15] provided evidence that by adjusting the pH during the synthesis of mesoporous silica, various structures can be generated. Also in this work to achieve the desired transformation from hexagonal to cubic structure, the amount of base added needed to be optimized to allow the packing parameter to reach a value associated with the cubic phase. It was observed that the NaOH to silica ratio required for the transition from hexagonal to cubic structure to occur needs to be adequate (0.74), but excess of base

results in the formation of hexagonal phase (Figure 3). During the MCM-48 synthesis not only the pH but also other factors such as temperature need to be considered. Material obtained using a higher NaOH to silica ratio (0.84) but prepared in relatively short RT precipitation period ($t_1 = 0.5$ h, $t_2 = 2$ d) reveals a small amount of cubic phase in the XRD pattern. When the synthesis gel reacts at room temperature for a longer period of time only the hexagonal phase is obtained due to extended condensation of the silica at that stage in the reaction and therefore less favorable H to C transition.

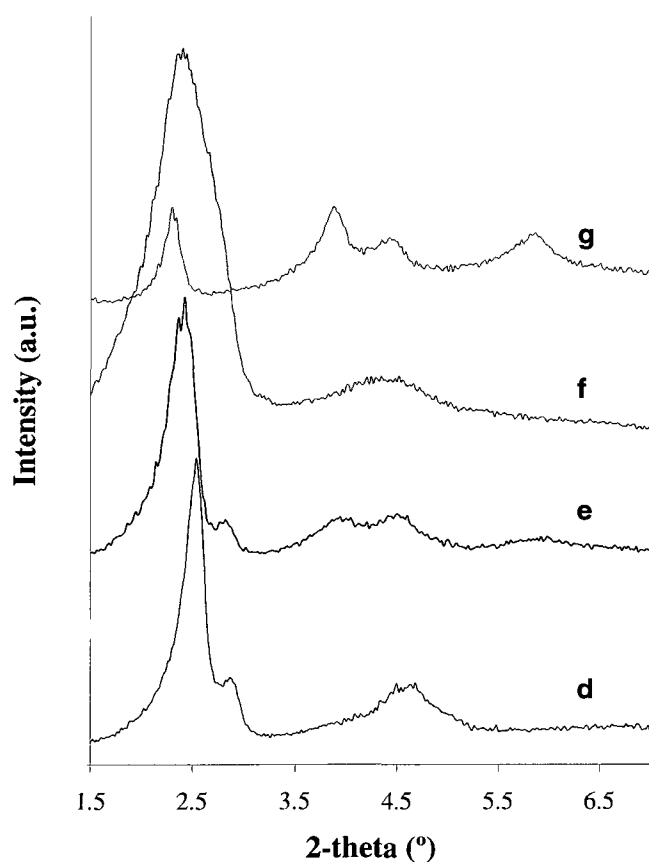


Figure 3.3. X-ray diffraction patterns of mesoporous materials obtained during $t_1 = 0.5$ h and $t_2 = 2$ d with the following gel compositions 1 TEOS:0.064 C_{16} -DMB- C_{16} :x NaOH:185 H_2O molar composition: (d) $x = 0.74$, (e) $x = 0.84$, (f) $x = 0.64$ and (g) using fumed silica.

In all cases the time allowed for the formation of hexagonal and lamellar phases at room temperature needs to be limited to prevent the framework from becoming too rigid before the cubic phase is formed. As the room temperature precipitation period is extended to more than 1h, due to increased degree of condensation, the time required for the hexagonal to cubic transformation to take place increases. As shown in Figure 1, the optimum conditions for obtaining cubic MCM-48 silica correspond to short precipitation periods (t_1) and long aging periods (t_2). Although, the results (Table 1) indicate that cubic mesophases with higher surface areas and pore volumes are obtained with longer precipitation (t_1) and aging (t_2) times, shorter t_1 leads to materials with narrower pore size distribution within a shorter t_2 period.

Table 3.1. Effect of temperature, precipitation and ageing periods on the characteristic of MCM-48.

molar composition ^a C ₁₆ -DMB-C ₁₆ /NaOH	precipitation time (h) / aging time (days) /temperature (°C)	S _{BET} (m ² g ⁻¹)	d _{KJS,ads} (nm)	V _{tot} (cm ³ g ⁻¹)	d ₂₁₁ (nm)	a (nm)
0.064/0.74	1/3/100	1164 ^b	2.5	0.58	2.5	4.1
0.064/0.74	0.5/2/100	1023	2.4	0.48	2.6	4.0
0.064/0.74	0/2/100	941	2.3	0.47	2.6	4.0

^a where TEOS = 1.0, H₂O = 185; ^b broad pore size distribution

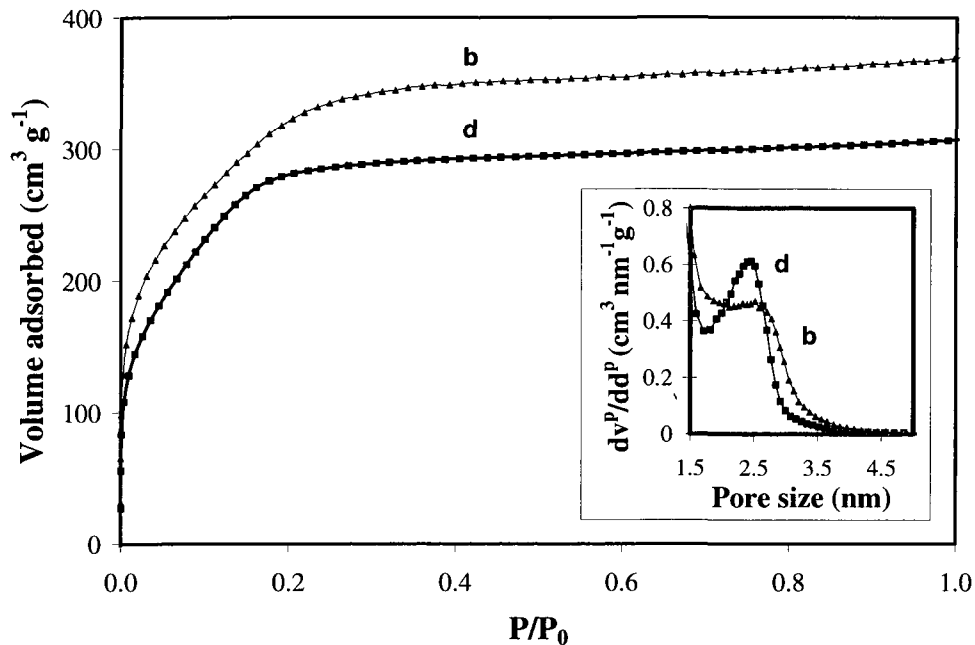


Figure 3.4. Adsorption isotherms and pore size distributions of products prepared after precipitation and aging for (b) $t_1 = 1$ h ; $t_2 = 3$ days and (d) $t_1 = 0.5$ h ; $t_2 = 2$ days.

The nitrogen adsorption isotherms of samples b ($t_1 = 1$ h ; $t_2 = 3$ days) and d ($t_1 = 0.5$ h ; $t_2 = 2$ days) are shown in Figure 4. The surface areas and pore volumes were, respectively, 1164 m²/g, 0.58 cm³/g and 1023 m²/g, 0.48 cm³/g. The isotherms were of type IV in IUPAC classification,[16] showing a capillary condensation at a relative pressure p/p_0 between 0.1 and 0.25 which is indicative of the occurrence of small size mesopores. A narrower pore size distribution is usually indicative of better pore ordering. Although material (b) exhibited a higher surface area than material (d), its pore organization was inferior which is also apparent in the shape of the adsorption isotherm that shows a broader condensation step.

As expected, when fumed silica was used as the silica source, no transition into cubic phase was observed (Figure 3).[8] The addition of 4 molar equivalents of ethanol with respect to SiO_2 to the synthesis did not induce the phase transition. The presence of ethanol generated in situ by the hydrolysis of TEOS showed to be necessary for the formation of the cubic structure. This is consistent with the fact that a low surface curvature mesophase is the favored product when organic compounds of low polarity are present in the synthesis mixture.[8, 17, 18]

The elevated temperature appears to be crucial as it provides heat to overcome the activation energy for the transition from hexagonal to cubic symmetry. Temperatures higher than 100 °C, however, lead to poor quality materials.

3.3. Conclusions

In conclusion, the MCM-48 mesoporous silica has been successfully synthesized by utilization of Gemini surfactant with a rigid spacer as template and TEOS as precursor. It was established that the slow hydrolysis of TEOS during the polymerization of the silicate structure causes the micelles to adopt the hexagonal symmetry. The effects of different reaction parameters on the mesostructures obtained have been investigated and optimized. The presence of coexisting hexagonal and lamellar phases prior to thermal treatment ($t_2 = 0$ h) appears to be essential for the transformation to bicontinuous cubic Ia3d mesophase. The cubic phase is obtained only upon heating to 100 °C, since the MCM-48 is the thermodynamically favored product. The dynamics of the phase curvature change appear to

be also affected by the base to silica ratio, which affects the packing of the surfactant species and the depolymerization of the silica species.

3.4. Experimental Section

3.4.1. (p-Phenylenedimethylene)bis(n-hexadecyldimethylammonium) dibromide.

C₁₆-DMB-C₁₆ cationic Gemini surfactant was prepared by quaternization of hexadecylamine with 1,4-bis(bromomethyl)benzene in anhydrous acetone.[19] 2.5 g (0.947 mmol) of p-xylylene dibromide was dissolved in 60 mL of warm acetone. 6.3 g (2.36 mmol) of N,N'-dimethyl-n-hexadecylamine diluted with 2 mL of acetone was introduced into the solution. A white precipitate formed almost immediately. 30 mL of acetone was added and the solution was allowed to stir overnight. The solid was filtered out, washed with 10 mL of acetone, and recrystallized from acetone/chloroform mixture to obtain 6.574 g (86.4%) of C₁₆-DMB-C₁₆ as a white powder. ¹H NMR (400 MHz, CDCl₃): δ 7.82 (s, 4H), 5.31 (s, 4H), 3.53 (m, 4H), 3.24 (s, 12H), 1.83 (m, 4H), 1.38 (m, 12H), 1.26 (m, 40H), 0.88 (t, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 134.1, 130.1, 66.2, 64.9, 49.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 26.4, 23.0, 22.7, 14.1. MS (EI, ethanol/acetonitrile): m/z 723(M-⁷⁹Br)⁺, 721(M-⁸¹Br)⁺.

3.4.2. Material Synthesis.

Mesoporous silica was prepared using C₁₆-DMB-C₁₆ and TEOS as a silica source in basic medium. The molar ratio of the reactants TEOS/C₁₆-DMB-C₁₆/NaOH/H₂O was 1/0.064/0.74/185. Typically the surfactant (0.513 g) was dissolved in water (33.3 g), NaOH (0.296 g) was then added under stirring and after 20 min, the silica source (2.08 g) was

introduced to the solution. A white, fine precipitate appeared within 5 minutes of stirring. After a certain time (t_1) of room temperature precipitation, the mixture was transferred to a Teflon-lined steel autoclave, the temperature was raised to 100 °C and the mixture aged for another period of time (t_2). The solid product separated by filtration was dried at ambient conditions and calcined in air at 550 °C for 5 hours (36.4% yield). Materials with NaOH to TEOS ratios of 0.64 and 0.84 and fumed silica as silica source were also prepared.

3.4.3. Analyses.

Powder X-ray diffraction (XRD) analysis was performed using a Philips PW3710 diffractometer with Cu K α radiation (45 kV, 40 mA), 0.02° step size and 2.5 s/step accumulation time. Nitrogen sorption isotherms were determined with a Coulter Omnisorp 100 gas analyzer at 77 K. Before analysis the samples were evacuated at 200 °C under vacuum. The BET specific surface area, S_{BET} , was obtained from the nitrogen adsorption data in the relative pressure range 0.05-0.15 and the total pore volume was determined from the amount of nitrogen adsorbed at $P/P_0 = \text{ca. } 0.99$. The pore size distributions were derived from the adsorption branches using the KJS method valid over a broad range of pore sizes.[12] Transmission electron micrographs (TEM) were recorded on a JEOL-2010 instrument operating at 200 kV. Before examination, specimens were dispersed in anhydrous ethanol and deposited on a holey carbon film on a microgrid.

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CHAPTER 4

Preparation of CO₂ Adsorbents by Organic Functionalization

Abstract: Pore-expanded MCM-41 (PE-MCM-41) was prepared and functionalized with 3-iodopropyl or 3-chloropropyl groups. Subsequent halogen substitution reaction with tetraethylpentaamine or tris(2-aminoethyl)amine afforded polyamine functionalized PE-MCM-41. The produced materials were examined by thermogravimetric analysis and nitrogen adsorption-desorption measurements in order to determine the effect of the quantity of polyamine introduced on the silica surface on the CO₂ adsorption capacity. The optimal pentaamine grafted PE-MCM-41 adsorbent exhibited a 6.06 %wt adsorption capacity for 5% CO₂ in N₂ at 25 °C. The reactivity of the halopropyl groups was discussed in relation to the structural differences.

