



Modification of Mesoporous Silica MCM-41 and its Applications- A review

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(Received: January 01, 2012; Accepted: February 03, 2012)

ABSTRACT

Recent research has looked to develop innovative and powerful novel functionalized mesoporous silica type MCM-41, controlling and tailoring their properties in a very predictable manner to meet the needs of specific applications. Surface functionalization of ordered mesoporous silica has garnered intense interest for use as solid supports due to its large surface area, fast adsorption kinetics and controllable pore size and pore arrangement in comparison to amorphous silica gel. After a brief introduction to mesoporous silica synthesis, the various methods to modify the surface of mesoporous silica materials, as well as applications in catalysis, adsorption, and guest-host chemistry, chemical separations, biosensors and chemosensors, will be discussed.

Key words: Mesoporous silica, Biosensors, Chemosensors.

INTRODUCTION

Over the past few decades studies in nanoscience and nanotechnology has emerged as one of the most intensively explored fields. The massive quantity of new literature pertaining to nanoscale materials in a wide range of scientific concentrations, such as materials sciences, chemistry, biology, physics, and engineering, has proven the seemingly unlimited potential these materials have to enhance the daily lives of all society.

One of the most promising classes of nanoscale materials are mesoporous silicates. These materials have many unique and advantageous properties such as high mechanical strength, thermal stability, stability under a wide pH range, and highly tunable pore diameters and

shapes which may be taken advantage of for size and shape selective organic syntheses under harsh experimental conditions. The covalent attachment of organic functionality by various methods allows for alteration of the hydrophilicity/-phobicity of the mesoporous silica or the addition of moieties which may catalyze organic transformations, used as efficient chromatographic packings for chemical separations, aid in the long-term stability of microelectronic components, or serve as heterogeneous chelates for toxic metal sequestration or sensing. In addition, mesoporous silicas are optically inert and semiconducting which allows for use in optic and electronic sensing applications for organic compounds such as explosives, volatile organic compounds (VOCs), and biological compounds or byproducts of biological processes.

History and Synthesis

Ordered mesoporous silica materials (OMS) were first synthesized in the early 1990's¹ by scientists at Mobil Corp. The prominent characteristics of these materials are high surface areas, narrow pore size distribution along with uniform pore size typically in the range of 3nm - 10

nm. Traditionally three mesophases were synthesized collectively known as M41S materials, and are described as mesoporous per the IUPAC nomenclature because of their pore² diameters ranging between $2 \text{ nm} < d < 50 \text{ nm}$. Perhaps the most widely recognized and used OMS is known as MCM-41 (a Mobil code for mesoporous catalytic

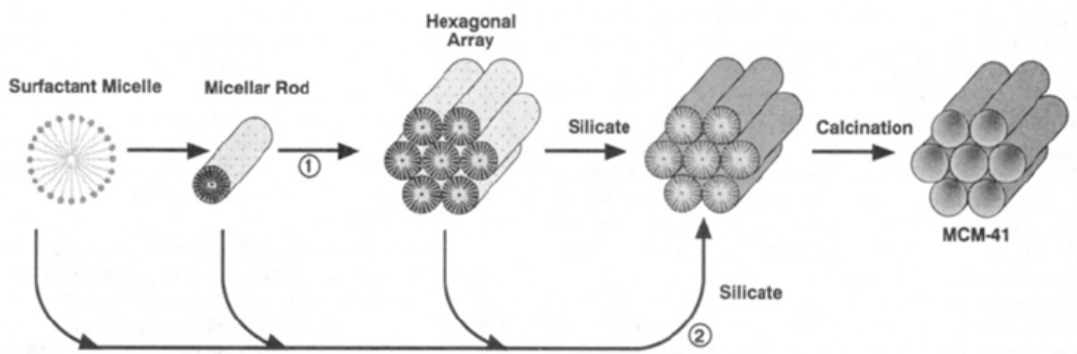


Fig. 1: Proposed mechanism of MCM-41 formation¹

material), with a regular hexagonal pore structure and 1D channels. The other two phases have cubic pore shapes (MCM-48), or lamellar structures (MCM-50).