4.1. Introduction

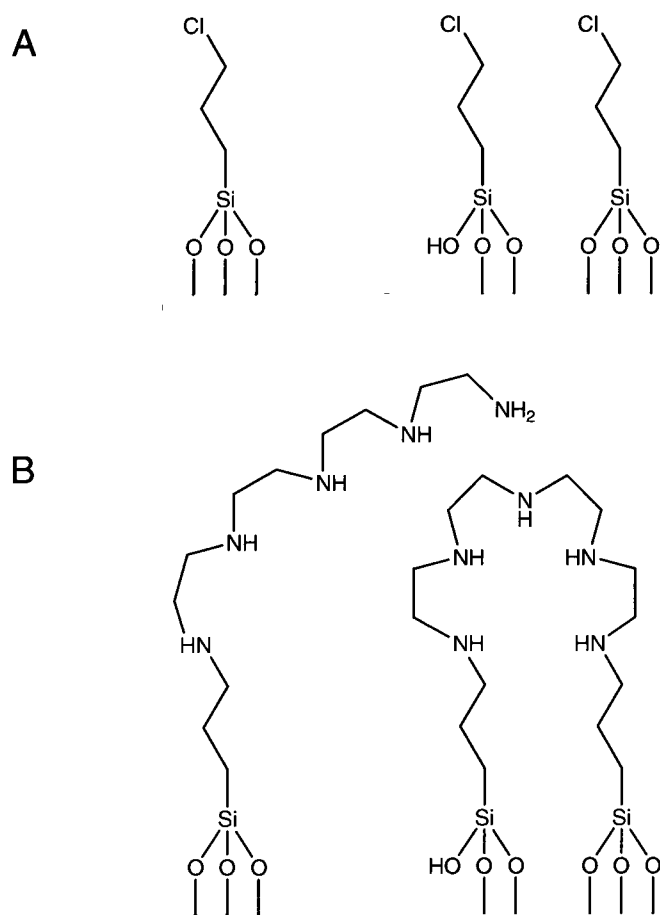
Since the discovery of ordered mesoporous silica, much attention has been centered on these materials because of their mesoporous structure, large surface area and high thermal stability. Grafting or post-synthesis modification of mesoporous silica have been widely studied to explore their potentials for use in various applications including carbon dioxide separation. In addition of conventional adsorbents such as zeolites and activated carbon, solid adsorbents for capture of carbon dioxide have to a large degree been based on porous silicas having amino groups grafted to the pore surface.[1-7] Although, this method

of preparation is simple, limited quantity of amine groups can be retained on the surface of these supports due to low density of surface silanol groups. The size of the guest molecules is also limited, so that the diffusion of the monomer can compete with the surface reactions at the pore windows. Introduction of bulky functional groups simply results in their inhomogeneous distribution on the surface, which may be crucial in chemical events where functional groups work cooperatively. Further, limited availability of the silane reagents allowed only for the preparation of mesoporous silicas with up to three amino groups in the grafted chain.[6,7] Increased adsorption capacity was found with increase of amino groups in the chain. This suggested, that higher adsorption capabilities could be obtained not only by increasing the number of amino groups available on the surface, but also by increasing number of groups per monomer, since the optimum number was not reached.[6]

Preparation of polyamine impregnated porous silicas was suggested to show improved performance, however, those materials suffered from problems such as low capacity particularly at ambient temperature, instability due to leaching and poor selectivity.[8] To address this matter, Jones et al.[7] synthesized hyperbranched aminosilica material prepared by surface-initiated polymerization of aziridine. The high amine loading of 7.0 mmolN/g in the resulting material, allowed for CO₂ adsorption capacity of 3.1 mmol/g at 10% CO₂ in humid environment. It also showed good recyclability. Although this is a promising type of materials, it requires the use of unstable and hazardous reagent, aziridine and therefore may not be advantageous for large scale application.

Post-synthesis modification by grafting of 3-halopropyl silane and subsequent nucleophilic displacement of halogen ion was suggested to be a promising route for obtaining bulky groups on the surface of mesoporous silica.[9] In fact chloropropylsilane

and bromopropylsilane groups has been investigated as a linker for introduction of amine groups on the silica surface for ion adsorption.[10,11] Formation of bicrural species in addition to linear amines was reported due to the substitution reaction occurring at two amino groups of the same molecule. Longer amine chain, higher density of the chloropropyl groups and their inhomogeneous distribution were identified as the factors increasing the amount of bridged species.



Scheme 4.1. (A) Grafted chloropropyl groups, and (B) subsequent formation of monocrural and bicrural amine species on the silica surface.

Earlier, our research group developed a method to enlarge the pore size of MCM-41 and by prehydration of the pore expanded silica (PE-MCM-41) surfaces prior to grafting. The obtained materials had high triamine loading (7.9 mmolN/g) and adsorption capacity of 2.65 mmol/g for dry 5% CO₂ in N₂. The high CO₂ adsorption capacity was attributed to the large pore size of PE-MCM-41 that allowed for a large quantity of amino groups to be grafted without inhibiting the adsorbate mobility. Prehydration of the silica surface enhanced the surface coverage of grafted species. Although, increased amine loading led to better adsorption capacity, beyond an optimum amine loading, poor CO₂ adsorption efficiency was observed due to diffusion limitations.[6,7]

To investigate the effect of higher density of amino groups, post-synthesis modification of grafted 3-halopropylsilane with amine was employed to generate long chain polyamines on the surface of PE-MCM-41. The performance of CO₂ adsorption will be discussed in relation to the structural changes caused by the choice of the synthetic method. Effect of different halogens on the final material will be determined. Performance of tetraethylpentaamine and tris(2-aminoethyl)amine grafted materials will be compared.

4.2. Results and discussion

Pore-expanded MCM-41 silica containing variable quantities of chloropropyl and iodopropyl groups were prepared by dry and wet grafting methods. The subsequent reaction with pentaamine silica produced corresponding amine-containing samples. All the materials were analyzed with TGA in order to determine the amount amine groups and compare it to the amine content expected based on the amount of grafted halopropyl groups. The results are summarized in Table 1.

Table 4.1. Properties of the prepared polyamine functionalized materials.

Sample	CO ₂ capacity (% wt)	CO ₂ capacity (mmol/g)	Amine content /expected (%wt)	Amine content (mmol/g)	CO ₂ /N ratio	Improved performance at T (°) / CO ₂ capacity (% wt)
PE-MCM-41/I/0	4.29	0.98	24.6 / 21.2	1.07	0.182	-
PE-MCM-41/I/0.3	5.20	1.18	30.9 / 27.1	1.34	0.176	-
PE-MCM-41/I/0.8	5.84	1.33	38.0 / 34.8	1.65	0.161	-
PE-MCM-41/I/1.0	5.64	1.28	44.5 / 41.7	1.93	0.133	40 / 6.57
PE-MCM-41/I/1.5	4.73	1.07	43.2 / 51.5	1.88	0.115	50 / 5.20
PE-MCM-41/I/2.0	0.107	0.03	57.9 / 64.9	2.52	0.002	85 / 1.26
PE-MCM-41/Cl/0.5	6.06	1.38	27.5 / 22.0	1.19	0.231	-
PE-MCM-41/Cl/0.8	4.13	0.94	32.3 / 48.9	1.40	0.134	-

The proper distribution of the organic groups on the porous support is crucial for the CO₂ adsorption capacity, since the amine groups work cooperatively. To increase the density of the grafted halopropyl groups, water was used in the surface functionalization process to enhance the surface coverage of the grafted species. Possibly due to the interaction of water with the silane reagent, the effect of water on the functionalization reaction was lower than that for polyaminopropyl silane reported in literature.[5] Further, the reactivity of halopropyl silane with the silica surface was different for chloro and iodo derivative. The organic loading in materials prepared in the presence of 0.8 mL of water per gram of silica was 1.51 mmol/g of iodopropyl groups, compared to 2.12 mmol/g of chloropropyl groups. As much as 1.5 mL of water was required during the grafting procedure to functionalize PE-MCM-41 with 2.23 mmol/g of iodopropyl groups.

The subsequent step towards the optimization of the density of the surface groups was the control over the substitution reaction. As previously reported by Corriu et al.,[9] the rate of the halogen substitution reaction with polyamine depends on the identity of the leaving group, since the strength of the halogen-carbon bond determines the rate of the substitution reaction. In the current study, the concentration of grafted halopropyl groups in the PE-MCM-41 material calculated using TGA was compared to the amount of resultant pentaaminopropyl groups to confirm completion of the reaction and its stoichiometry. It was found that complete reaction of the pentaamine with surface grafted iodopropyl groups was achieved in less than 15 minutes at 80 °C. While treatment of chloropropyl groups under the same conditions for 1 h was necessary to obtain quantitative substitution of chloro groups with pentaamine. The optimal reaction temperature for efficient diffusion of the reactants into the pores was found to be 80 °C, consequently providing optimal conditions that allow

for the reactants to reach the equilibrium at a reasonable time. Unreacted amine can be retained inside the mesopores despite the numerous washings, due to the interaction with the surface of the grafted amines. Therefore, optimization of the material as CO₂ adsorbent also involved minimizing the amount of the amine added to the reaction to achieve maximum amine loading without excess amine adsorbing on the surface and occupying pore volume, crucial for efficient adsorbate performance. The molar amount of halopropyl groups at lower loadings was close to that of produced amine, indicating 1:1 stoichiometry between the amine and halopropyl groups, consistent with a linear mode of amine attachment to the propyl chain on the PE-MCM-41 silica surface. The concentration of amine in the materials prepared from PE-MCM-41 with larger amount of grafted halopropyl groups was lower than expected due to the structural and chemical differences discussed later.

The uptake of 5% CO₂ in N₂ at 25 °C was measured using a thermogravimetric analyzer. Good CO₂ capacities of up to 6.06 wt% at RT were obtained. The adsorption data was examined in terms of amine efficiency and presented as CO₂/N ratio (Table 1). During carbamate formation two equivalents of amine groups are required to adsorb a given amount of CO₂, the CO₂/N ratios for primary, secondary and tertiary amines should be about 0.5, 0.3 and 0.05, respectively.[12] Therefore pentaamine functionality is expected to give a maximum efficiency per amino group of 0.34. However, the basicity of secondary amines further away from the terminal end is expected to be lower, resulting in lower CO₂ efficiency than 0.3. The maximum ratio obtained for PE-MCM-41/I samples of 0.182 suggests that not all of the amine groups are accessible. The decrease in the efficiency of grafted amine groups was observed with higher concentration of amine groups indicating the occurrence of diffusion limitations of CO₂ molecules. Increase in adsorption temperature of

materials containing 1.93 mmol/g or higher concentration of amine groups, led to the enhancement of sorption capacity, indicating kinetic barrier for diffusion of the adsorbed CO₂. Although, low temperature thermodynamically favors the adsorption of CO₂, in a case of kinetically controlled diffusion of the sorption gas, temperature increase facilitates the transfer of the CO₂ molecules to the sorption sites. The optimum temperature allowing for the maximum CO₂ uptake increased to 40 and 50 °C (PE-MCM-41/I/1.0 and PE-MCM-41/I/1.5) on loading higher concentration of pentaamine. The change in the diffusion kinetics as the amount of amine groups increased from 1.65 to 1.93 mmol/g is illustrated in Figure 1. The adsorption profiles of PE-MCM-41/I/0.8 and PE-MCM-41/I/1.0 (dotted line) samples were analyzed and the CO₂ uptake after 20 and 60 minutes were calculated. After exposure to CO₂ for 20 min, PE-MCM-41/I/0.8 material achieved 96% of the capacity obtained at 60 min, this value was 90% for PE-MCM-41/I/1.0.

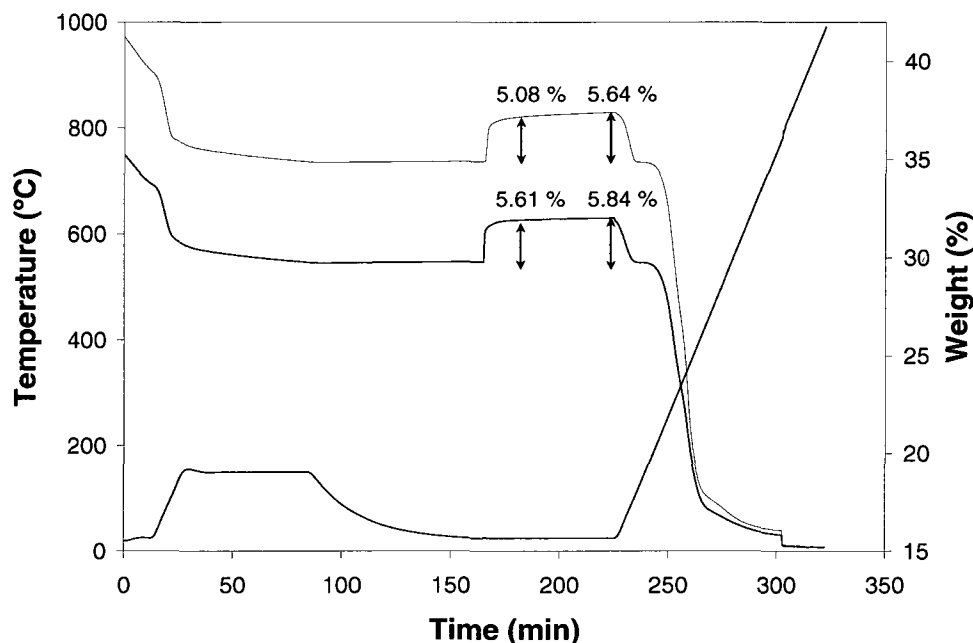


Figure 4.1. Adsorption and decomposition profiles of PE-MCM-41/I/0.8 and PE-MCM-41/I/1.0 (shaded line).

Material prepared in the presence of 2 mL of water per gram of silica gave a significantly lower adsorption capacity of 0.024 mmol/g at room temperature. Temperature of 85 °C slightly improved the sorption capacity to 0.13 mmol/g. The nitrogen adsorption isotherms of the parent material and the amine functionalized PE-MCM-41/I materials were obtained and are presented in Figure 2. The isotherms confirmed that the surface was functionalized, with increased amine loading the adsorption branch shifted towards the lower pressures and surface area decreases from 1138 m²/g for PE-MCM-41/I/0.3. As the amount of amine in the material increased the pores became more occupied by the guest molecules, until they were completely filled in the pentaamine material obtained in the

presence of 2 mL of water per gram of silica. This resulted in 5 m²/g surface area and therefore substantially suppressed amine efficiency.

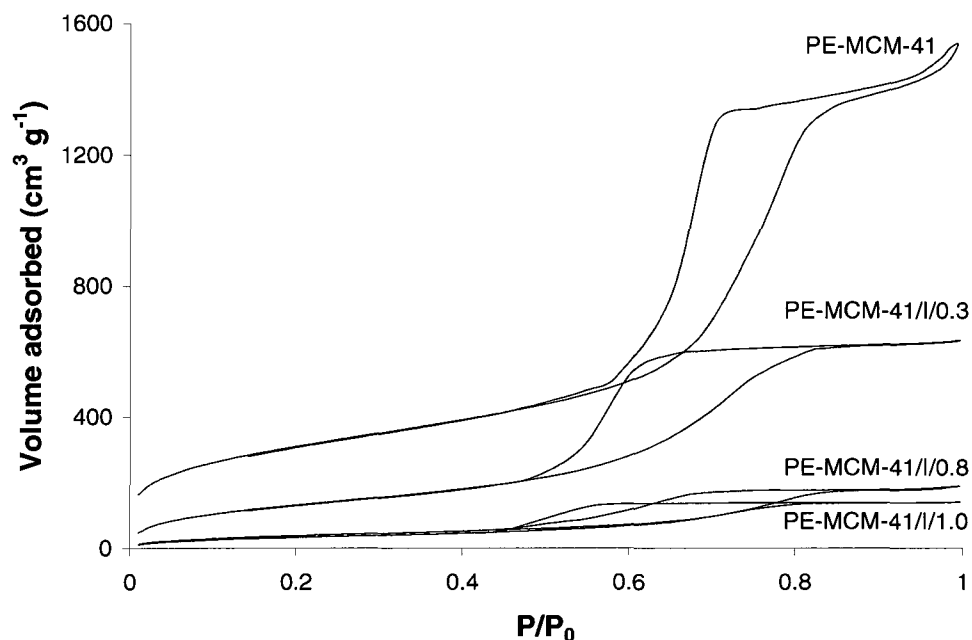


Figure 4.2. Nitrogen adsorption-desorption isotherms for parent PE-MCM-41 silica and PE-MCM-41/I/0.3, 0.8, 1.0 materials, with surface areas of 1138, 507, 153, 133 m²/g, respectively.

The materials prepared from PE-MCM-41 functionalized with chloropropyl groups in the presence of 0.8 mL of water per gram of silica shows lower CO₂ uptake compared to PE-MCM-41/Cl/0.5 material, as a result of lower amine content than expected. The high surface area of PE-MCM-41/Cl/0.8 of 340 m²/g signifies that the pore volume was not completely occupied. However, the yield of the halogen substitution reaction increased by only 6% by increasing the reaction time to 24 h and doubling the amount of reactants. Drastic decrease in the amine efficiency from 0.231 for PE-MCM-41/Cl/0.5 to 0.134 for PE-

MCM-41/Cl/0.8 suggests the formation of bridged species.[10] The formation of bicrural species exclusively during the reaction with chloropropyl groups may be due to the slower reaction as compared to that with iodopropyl functionalized material.

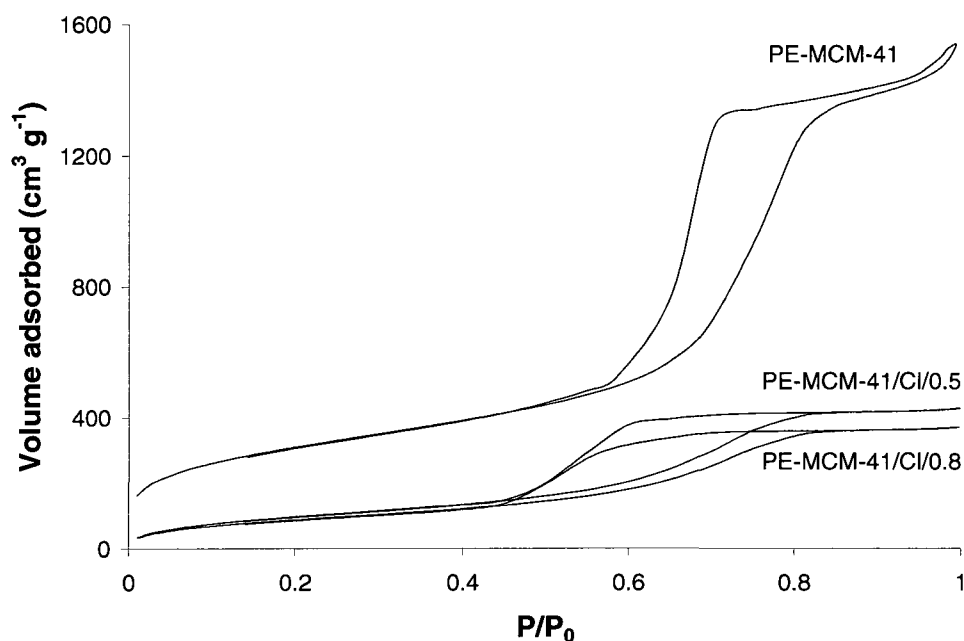


Figure 4.3. Nitrogen adsorption-desorption isotherms for parent PE-MCM-41 silica and PE-MCM-41/Cl/0.5, 0.8 materials, with surface areas of 1138, 382, 340 m²/g, respectively.

The recyclability of adsorbent during prolonged operation is important for practical use. Figure 4 shows cyclic adsorption profiles of PE-MCM-41/I/1.0. The expected value of 5.08 % was obtained in the in the first cycle. The adsorptive capacity in the fifth cycle was 13% lower than initial. From the decrease in mass, it was calculated that 8% of the organic content is removed. Recently published study on a similar material, revealed that the desorption temperature of 150 °C exceeds that of the stability of this type of material.[13]

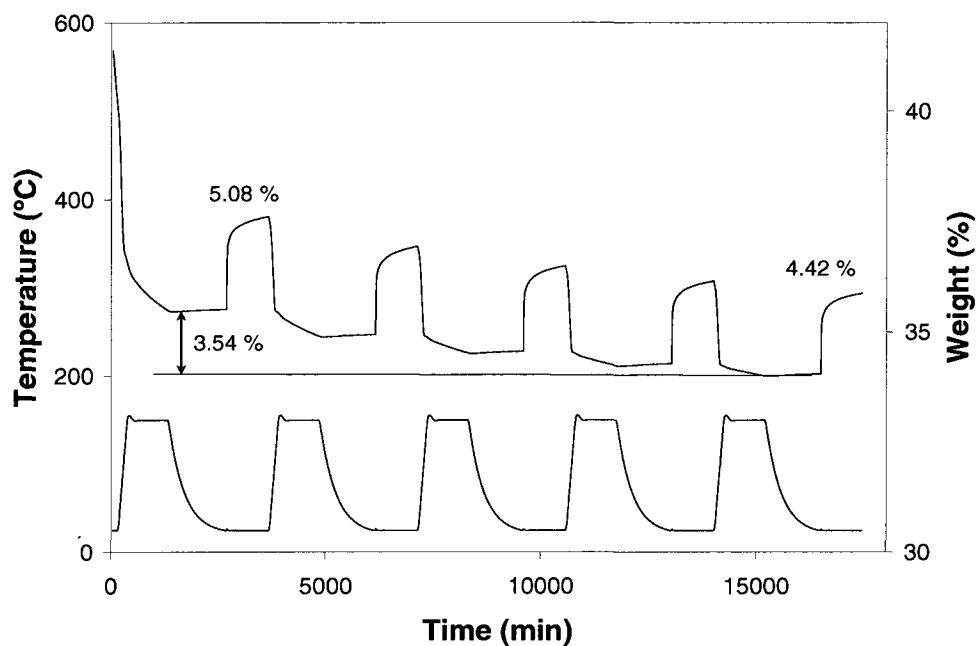


Figure 4.4. Cyclic adsorption-desorption profiles for PE-MCM-41/I/1.0.

The surface of PE-MCM-41 silica was also functionalized with branched tris(2-aminoethyl)amine in order to compare the performance of this functional group with that of the pentaamine. Since the branched tetraamine contains two primary amine groups, therefore regardless of the presence of tertiary amine, the average CO_2/N ratio is expected to be the same as that of the linear pentaamine. Branched amine functionalized PE-MCM-41/I/1.0 and PE-MCM-41/Cl/0.5 materials were prepared. The molar amounts of amine introduced into the materials and the amine efficiency were found to be close to that of corresponding pentaamine materials.

4.3. Conclusion

In conclusion, the polyamine functionalized PE-MCM-41 mesoporous silica for CO₂ adsorption has been successfully synthesized by reacting polyamine groups with halopropyl groups grafted with the aid of water on the silica surface. This preparation method allowed to introduce pentaamine and tris(2-aminoethyl)amine functionalities not available commercially as silane derivatives. The resulting materials showed maximum CO₂ adsorption of 6.06 %wt at room temperature. The materials with high quantity (1.93 mmol/g) of polyamine showed higher CO₂ uptake at higher temperatures due to the diffusion limitations. Ultimately, complete pore filling at amine loading of 2.52 mmol/g resulted in amine inefficiency. By comparison with iodopropyl groups, it was observed that the chloro groups react more readily with the surface in the presence of water resulting in better amine efficiency at lower amine loadings. However slower chemical reaction with amines results in bridged species and therefore lower than expected amine loading and efficiency.

4.4. Experimental

4.4.1. PE-MCM-41.

MCM-41 was prepared as previously reported and subsequently pore-expanded by post-synthesis treatment.[6]

4.4.2. 3-iodopropyltriethoxysilane grafted PE-MCM-41.

PE-MCM-41 was dehydrated at 393 K under vacuum to remove any water adsorbed to the surface. In a round bottom flask 1.00 g of silica was dispersed in 150 mL of toluene and preheated to 80 °C. 2.5 mL of 3-iodopropyltriethoxysilane was added and the solution stirred vigorously for 16 h. The sample was collected by filtration, washed with toluene and dried at RT overnight.

4.4.3. 3-iodopropyltriethoxysilane grafted PE-MCM-41.

The sample was prepared according to the above procedure, 2.33 mL of 3-chloropropyltriethoxysilane was added.

4.4.4. Pentaamine functionalized PE-MCM-41 (PA- PE-MCM-41).

To a solution of tetraethylpentaamine (0.24 mL) and triethylamine (0.20 mL) in 15 mL of toluene 0.2 g of chloropropyl- or iodopropyl-PE-MCM-41 was added. The mixture was immersed in a preheated oil bath and stirred for 15 min at 80 °C. The solid was then filtered, washed with toluene and dried at RT. The obtained materials were designated PE-MCM-

41/X/Y, where X is the halogen of the halopropyl group and Y is the amount of water used during the grafting procedure.

4.4.5. Branched tetraamine functionalized PE-MCM-41 (BTA- PE-MCM-41).

The sample was prepared using the above procedure, tris(2-aminoethyl)amine, triethylamine and toluene were mixed under inert conditions. The mixture was immersed in a preheated oil bath and stirred for 1 h at 80 °C.

4.4.6. Characterization.

Nitrogen adsorption–desorption isotherms of the amine functionalized materials were obtained at 77 K using a Micromeritics ASAP 2020 volumetric adsorption analyzer. Before measurements, the sample was degassed in vacuum overnight at ambient temperature. The BET specific surface area was calculated from the nitrogen adsorption data in the relative pressure range from 0.06 to 0.2. The total pore volume was determined as the volume of liquid nitrogen adsorbed at a relative pressure of 0.99.

The amount of halopropyl functional groups grafted was determined by a thermal decomposition method using thermogravimetric analyzer (TGA). The sample was heated at a rate of 10 °C/min up to 800 °C under flowing nitrogen, followed by complete combustion of the organic material under air up to 1000 °C.