The synthetic protocol utilizes quaternary alkylammonium salts such as cetyltrimethylammonium bromide (CTABr) in an aqueous solution under basic conditions. Under these conditions the

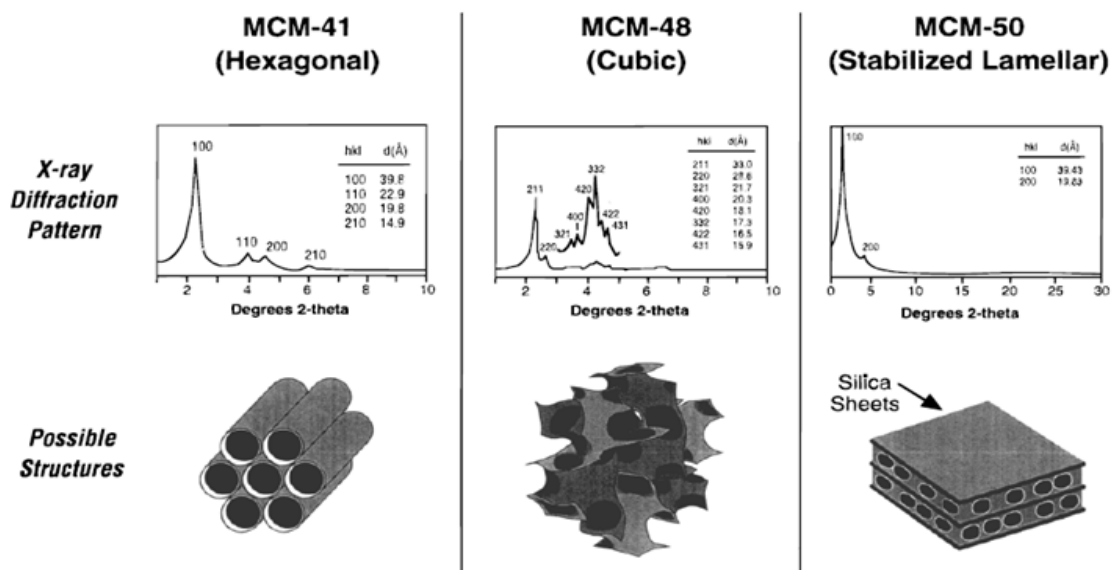


Fig 1 : The X-ray diffraction patterns and proposed structures of MCM-41, MCM-48, and MCM-50⁵.

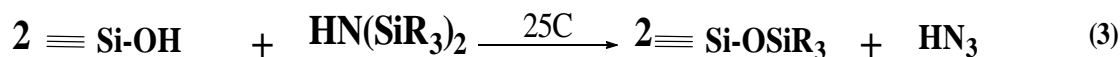
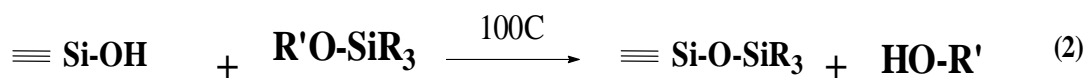
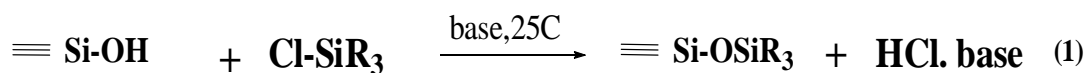
ionic surfactants form spherical micelles which form supramolecular aggregates of micellar rods that act as structure-directing agents (SDAs) or templates, by forming a liquid crystalline phase³. The hydrolysis and condensation of silica precursors, such as tetraethylorthosilicate (TEOS) or tetramethylorthosilicate (TMOS), forms a solid silicate mesostructure around the template (Path 1 in Fig. 1) due to electrostatic interactions between the negatively charged silica species and head groups of the surfactant, or by hydrogen bonding interactions. It is also proposed that the mechanism of formation of the liquid crystalline phase is promoted by the introduction of the silicate species. (Path 2 in Fig. 1).