TGA was also employed to monitor the adsorption of CO₂ of the amine containing samples, as a weight change. Before the sorption test the samples were activated by pre-heating in N₂ flow at 150 °C. Materials were then cooled down to 25 °C (or higher) and CO₂ (5% in N₂, UHP) introduced into the system at a flow rate of 100 mL/min. The flow of CO₂ mixture

was continued for 1 h. The organic content was obtained by subsequent decomposition (as described above). Gas cyclic adsorption-desorption experiments were performed by repeating activation (regeneration) and adsorption steps.

4.5. References

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CHAPTER 5

Photoresponsive Azobenzene-Bridged Mesoporous Organosilica

Abstract: A bridged photoresponsive arylorganosilane 1,4'-bis(triethoxysilyl)azobenzene is used as a precursor for the synthesis of pure mesoporous azobenzenesilica. For the first time, palladium catalyzed silylation using triethoxysilane is used for the preparation of a silsesquioxane from its iodo-derivative. The novel organosilica material with pore diameter of 39 Å and specific surface area of 384 m²g⁻¹ also exhibits molecular-scale periodicity within the pore walls. Reversible *trans*-to-*cis* isomerization of the azobenzene moieties integrated in the framework indicates that the organosilica remains flexible enough to undergo such contractions under UV irradiation.

5.1. Introduction

The majority of PMOs synthesized up to date, have organic functionalities that consist mainly of alkanes, alkenes and aromatic rings that serve primarily 'passive' roles such as reducing the dielectric constant of the framework or enhancing hydrophobicity. Introduction of more diverse functionalities was achieved by several groups,[8,9] although incorporating large content of organosiloxanes into the framework remained a challenge.[9] Obtaining PMOs that are responsive to external stimuli in a controlled manner is a highly desirable achievement. Therefore recently, several groups began to study luminescent properties of materials with conjugated organic groups. Other materials with potential

optoelectronic applications were prepared such as, PMOs consisting of an energy donor and acceptor incorporated into the framework and the surfactant micelles, respectively (see Chapter 1).

Particularly promising candidates for optical applications are photoisomerizable azobenzene derivatives owing to their efficient and fully reversible photochromism. These compounds, existing usually in *trans* configuration, can be isomerized to their *cis* isomers by photoirradiation. The *cis* isomer is less stable and therefore thermally relaxes back to the *trans*-azobenzene derivative.

Photoresponsive materials containing azobenzene functionality including surface modified mesoporous silicas are widely studied.[10] Self assembly of organosilicas derived from an azobenzene-bridged silsesquioxane was studied by X-ray diffraction.[10a] Optical control of d-spacings corresponding to lamellar mesostructures of the *trans* and *cis* isomers was achieved through photoisomerization of the azobenzene moiety before or after assembly. The photo and thermal responsiveness was also evidenced by UV-vis spectroscopy for azobenzene derivatives grafted inside the channels of mesoporous silica films.[10b] Changing the length of the grafted moiety by photoisomerization enabled dynamic photocontrol of the pore size and hence regulated mass transport through the thin film.[10c] Immobilization of small amounts of azobenzene derivatives in a mesoporous silica matrix through co-condensation with tetraethyl orthosilicate (TEOS) was achieved while maintaining the photoswitchable property. It was, however, observed that the isomerization does not occur in materials prepared by the sol-gel method without added TEOS.[10d]

Herein, we report for the first time the synthesis of pure azobenzene-bridged porous organosilica, and we demonstrate that the photoisomerization of the azobenzene moieties integrated in mesoporous organosilica network is not limited to materials with chromophores diluted in silica, but can take place in pure PMO. Also, for the first time palladium catalyzed reaction is used for the preparation bis(trialkoxysilyl) organic precursors by silylation of its iodo-derivative with triethoxysilane.[11,12]

5.2. Results and Discussion

Examination of the material by X-ray diffraction (Figure 5.1) revealed a low angle Bragg-diffraction peak at $2\theta \approx 2.7^\circ$ attributed to a mesophase with a lattice constant of 39 Å. The XRD patterns lack the higher order reflections indicating the occurrence of a disordered wormhole pore system which is consistent with TEM micrograph (Figure 5.2). Typically, the XRD peak intensity doubled upon surfactant removal; however, the peak broadened indicating that the pore size distribution widened. In addition to the small angle diffraction a series of broad but distinct peaks appeared (see arrows in Figure 5.1), indicative of the occurrence of molecular-scale order within the pore walls, similar to that observed in other aromatic-containing PMOs.[5,6,7,8] Although, increasing the TEOS content from 0% to 20% gave rise to improved periodic organization, it understandably decreased the molecular order within the sample (Figure 5.1). The nitrogen adsorption isotherm featured quite broad hysteresis loop confirming the occurrence of mesopores (Figure 5.3). The BET surface area was $384 \text{ m}^2 \text{ g}^{-1}$ and the total pore volume was $0.58 \text{ cm}^3 \text{ g}^{-1}$.

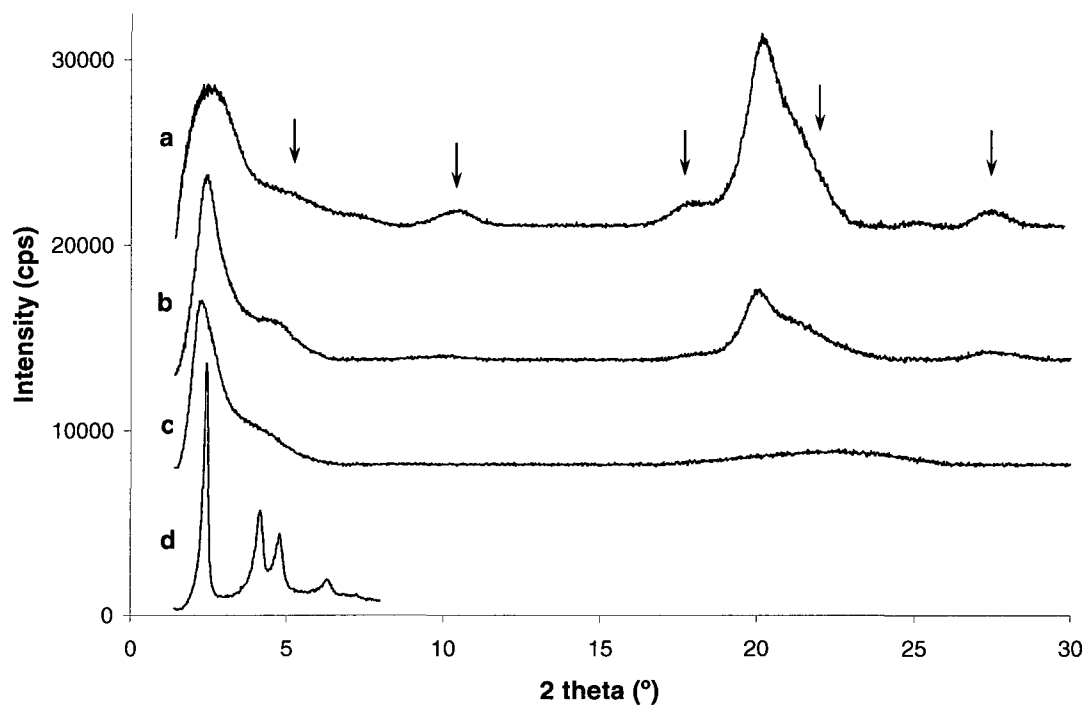


Figure 5.1. X-ray diffraction pattern of the extracted organosilica samples with (a) 0%, (b) 60%, (c) 20% TEOS added, and (d) pure silica sample.

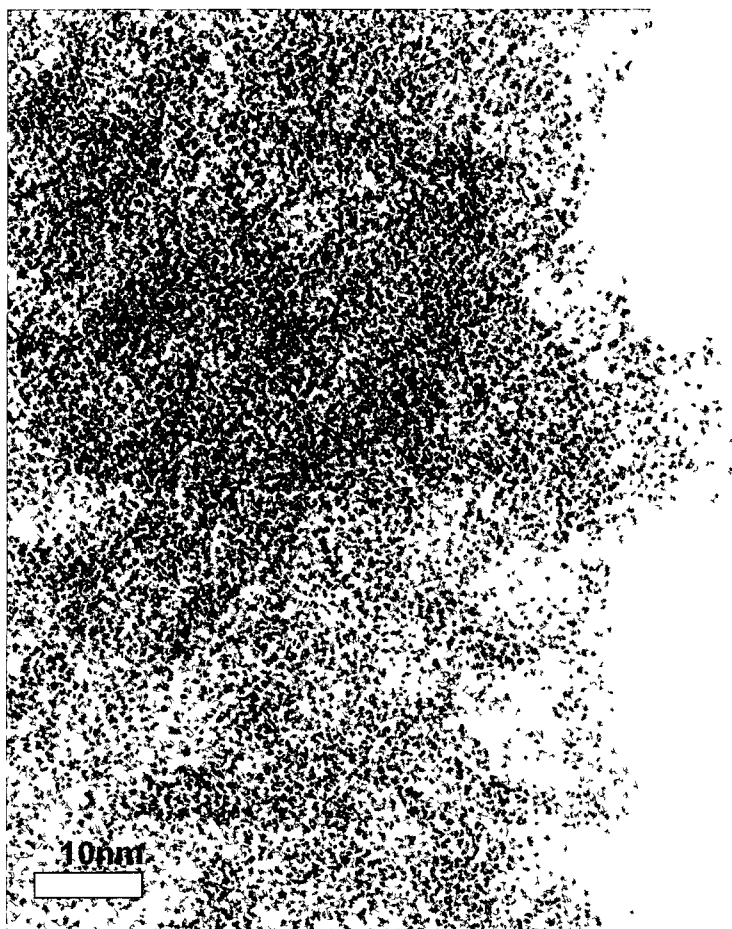


Figure 5.2. TEM of azobenzene-bridged mesoporous organosilica.

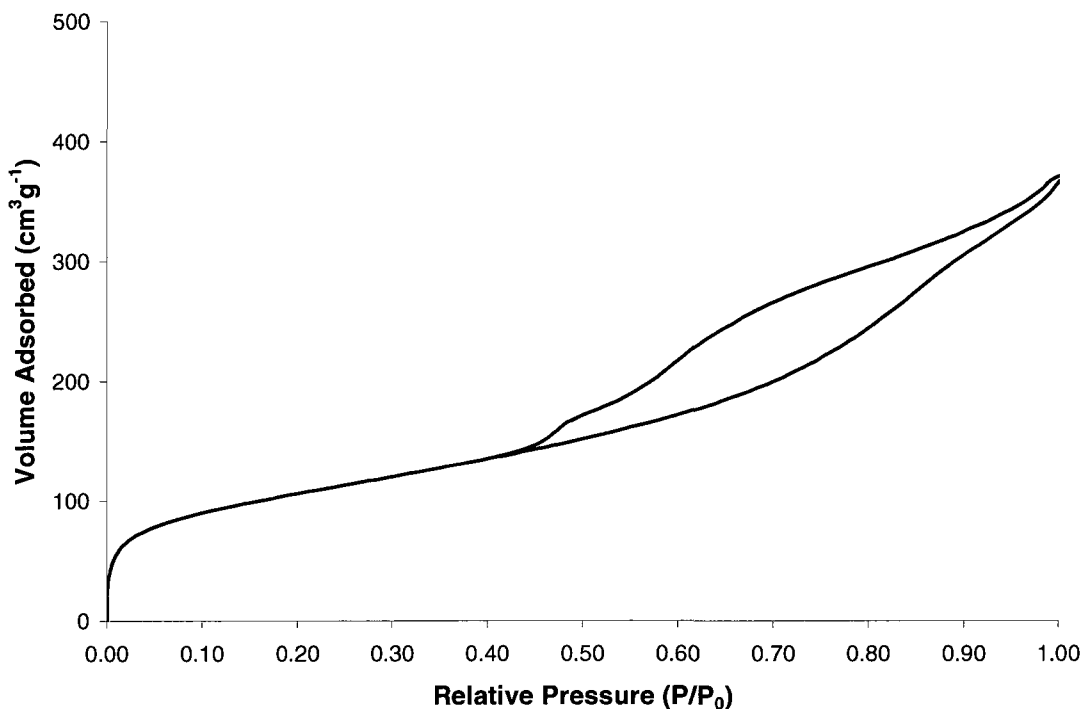


Figure 5.3. Adsorption isotherm of the azobenzene-bridged organosilica.

The ^{13}C cross polarization MAS NMR spectrum was comprised of four aromatic resonances attributable the four distinct carbon atoms of the azobenzene moiety. This indicates that all the bonds remained intact during the material synthesis and that the organic functionality covalently bonded to silicon consists of 1,4-substituted benzene units. Similar groups of four peaks are apparent in lower and higher regions, those are spinning sidebands. No signal was observed at 30 ppm indicating complete surfactant removal. The peaks in ^{13}C cross polarization MAS NMR spectrum (Figure 5.4) were assigned using dipolar dephasing sequence and on the basis of liquid state chemical shifts of the precursor. Assignment of the NMR signals to specific carbon atoms is given in Figure 5.4. The ^{29}Si CP MAS NMR spectrum (Figure 5.4) resembles a typical spectrum for symmetrically bridged mesoporous

organosilica.[13] It consists of a major T³ (-79 ppm) resonance and a weak T² (-70 ppm) resonance representative of Si species covalently bonded to carbon atom.

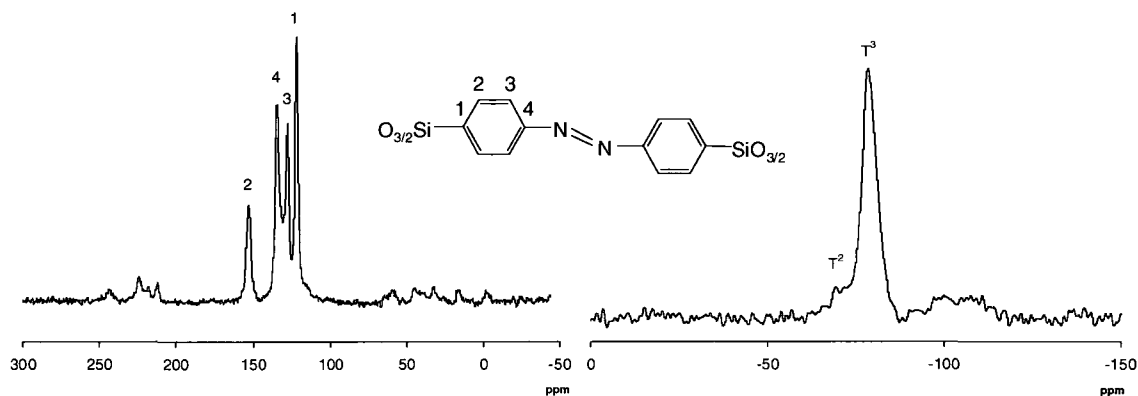


Figure 5.4. ¹³C and ²⁹Si CP MAS NMR of the azobenzene-bridged mesoporous organosilica.

Thermogravimetric analysis was used to investigate the thermal stability of the material and for quantitative verification that the framework consists of the same relative amount of organo-bridged siloxane as predicted based on the composition of the synthesis mixture. High thermal stability of the material was observed as no substantial weight loss was detected under flowing nitrogen up to 320 °C. Thermal degradation of the organosilicate framework occurred over the 320-1000 °C range. The total weight loss of the pure organosilica sample was 69.1%. This experimental value is in acceptable agreement with the calculated content (63.4%) of azobenzene groups based on a framework composition of O_{3/2}Si-C₆H₄-N=N-C₆H₄-SiO_{3/2}. The percentages of the azobenzene incorporated in the samples with TEOS also agree with the calculated values based on the initial BTS AZB to TEOS ratios (Table 5.1). The decomposition temperature was higher than that of the

materials prepared *via* surface modification which underwent decomposition of the organic moieties between 140 and 620 °C. [10]

Table 5.1. Structural properties of the mesoporous materials.

organosilica/TEOS molar ratio	% of organics		S_{BET} (m^2g^{-1})	V_{tot} (cm^3g^{-1})	d_{211} (nm)
	calculated	from TGA			
100	63.4	69.1	384	0.58	3.9
80	60.2	60.5	430	0.52	3.7
60	55.5	59.8	471	1.23	4.2
40	48.1	45.9	725	1.00	3.9
20	34.3	26.0	945	0.53	4.4
0	0	--	869	0.72	4.2

The Raman spectrum of the pure organosilica sample (Figure 5.5) revealed distinctive features of motions related to azobenzene moiety. In-plane benzene ring vibrations and C-H out-of-plane bending appear at 1593 cm^{-1} and 999 cm^{-1} respectively, whereas Raman scattering features in the $1380 - 1470\text{ cm}^{-1}$ region correspond to $-\text{N}=\text{N}-$ stretching vibrations.[14]

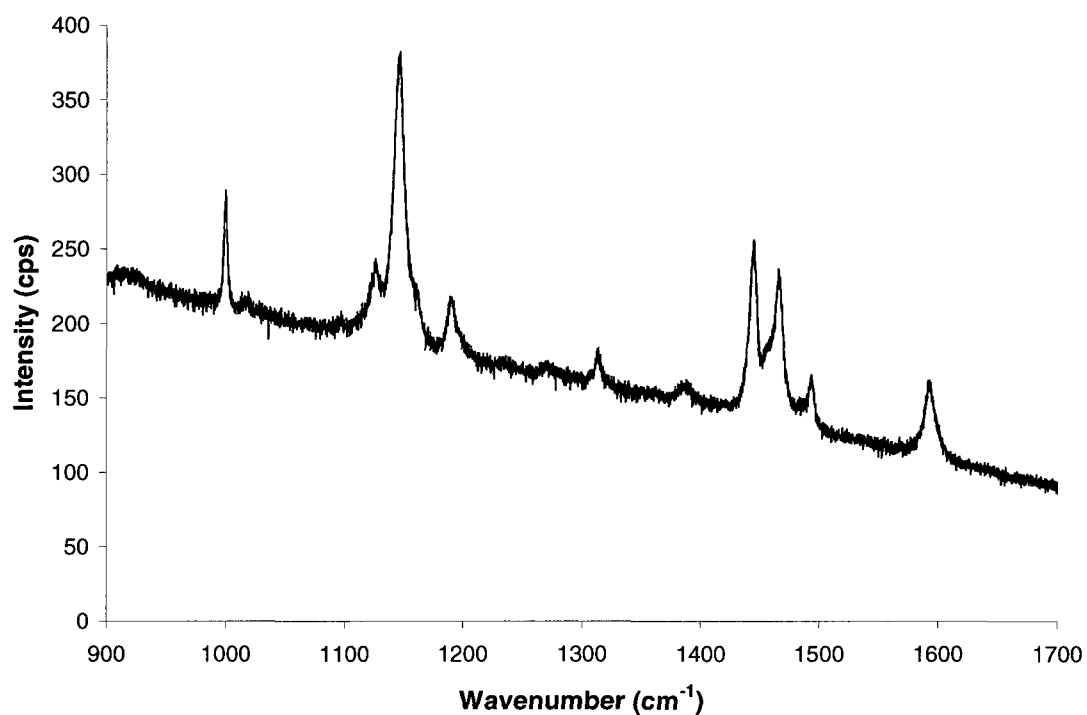


Figure 5.5. Resonance Raman spectrum of azobenzene-bridged mesoporous organosilica.

Table 5.2. Tentative assignments of the Raman bands.

Raman lines (cm ⁻¹)	Tentative assignments
999	CH out-of-plane bending
1146	CN stretching
1388	NN stretching coupled with ring vibrations
1444	
1465	
1593	ring vibrations

The UV-vis spectroscopy was used to characterize the photo-responsiveness of azobenzene moieties within the organosilica framework. It also permitted to study the flexibility of organosilica network based on the mobility of the organic molecules. In the photoexcitation experiment, the material was pressed into a pellet and irradiated with UV-A lamps with overall power of 8 W. The exposure time of 15 minutes was sufficient to produce apparent *trans*-to-*cis* isomerization (Figure 5.6). Absorption spectra were recorded 5 minutes after switching the light source off until the difference in absorbance between subsequent spectra was minimal. The spectrum of the material exhibited an absorption band at 325 nm attributed to the π - π^* transition of the *trans* isomer and a weaker band at 450 nm due to n- π^* transition of the *cis* form. Time difference of 5 minutes between the measurements was satisfactory to observe changes in *cis/trans* population as the exposure to the room light caused reverse isomerization to the thermodynamically more stable *trans* isomer. The initial *trans* population was nearly restored after 1 day. These results are completely reversible and indicate that the *trans*-to-*cis* isomeration is possible in pure azobenzene-bridged mesoporous organosilica.

5.3. Conclusion

A novel palladium catalyzed reaction was used for the preparation of bis(trialkoxysilyl) organic precursor by silylation of its iodo-derivative with triethoxysilane. A bridged photoresponsive arylorganosilane was synthesized and used for the surfactant-assisted synthesis of PMO. It was demonstrated that the reversible photoisomerization of the azobenzene moieties integrated in mesoporous organosilica was possible. The UV-vis

spectra of the material prepared only from bis(triethoxysilyl)azobenzene revealed the mobility of incorporated azobenzene functionality upon UV irradiation. The product exhibited also some molecular order attributed to the formation of a lamellar structure within the pore wall.

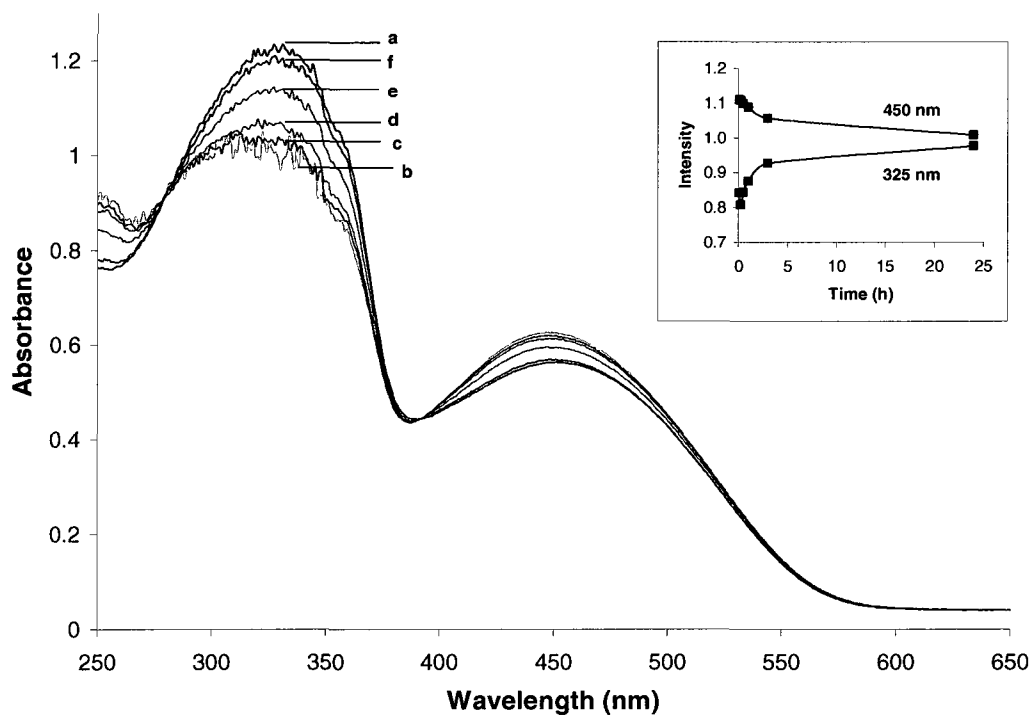
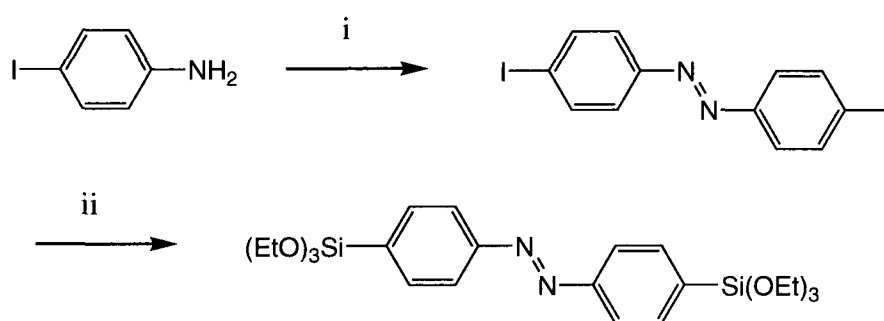


Figure 5.6. UV-vis absorption spectra of the azobenzene-bridged mesoporous organosilica sample (a) before exposure to UV-A for 30 min and (b) 5 min, (c) 30 min, (d) 1 h, (e) 3 h and (f) 1 day after the exposure.

5.4. Experimental

The azobenzene-containing organosiloxane precursor was prepared according to Scheme 5.1. Coupling of 4-iodoaniline afforded 4,4'-diiodoazobenzene.[15] The arylsilane was then synthesized via palladium catalyzed silylation of 4,4'-diiodoazobenzene with triethoxysilane.[11] The use of hydrotriethoxysilane instead of tetraethoxysilane led to higher yield.[12] The corresponding porous organosilica was prepared by self-assembly of the precursor in the presence of cetyltrimethylammonium bromide (CTAB) in basic aqueous medium.



[i] MnO_2 , benzene, 90 °C; [ii] $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$, $\text{P}(o\text{-tol})_3$, $i\text{-Pr}_2\text{NEt}$, $(\text{EtO})_3\text{SiH}$, NMP, rt to 80 °C

Scheme 5.1. Preparation of bis(triethoxysilane)azobenzene precursor.

5.4.1. Synthesis of 4,4'-diiodoazobenzene.

An amount of 4.60 g of 4-iodoaniline (21 mmol) and active manganese (IV) oxide (9.13 g, 105 mmol) in benzene (100 ml) were refluxed for 6 h. The hot solution was filtered and washed with benzene until the filtrate was colorless. The filtrate was concentrated and

crystallized by addition of hexanes forming orange plates (55% yield). The product was characterized as 4,4'-diiodoazobenzene by ^{13}C and ^1H NMR.