Upon formation of the silicate mesostructure, the template is removed by either extraction with solvents such as ethanol or ethanol/diethyl ether mixtures, or high temperature calcinations at 400-550°C. Careful modification of experimental parameters (i.e. alkyl chain length, pH, and surfactant concentration) has yielded mesoporous silicas with hexagonal pore structure, cubic pore shapes, and laminar structures (**Fig.2**) coined MCM-41, MCM-48, and MCM-50, respectively with varied pore size distributions, pore wall thicknesses and surface areas⁴.

Surface Modification of MCM-41

Various methods have been developed to modify the surface of mesoporous silica materials. Chemical modification of the surface attempts to functionalize the surface with inorganic or organic groups so that the surface properties become better suited for specific applications. Inorganic modification, especially direct doping of the silica surface with metal ions, while important, is outside the scope of this work and therefore will not be discussed.

Introducing organic groups in the readily accessible pores of MCM-41 provide a way of manipulating the chemical and physical properties of these materials without compromising the basic geometry and mechanical strength. Modification of the surface can be achieved chemically (covalent attachment), or physically by adsorption of the functional group⁶. The framework of MCM-41 silica material has SiO₂ tetrahedra terminating in either siloxane (Si-O-Si) or silanols (Si-OH) on the surface. Both of these groups are reactive towards functionalization, though reaction with silanols is considered to be the main modification pathway⁶. Covalent attachment of organic moieties on the surface is termed chemisorption and can be achieved in two major ways co-condensation and post-synthetic modification, or grafting.



Grafting Methods

Grafting is a post-synthesis method and it is the most commonly employed functionalization method because of its relative synthetic simplicity and the flexibility in introducing surface groups. This is achieved after surfactant removal and drying of the mature MCM-41. Presence of silanols on the surface in high concentration is an important criterion in this approach. Surface functionalization with organic groups by grafting is most commonly

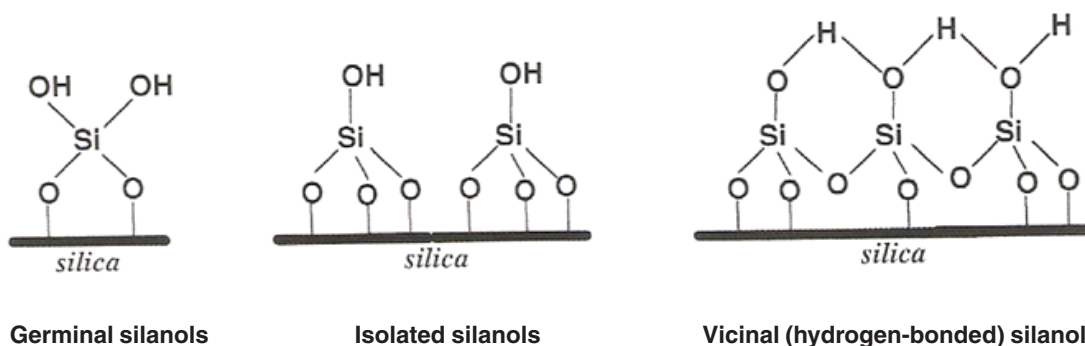
carried out by silylation, which is accomplished by one of the three procedures (Eq. (1) to (3))⁷. Moreover, esterification is another reaction to carry out surface modification^{8, 9}.

As mentioned earlier, high concentration of silanols is important for chemisorptions reaction. The silanols on the surface can be single (isolated or hydrogen bonded), or geminal (two hydroxyls on one silicon) as shown in Fig. 3¹⁰. Silylation occurs

on all surface groups of the silica including the free or geminal silanols. However, hydrogen-bonded silanol groups are less accessible to the modification because of the formation of hydrophilic networks¹¹.