5.4.2. Synthesis of bis(triethoxysilyl)azobenzene (B TSAZB).

A Schlenk flask was charged with $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (80 mg, 0.08 mmol), $\text{P}(o\text{-tol})_3$ (91 mg, 0.30 mmol), iodoazobenzene (1 g, 2.45 mmol) and N-methylpyrrolidone (NMP) (20 mL; distilled from CaH_2 before use). The reaction vessel was purged with nitrogen, subsequently *i*- Pr_2NEt (2.6 mL, 15 mmol) and triethoxysilane (1.24 g, 7.5 mmol) were added via syringe. The mixture was stirred for 1 h at room temperature, then at 70 °C for 5 h. The reaction mixture was taken up in chloroform, extracted three times with water to remove NMP, dried over MgSO_4 and concentrated. Purification by column chromatography (hexanes:ethanol = 9:1) afforded 410 mg (32% yield) of product as orange oil identified as B TSAZB. ^1H NMR (400 MHz, CDCl_3 , δ): 1.19 (t, 18H, $\text{SiOCH}_2\text{CH}_3$), 3.78 (q, 18H, $\text{SiOCH}_2\text{CH}_3$), 7.4-8.0 (ArH); ^{13}C NMR (100 MHz, CDCl_3 , δ): 18.3 ($\text{SiOCH}_2\text{CH}_3$), 58.9 ($\text{SiOCH}_2\text{CH}_3$), 122.7, 129.1, 135.7 and 152.7 (ArC); ^{29}Si NMR (99.4 MHz, CDCl_3 , δ): -58.3.

5.4.3. Synthesis of azobenzene-bridged organosilica.

This material was prepared using B TSAZB as precursor and CTAB as template. The synthesis mixture had the following molar composition B TSAZB/CTAB/ NH_4OH / H_2O /EtOH: 0.5/0.24/16/327/16. Initially the surfactant was dissolved in water, then NaOH was added under stirring and after complete dissolution, the precursor dissolved in ethanol was added to the solution at room temperature. An orange precipitate appeared upon stirring. After 30 minutes of stirring, the temperature was raised to

80 °C and the mixture aged for another 4 days under static conditions. The solid product separated by filtration was dried at ambient conditions and the surfactant removed by two consecutive solvent extractions using 150 mL of ethanol with 2 g concentrated HCl for 1.0 g sample at 50 °C for 6 h. Samples containing BTSAZB in mole fractions of 80%, 60%, 40%, 20% and 0% as a mixture with TEOS were also prepared.

5.4.4. Characterization.

Powder X-ray diffraction (XRD) analysis was performed using a Philips PW3710 diffractometer operated at 45 kV, 40 mA, with CuK α radiation, 0.02° step size and 1.0 s accumulation time per step. Nitrogen sorption isotherm was determined with a Coulter Omnisorp 100 gas analyzer at 77 K. Before analysis the sample was evacuated at 200 °C under vacuum. The BET specific surface area, SBET, was obtained from the nitrogen adsorption data in the relative pressure range 0.05-0.15 and the total pore volume was determined as the amount of liquid nitrogen adsorbed at $P/P_0 = \text{ca. } 0.99$. The pore size distribution was derived from the adsorption branches using the KJS (Kruk-Jaroniec-Sayari) method.[16] UV-visible spectra were recorded with a Varian Cary 300 spectrometer. Transmission electron micrograph (TEM) was recorded on a JEOL JEM-2100F instrument. ^{29}Si and ^{13}C CP MAS NMR spectra were recorded at room temperature on a Bruker AVANCE 500 instrument in a magnetic field of 11.7 T. The weight loss curves were recorded on a TGA thermogravimetric analyzer (model Q500-TGA, TA Instruments). The sample was heated from ambient temperature to 1000 °C at a heating rate of 15 °C/min. The atmosphere was switched from flowing nitrogen to air at the temperature of 900 °C. Raman spectrum of the material was collected with a HORIBA Jobin Yvon LabRam-IR HR800

system. The powdered sample was irradiated with an Ar-ion laser (λ 785 nm) and the signal detected by a CCD camera.

5.5. References

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CHAPTER 6

Investigation of Periodic Mesoporous Organosilica with Dimethylphenyl and Ethylene Spacers by Correlation NMR Spectroscopy

Abstract: Periodic mesoporous organosilicas (PMOs) were synthesized using two silsesquioxane precursors containing bulky dimethylphenyl (DMB) and smaller phenylene (Ph) or ethylene (E) spacers. The synthesized DMB-E-PMO and DMB-Ph-PMO materials exhibited high surface areas of 1100 and 1055 m²/g, with improved organization over the pure dimethylphenyl organosilica, with a surface area of 515 m²/g. Successful incorporation of both organic spacers was demonstrated by NMR and TGA. The 2D ²⁹Si-¹H heteronuclear correlation technique was employed to specifically address the issue of structural homogeneity in the bifunctional DMB-E-PMO. The heteronuclear correlation experiment showed that the two distinct moieties were in close contact, indicating the formation of a chemically homogeneous network with the spacers randomly distributed, regardless of differences in the size of the organic bridges.

6.1. Introduction

Periodic mesoporous organosilicas (PMOs) with ordered pore network and homogenous distributions of organic moieties in the framework are an important class of materials with potential applications in many areas such as catalysis, adsorption and optoelectronics.[1,2] Precursors with a large variety of organic spacers (R') have been used for the synthesis of pure PMOs.[1] Most single precursors used had simple organic spacers such as methylene, ethane, ethylene, phenylene, biphenylene, naphthalene, thiophene, etc,

and a limited number of bifunctional species.[3] However, silsesquioxane molecules with bulky or flexible spacers were difficult to self assemble without the addition of a silica precursor such as tetraethylorthosilicate. Another route, introduced recently to increase the diversity of PMOs, consisted of co-condensation of multiple organosiloxane precursors to achieve different functionalities within the pore walls.[4] Numerous PMOs using two[4-14] or three[4,15] precursors have been reported. Elaboration of materials with multiple functional bridging groups allowed the further expansion of the range of PMOs with finely tailored properties by varying the content and the nature of the functionalities.[11] Another advantage of using multiple precursors is the fact that organosilica precursors with small bridging groups were found to facilitate the condensation of silsesquioxanes with large bridging groups by stabilizing the porous network, without greatly affecting the surface properties of the material such as the hydrophobicity.[5,13] Nevertheless, a major limitation to the synthesis of well organized PMOs using multiple precursors is the discrepancy in hydrolysis and condensation rates of the structurally different precursors, due to their different hydrophobic characters. Thus, judicious choice of the precursors and synthesis conditions is required to obtain well ordered and homogenous materials.[15]

Multiple precursor-derived PMOs were characterized mostly by standard techniques such as microscopy, ^{29}Si and ^{13}C MAS NMR, XRD, nitrogen adsorption and the results were interpreted based on the implicit assumption of the formation of a single homogeneous mesophase with organic spacers randomly distributed within the pore walls.[4,6] However, since the surface properties of such materials are likely to depend on the details of the local structure, probing the organization of the organic spacers within the pore walls at the molecular level is an important endeavor to fully understand the properties of these

materials. Specifically, the question as to whether one or more phases form or the possible occurrence of molecular segregation within the same mesophase when multiple precursors are used should be systematically addressed. Most of the aforementioned techniques are not highly discriminating, except under some exceptional circumstances. For example, Yang and Sayari[9] co-condensed organosilica precursors containing phenyl and biphenyl bridging groups under basic conditions, favorable for the formation of molecular order within the pore walls to evaluate the distribution of the organic spacers. Structure determination of the resulting material using XRD revealed two distinct series of molecular-scale periodicities associated with phenylene and biphenylene species. These results indicated the formation of separate domains of phenyl and biphenyl silicas sufficiently large to generate a series of equidistant XRD peaks. However, this technique did not provide an unambiguous answer as to whether this is the result of phase segregation or phase separation. All the other techniques used to characterize these materials such as nitrogen adsorption, SEM, TEM, ^{29}Si and ^{13}C CP MAS NMR were not helpful to shed light on the homogeneity of the materials. Notice that even XRD would have not been appropriate if the material did not exhibit the pore wall molecular order, since the low angle peak associated with the occurrence of the mesophase(s) was too broad and unresolved. Khimyak et al.[7,10] made significant contributions in this area through their investigation of a PMO with ethane and ethylene bridging groups using NMR as the main characterization tool. Although NMR spectra are not sensitive to long range order, the detail and the unambiguous nature of the information make it an effective tool for short range structural identification and elucidation. Khimyak et al. [7,10] made use of the differences between the cross polarization dynamics of the T sites $[\text{CSi}(\text{OSi})_n\text{OH}_{3-n}]$, $n = 1-3$ in single and two precursor-derived PMOs to

characterize the level of homogeneity of the mixed-precursor material. Interestingly, only ^1H - ^{29}Si HETCOR experiments provided an unambiguous answer concerning the through-space dipolar interactions of the two organic bridges. The presence of cross-peaks correlating the ^1H resonance of one bridging group to the silicon sites of the other linking moiety indicated that the two functionalities were homogeneously distributed throughout the framework.

In order to gain further insights into the organization of multiple precursor organosilicas, we used ^1H - ^{29}Si heteronuclear correlation (HETCOR) to investigate a PMO containing bulky 2,5-dimethylphenyl and smaller ethylene bridging groups synthesized under basic conditions. Our objective was to unambiguously determine the spatial proximity of the organic moieties in this PMO synthesized from precursors with different Si-Si distances, as well as spacers with different sizes and hydrophobic characters.

6.2. Results and discussion

Figure 1 shows the low and high angle XRD patterns of the materials. A single peak observed in the small-angle range for DMB-PMO and DMB-E-PMO corresponds to the formation of periodically structured mesophase with lattice spacing of $d = 4.4$ nm for DMB-PMO and 3.5 nm for DMB-E-PMO. Assuming hexagonal symmetry, this spacing would correspond to a unit cell dimension ($a_0 = 2d_{100}/\sqrt{3}$) of 5.08 and 4.04 nm, respectively. The broad diffraction peak at ca. 10 degree was attributed to the occurrence of molecularly ordered pore walls with an interlayer spacing of $d = 9.4$ Å.[16] The expected spacing based on fully condensed periodic mesoporous dimethylphenyl-silica would be 7.6 Å.[16] The

larger than anticipated interlayer distance (9.4 vs. 7.6 Å) for the current materials containing the dimethylphenyl spacer can be associated with the occurrence of hydrogen bonding. It has been demonstrated that if the PMO material does not fully condense, the hydroxyl groups formed via hydrolysis of the silane alkoxy groups may stabilize the structure via interlayer hydrogen bonding. As a result, the interlayer species would be substantially longer and the resulting interlayer distance may be up to 2.5 Å larger than in the fully condensed PMO.[18] The influence of the hydrogen bonding on the average lattice spacing varies with the degree of silicate condensation. Consistent with our finding, Inagaki and coworkers¹⁸ reported that phenylene-bridged silica with mostly T² and T³ species as detected by ²⁹Si NMR, exhibits an interlayer spacing $d = 9.3$ Å compared to 7.6 Å for the fully condensed material.[10] The lack of periodicity representative of the ethylene moiety, in the case of the DMB-E-PMO material, which would correspond to an interlayer distance of 5.6 Å indicates that the molecular organization of this material is dominated by the dimethylphenyl functionality.[19] Comparable intensity of the peaks in the diffractograms of DMB-Ph-PMO and DMB-PMO suggests that addition of the phenylene-bridged precursor to synthesize the PMO containing dimethylphenyl-bridges does not lead to better organization of the final material.

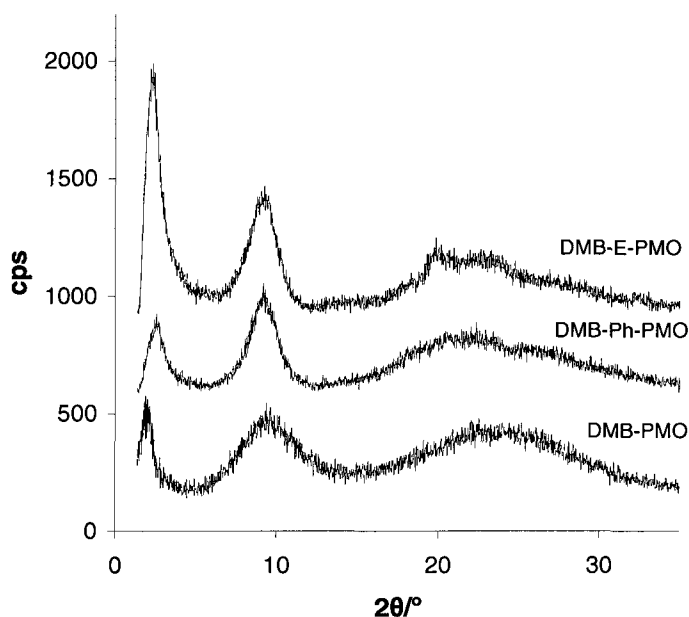


Figure 6.1. Powder X-ray diffraction patterns of the template extracted PMO materials: DMB-E-PMO, DMB-Ph-PMO and DMB-PMO.

The structural properties of the materials, as derived from the nitrogen adsorption data (Figure 2), indicate that addition of less hydrophobic ethylene or phenylene silica precursor to the dimethylphenyl-bridged precursor improves the overall organization of the resulting organosilica. The DMP-PMO displayed a surface area of 515 m²/g, attributed largely to the occurrence of micropores. The two precursor-derived PMO materials were highly porous. The surface areas were 1100 and 1055 m²/g for DMB-E-PMO and DMB-Ph-PMO, respectively. The PMO material containing ethylene and dimethylphenyl displayed larger pore volume than DMB-Ph-PMO (0.85 vs. 0.69 cm³/g). The adsorption measurements also indicated the occurrence of a larger ratio of mesopores compared to micropores within the DMB-E-PMO material, as suggested by XRD results.

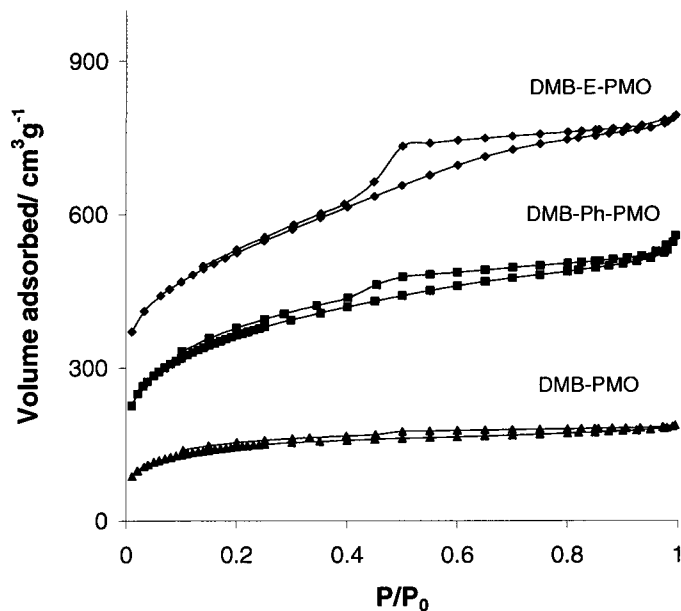


Figure 6.2. N₂ adsorption-desorption isotherm of the DMB-E-PMO, DMB-Ph-PMO and DMB-PMO organosilica samples.

The TEM images of the DMB-E-PMO material are indicative of a well organized mesoporous silica structure (Figure 3a). The micrograph viewed perpendicular to the pore channel axis clearly shows highly ordered parallel channels throughout the sample. Examination of several TEM images indicated uniform 3.5 nm interline spacing. Considering a hexagonal arrangement of the pores, the distance δ between the parallel lines is related to the unit cell dimension a_0 as follows $\delta = a_0 \cos(30)$ resulting in $a_0 = 4.1$ nm, that is in reasonable agreement with the average unit cell dimension (4.0 nm) determined by XRD.[20]



Figure 6.3. TEM image of DMB-E-PMO material viewed (a) perpendicular to the pore channel axis, (b) down the $[110]$ zone axes.

The ^{29}Si NMR spectra of the three PMO samples are shown in Figure 4. The signals associated with silicon bonded to the dimethylphenyl species appeared at $-61(\text{T}^1)$, $-70(\text{T}^2)$ and $-77(\text{T}^3)$ ppm (Figure 4c). The DMP-Ph-PMO material displayed three similar resonance peaks assigned to the overlapping T^n signals due to silicon atoms attached to dimethylphenyl and phenyl moieties. However, good resolution within the T^2 and T^3 species of the dimethylphenyl and the ethylene bridging groups in the DMP-E-PMO material was obtained. The peak separation is necessary to confirm the presence of the cross-peaks in the ^{29}Si - ^1H HETCOR spectrum and therefore to draw a definite conclusion about the homogeneity of the material. The hydrolysis and condensation rates of the individual precursors influence the ratio of the organic moieties in the final material.[5] Equal amounts of the appropriate organosilica precursors were used in the initial reaction mixture for the synthesis of DMP-Ph-PMO and DMP-E-PMO materials. However, despite the fact that the ^{29}Si CP MAS spectra are only semiquantitative, the relative intensity of the silicon species attached to the ethylene and dimethylphenyl functionalities in DMP-E-PMO material indicates that a smaller amount of ethylene groups was incorporated into the material compared to DMB groups. The exact amounts of organic functionalities could not be calculated from the TGA analysis due to the presence of variable amounts of unhydrolyzed ethoxy groups in the materials. Although, approximate calculations confirmed that a smaller amount of ethylene moieties was incorporated into DMP-E-PMO material. The DMP-Ph-PMO material, on the other hand, consisted of nearly equal amounts of the two functionalities.

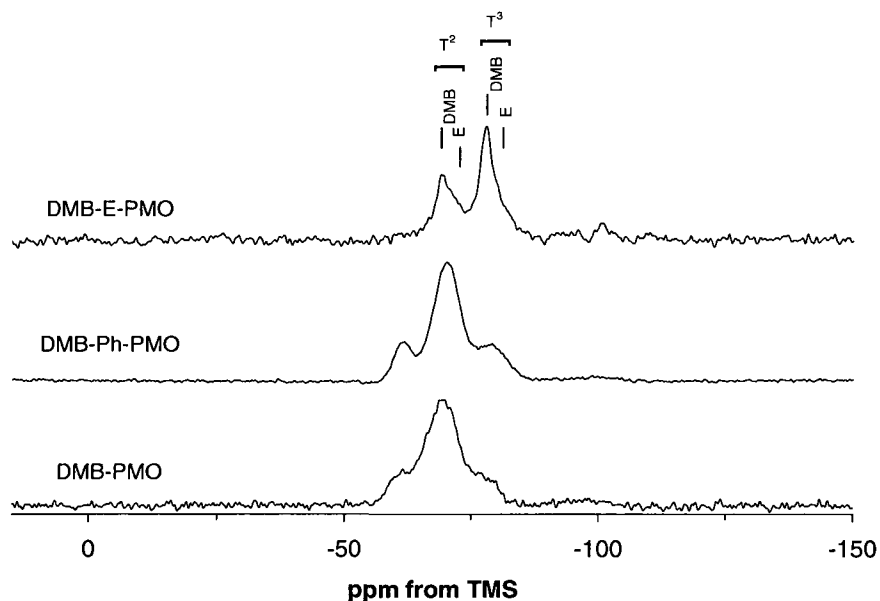


Figure 6.4. ^{29}Si MAS NMR spectra of the DMB-E-PMO, DMB-Ph-PMO and DMB-PMO.

^{13}C CP MAS NMR data were collected to verify the composition of the organosilica framework. The spectra of the single and two precursor-derived PMOs are shown in Figure 5. The spectrum of DMP-PMO exhibited resonance peaks at 21, 133, 136 and 139 ppm corresponding to the methyl and phenyl groups of the dimethylphenyl moiety. The ^{13}C CP MAS NMR spectra of the DMP-Ph-PMO and DMP-E-PMO material also exhibited peaks at 133 and 144 ppm, assigned to the carbon of the phenyl and ethylene bridging groups, respectively (indicated by arrows).[21] These results indicate the occurrence of both organic spacers in the prepared materials. Additional resonances due to residual ethoxy groups were also observed at 16 and 58 ppm.

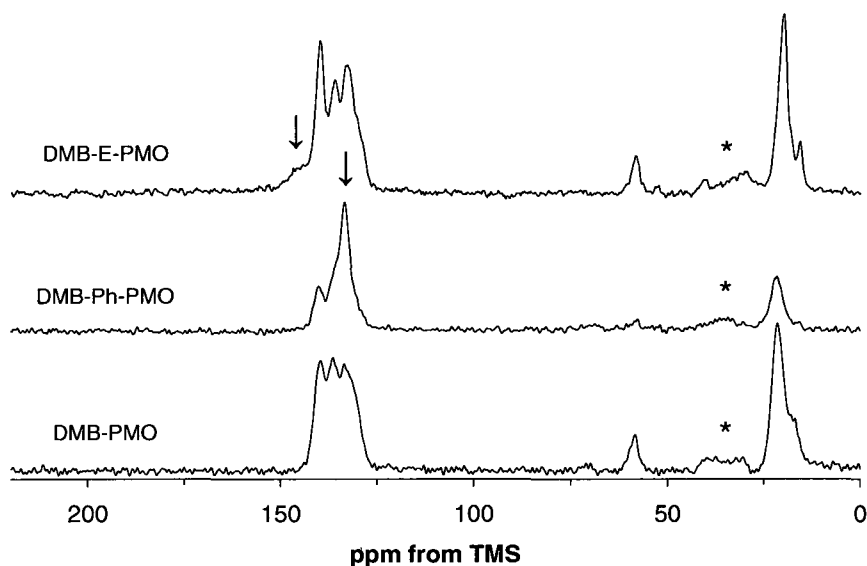


Figure 6.5. ^{13}C MAS NMR spectra of the DMB-E-PMO, DMB-Ph-PMO and DMB-PMO.

^1H - ^{29}Si HETCOR spectrum of DMB-E-PMO was acquired at 21.1 T to obtain the highest spectral resolution possible (Figure 6). The ^{29}Si spectrum plotted on the top is a projection and the ^1H spectrum plotted on the left-hand side is the 900 MHz ^1H MAS spectrum. The silicon dimension of the spectrum revealed four peaks: two T^2 [$\text{CSi}(\text{OSi})_2\text{OH}$] and two T^3 [$\text{CSi}(\text{OSi})_3$] framework sites, one in each pair corresponding to each of the bridging groups. ^1H resonances were observed at low frequency (0.5, 2.9, 3.8 ppm), which were attributed to unhydrolyzed ethoxy and uncondensed hydroxyl groups. A resonance associated with the methyl groups of the 2,5-dimethylphenyl bridge was also observed at 1.9 ppm. The high frequency region of ^1H MAS NMR provided sufficient resolution between ethylene and phenylene protons to assess their environments in the PMO.

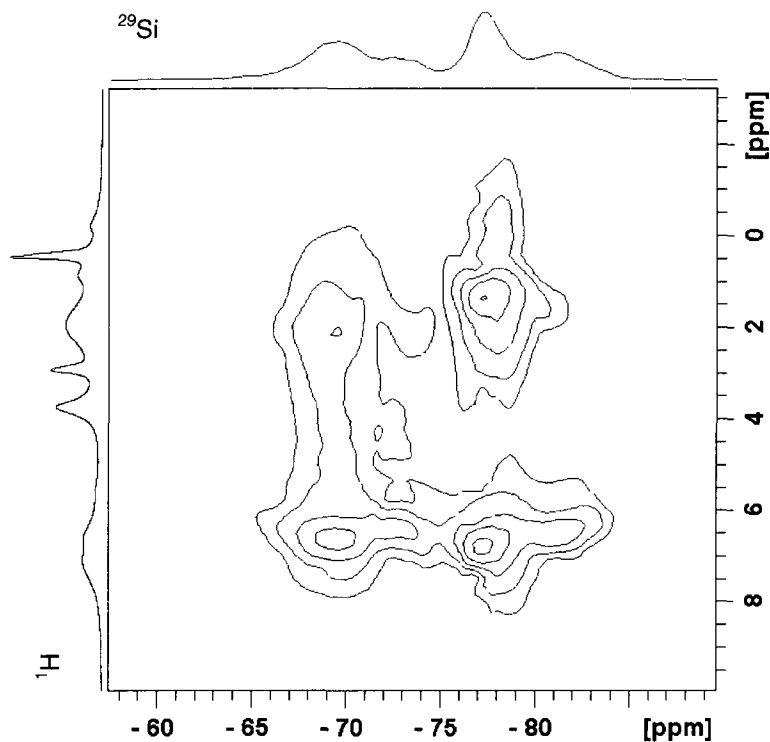


Figure 6.6. ^1H - ^{29}Si HETCOR spectrum of DMB-E-PMO bifunctional organosilica.

The correlation experiments were analyzed to extract information regarding not only the proximity of the two bridging groups but also the connectivity between framework silicon sites and hydroxyl and ethoxy groups. The HETCOR spectrum correlates the proton resonances of the bridging moieties to those of the corresponding silicon atoms, confirming the assignment of the proton and the silicon dimensions. The ^1H resonance of the methyl groups of dimethylphenyl moiety did not show significant interactions with ^{29}Si resonances of the ethylene bridge. However, the presence of a low intensity cross peak, correlating the protons of the methyl groups with T^3 Si species attached to ethylene groups, suggests that the interactions become apparent in the regions where the silica framework is more condensed and the two organic moieties are forced closer together (Figure 7a, 0 - 4 ppm

slice). In addition, the direct relation of the protons of ethylene moiety and all four silicon peaks indicates the occurrence of interactions between the two bridging moieties. This is indicative of homogenous (random) distribution of the organic functionalities in the framework (Figure 7b, 6 - 9 ppm slice). Further, the protons of the hydroxyl groups correlate strongly to the silicons attached to the dimethylphenyl moieties. This confirms the presence of stronger hydrogen bonding at those locations that contributes to the molecular periodicity with a longer spacing than has been typically found for fully-condensed phenylene-bridged PMO.

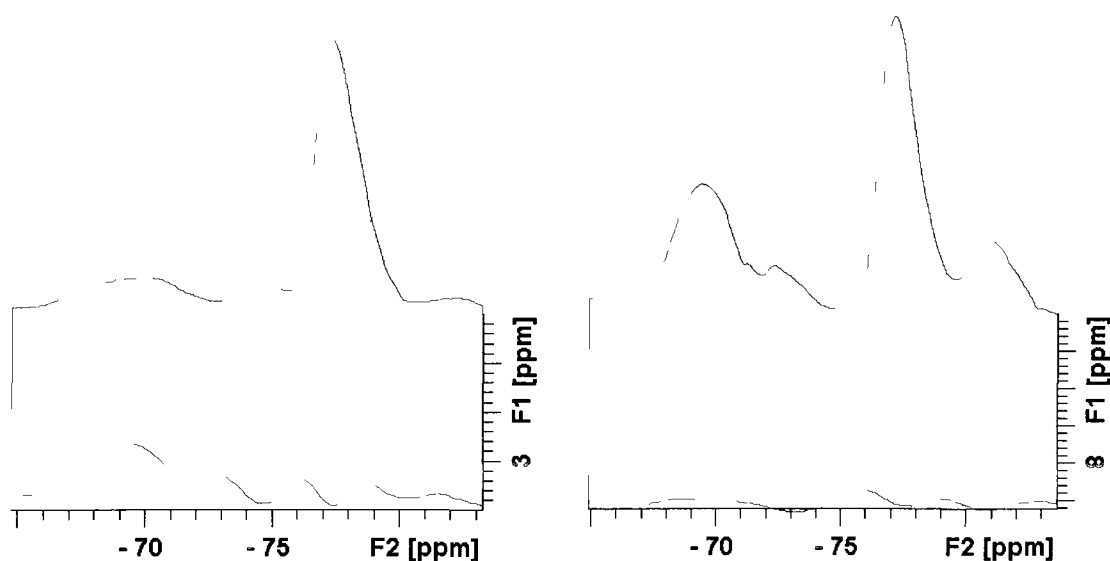


Figure 6.7. The (a) aliphatic and (b) aromatic region of ^1H - ^{29}Si HETCOR spectrum of DMB-E-PMO material.

6.3. Conclusion

PMOs were synthesized from multiple precursors using the supramolecular templating technique. The bulky dimethylphenyl-bridged precursor was incorporated into the PMO framework by adding ethylene- and phenylene-bridged silsesquioxane precursors to enhance condensation and improve the organization of the final material. The synthesized DMB-E-PMO and DMB-Ph-PMO materials exhibited high surface areas of 1100 and 1055 m²/g. Various techniques were used to confirm the presence of the two distinct spacers in the PMO materials, and the 2D ²⁹Si-¹H heteronuclear correlation technique was employed to specifically address the issue of structural homogeneity in the bifunctional PMO. Sufficient resolution in the H and Si dimensions is necessary to successfully employ HETCOR for molecular scale structure determination. Therefore, this technique is limited by the nature of the starting organosilane compounds and could only be used to identify through-space interactions in DMB-E-PMO, but not in DMB-Ph-PMO. The heteronuclear correlation experiment showed that the two distinct moieties were in close contact indicating the formation of a chemically homogeneous network regardless of differences in the size of the organic bridges. The current findings demonstrate that the NMR correlation experiment is a useful tool for the determination of structure homogeneity of multifunctional PMOs.

6.4. Experimental

6.4.1. Synthesis of 1,4-bis(triethoxysilyl)-2,5-dimethylbenzene.

The precursor was prepared via Grignard reaction.[22] In a typical synthesis, magnesium turnings (1.95 g), chlorotriethoxysilane (8.65 mL, 43 mmol) and dry THF (100 mL) were mixed in a three-necked flask, under nitrogen gas. 1,4-Dibromo-2,5-dimethylbenzene (5.28 g, 20 mmol) in THF was added dropwise. After 24 h of stirring at RT, the reaction mixture was filtered through Celite to remove the Mg salts, and the solvent was removed by vacuum distillation. Subsequently, hexane was added and the mixture filtered again, dried over MgSO_4 and concentrated. The oily residue was purified by column chromatography (hexanes:ethanol = 9:1) and distillation to afford 1.23 g of product identified as 1,4-bis(triethoxysilyl)-2,5-dimethylbenzene. ^1H NMR (400 MHz, CDCl_3 , δ): 1.25 (t, $\text{SiOCH}_2\text{CH}_3$), 2.45 (Ar- CH_3), 3.86 (q, 18H, $\text{SiOCH}_2\text{CH}_3$), 7.48 (ArH).

6.4.2. Material preparation.

1,4-bis(triethoxysilyl)-2,5-dimethylbenzene (1.33 g, 3.09 mmol) was suspended in aqueous solution of octadecyltrimethylammonium bromide surfactant (ODTMA, 1.04 g) in 51.3 g of water containing NaOH (0.50 g), and stirred at ambient temperature for 20 h to promote hydrolysis. After the mixture was aged at 95 °C for 2 days, the resultant precipitate was filtered and washed thoroughly with water. The as-synthesized material was subjected to a hydrothermal treatment in 85 mL of water containing 0.42 g of NaCl per gram of material, at 80 °C for 20 h. To remove the template surfactant, the sample was stirred in 150 mL of

ethanol acidified with 2 g of HCl, for 1 g of sample, at RT for 12 h. The final material will be referred to as DMB-PMO.

Two other PMO samples were synthesized under the same conditions by co-condensing equimolar amounts of dimethylphenyl-bridged precursor with ethylene- or phenylene-containing precursor, and were denoted DMB-E-PMO and DMB-Ph-PMO, respectively.

6.4.3. Characterization.

X-ray powder diffraction (XRD) data were acquired on a Philips PW3710 diffractometer using a nickel-filtered CuK_α radiation of 0.15405 nm, at 40 kV and 40 mA. The data were collected between 1.4° and 40° (2θ) with resolution of 0.02° and 1.0 s accumulation time per step. Nitrogen adsorption–desorption isotherms at 77 K were obtained using a Micromeritics ASAP 2020 volumetric adsorption analyzer. Before measurements, the sample was degassed in vacuum overnight at ambient temperature. The BET specific surface area was calculated from the nitrogen adsorption data in the relative pressure range from 0.06 to 0.2. The total pore volume was determined as the volume of liquid nitrogen adsorbed at a relative pressure of 0.99. Transmission electron microscopy (TEM) was performed on a JEOL JEM-2100F instrument operated at 200 kV. The samples were dispersed by sonication in a mixture of ethanol and chloroform, and then suspended over a carbon-coated Cu grids for imaging. The weight loss curves were recorded on a TGA thermogravimetric analyzer (model Q500-TGA, TA Instruments). The sample was heated from ambient temperature to 1000°C at a rate of $15^\circ\text{C}/\text{min}$. The atmosphere was switched from flowing nitrogen to air at the temperature of 900°C .

^{29}Si CPMAS NMR spectra for DMB-PMO and DMB-Ph-PMO were collected on a Bruker AVANCE III 200 equipped with a 7 mm CPMAS probe using a spinning speed of 5 kHz. The ^1H 90° pulse, contact time and recycle delay were 4 μsec , 2 msec and 2 sec, respectively. The ^{29}Si CPMAS NMR spectrum of DMB-E-PMO was collected on a Bruker AVANCE II 900 NMR spectrometer equipped with a 4 mm CPMAS probe using a spinning speed of 15 kHz. The ^1H 90° pulse, contact time and recycle delay were 3.5 μsec , 10 msec and 2 sec, respectively. All ^{13}C CP MAS NMR spectra were collected on a Bruker AVANCE III 200 equipped with a 7 mm CP MAS probe using a spinning speed of 5 kHz. The ^1H 90° pulse, contact time and recycle delay were 3.9 μsec , 2 msec and 2 sec, respectively. The ^1H MAS NMR spectrum of DMB-E-PMO was acquired on a Bruker AVANCE II 900 equipped with a 4 mm CPMAS probe using a spinning speed of 15 kHz. The ^1H 90° pulse and recycle delay were 3.5 μsec and 4 sec, respectively. ^1H - ^{29}Si CP MAS HETCOR NMR spectrum of DMB-E-PMO was obtained on a Bruker AVANCE II 900 NMR spectrometer equipped with a 7 mm CPMAS probe using a spinning speed of 15 kHz. The ^1H 90° pulse, contact time and recycle delay were 3.5 μsec , 2 msec and 2 sec, respectively. 1280 scans were collected for each of 32 increments using spectral widths of 43860 Hz in both the ^{29}Si and ^1H domains.

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CHAPTER 7

Summary and future outlook

The primary objective of this work was to synthesize novel organic-inorganic hybrid mesoporous silica materials and characterize them in order to better understand their formation and the resulting structure. Since tools that are necessary to design desired mesoporous materials are not always available, exploring the structure of these novel hybrid materials provides information necessary to increase the likelihood of designing successful future experiments. Furthermore, combining the nature of dissimilar organic and inorganic materials leads to novel structures and functions giving access to a wider spectrum of applications.

In **Chapter 3** the synthesis of MCM-48 materials by a temperature induced phase transition in the presence of novel Gemini surfactant with rigid organic spacer is described. It was observed that ethanol partitioning induced the structure transformation from coexisting hexagonal and lamellar phases to bicontinuous cubic. The dynamic of the phase curvature change was shown to be also influenced by the base to silica ratio and the degree of silicate polymerization.

The synthesis of MCM-48 in the presence of the dimeric surfactant and under various conditions, helps to emphasize the importance of the packing parameter of the surfactant (g value) for the successful reproducible synthesis, and to discover the conditions affecting it.

Future utilization of in situ X-ray diffraction would help to observe the details of the phase transformation process.

Chapter 4 describes the fabrication of amine functionalized PE-MCM-41 prepared by grafting of halopropyl groups in the presence of water and subsequent reaction with polyamine. In contrast with a typical grafting strategy, this method allowed to introduce larger than commercially available amine-containing species onto the mesoporous silica surface. The optimal pentaamine grafted PE-MCM-41 adsorbent exhibited adsorption capacity of 6.06 %wt for 5% CO₂ in N₂ at 25 °C, however, complete pore filling at amine loading of 2.52 mmol/g resulted in amine inefficiency. Overall, the materials exhibited lower than expected amine efficiency (CO₂/N = 0.3) and therefore displayed lower CO₂ capacity than anticipated. Optimization of the material based on the adsorption performance, as supposed to amine loading, should be the future approach.

This method can further be used to incorporate other amines into mesoporous materials. Also, the stability of high molecular weight polyamine loaded materials can be improved by attaching them to the surface of functionalized mesoporous silica with the aid of grafted halopropyl groups.

Since, in addition to CO₂ removal, amines are versatile starting groups for a large library of catalytic functional groups, these PE-MCM-41 based materials with high amine loading and high surface density could be further explored as precursors for the synthesis of amine-anchored metal complexes for catalysis and separation.

In **Chapter 5** azobenzene-bridged precursor was used to synthesize photoreponsive organosilica material. Reversible *trans*-to-*cis* isomerization of the azobenzene moieties

integrated in the framework indicated that the organosilica remains flexible enough to undergo such change under UV irradiation.

Azobenzene moiety as a reversible photochrome is useful in various optical applications, this property could be exploited to produce an optical device, such as a UV sensor. To improve the operation of the device, reverse isomerization could be enhanced using stronger visible light source or heat treatment. Further condensation of the framework would add strength to the material; however, complete removal of the T¹ and T² species could lower the response of the azobenzene groups. Although the material could be used in the powder form, many applications would require thin films to be shaped for certain applications.

The last part of this work (**Chapter 6**) deals with synthesis of bifunctional organosilica material and its characterization using correlation NMR spectroscopy. The heteronuclear correlation experiment showed, that despite the difference in the size of the two precursors, the two moieties are in close contact, indicating formation of a chemically homogenous network.

Further research should measure the strength of the interactions in materials prepared under different conditions and using different organic bridges, in order to further understand the degree of homogeneity in various frameworks.

All of the materials reported in this dissertation are novel contributions to the field of hybrid mesoporous materials. Overall, organic-inorganic hybrid materials have become important in a variety of fields, due to the ability to design these materials for specific applications. Due to their limitless applications and design, hybrid materials will continue to be a topic of much research for years to come.

Novel Contributions

While discussions in this thesis cover a range of topics, it may be helpful to distinguish specific novel contributions made in each area. These contributions were developed at various times during the completion of this work from 2004 to 2009.

- Novel Gemini surfactant with unique rigid spacer was introduced. Also, for the first time synthesis of MCM-48 mesophase in the presence of Gemini surfactant was optimized with respect to the combination of the control parameters (Chapter 3). This work was published in peer reviewed journal (Czechura, K.; Sayari, A. *Chemistry of Materials* **2006**, 18, 4147).
- For the first time pentaamine-grafted PE-MCM-41 synthesized via post synthesis chemical modification was used as CO₂ adsorbent (Chapter 4).
- Novel photo-responsive azobenzene organosilica was synthesized. This is first type or pure organosilica material displaying light-induced isomerization (Chapter 5). This work was published in the Nanoporous Materials V conference proceedings (Czechura, K.; Sayari, A. *Nanoporous Materials V*, World Sci. Publ. Co., Singapore **2008**, p. 108-116).
- Heteronuclear correlation NMR spectroscopy was used to describe organization of novel bifunctional organosilica material. In this work, advanced novel bifunctional material containing bulky and smaller organic precursors with different Si-Si spacing was characterized (Chapter 6).