The calcination process of making OMS results in loss of most of the surface silanols due to the high temperatures employed. Zhao and Lu demonstrated that the calcinations temperature

during the synthesis of MCM-41 materials affects the density of surface silanols¹². Ideally a larger concentration of silanol groups is desired because they act as active sites for anchoring organic groups on the surface. At lower calcinations temperatures a large number of the silanols were unavailable for covalent grafting because of hydrogen bonding between them, while at higher temperatures many of the silanols are lost due to condensation reactions. The surface can be rehydrated by boiling the OMS



(such as MCM-41) in water followed by azeotropic distillation with benzene or toluene to remove excess water. Secondly, in a more direct method, a stoichiometric amount of water is added based on the surface area of MCM-41. The latter method was developed by scientists at PNNL. By employing just enough water to form a monolayer on the pore surface, a more uniform coat of organosilane is obtained¹³. This process is termed "self-assembled monolayer on mesoporous supports" (SAMMS). The organosilanes are hydrolyzed to form trishydroxysilanes which undergo self assembly resulting in dense coverage of silica surface¹⁴. Adding excess water must be avoided as it may cause the organosilane reagent to form non-surface bound silanol clumps that may block the pores. In other words the silane polymerizes.

Co-condensation Methods

This method was first proposed by Mann et al¹⁵. Co-condensation is a one-pot synthetic method analogous to MCM-41 syntheses where trialkoxyorganosilane species are incorporated into the TEOS (or TMOS) solution and undergo hydrolysis and condensation in the presence of structure directing agents or templates. This method

produces mesostructures with organic functionalities covalently attached within the pore walls.

Compared with the grafting method in which the distribution of functional groups often tends to be inhomogeneous, the co-condensation is able to give homogeneously distributed organic groups on the entire inner pore surfaces. Even though the organo-silane may become buried within the walls of the silica matrix and therefore is inaccessible. Since each of the functionalized organo-silane group is in fact a defect in the silica matrix, it adversely affects the stability of the silica structure. This limits the concentration of surface silane groups because the larger the concentration of the silane, the more unstable the silica structure becomes.

There are some readily apparent drawbacks to this methodology, however. One of the major issues is the subsequent removal of templating agent. While calcination is shown to almost completely remove the structure directing agent, such high temperatures will also destroy the covalently attached organic functionality. This leaves

Table 1: Surface Modification of MCM-41 in the recent years (2000–2012) and their application

Modified group	Application	References
Amino group(NH ₂ -)	CO ₂ sorption Removal of Ni(II), Cd(II), and Pb(II)	18,19
Iron complex meso-tetrakis (2,6-dichlorophenyl)porphyrin (FeIIIP)	Catalyst	20
Iminodiacetamide ("IDA-Amide)	Ce ³⁺ , Nd ³⁺ , Eu ³⁺ , Gd ³⁺ , and Lu ³⁺ sorption	21
Polyacrylonitrile-derived carbon	Removal of methyl-ethyl ketone	22
4-amino-1,8-naphthalimides	----	23
Mercaptopropyl (MP) and diethylenetriamine (DETA)	Extraction of mercury (II)	24
Lanthanum (III)- diamino	Phosphate Adsorption	25
Calix[4]arene and Calix[4]areneBr	-----	26
β-cyclodextrin	-----	27
Trimethylchlorosilane and methyltrimethoxysilane	Phenol and hydroquinone adsorption	28
Cu diamine ligands (N,N'-dimethyl-1,2-ethanediamine, N,N-dimethyl-1,2-ethanediamine, and N,N-diethyl-1,2-ethanediamine)	Catalyst	29
Polyethylene oxide	-----	30
Chiral Ru complex	Catalyst	31
Sulfonated polyimide	Polymer electrolyte fuel cell	32
Glycopyranose	Borate Adsorption	33
Aminopropyl	Preconcentration of gold and palladium in	34
Alkyl chain	Chromatographic applications	35
Transition metal (Ni, Rh and Pd)	Hydrogen sorption	36,37
Aluminium 8-hydroxyquinoline derivatives	For tuning of the light emitting color	38
Platinum group metals (Pd, Pt, Rh, Ir)	Catalyst.	39-42
5-nitro-2-furaldehyde (fural)	Extraction of uranium(VI) and thorium(IV)	43

Ammonium	Adsorption of anionic dyes	44
2-(3-(2-Aminoethylthio)propylthio)ethanamine	Hg(II) sorption	45
3,4,9,10-perylenediimides (PDI)	-----	46
Fe, Mn and Co, tetraphenylporphyrin complexes	Catalysts	47
3-aminopropyl trimethoxysilane	<ul style="list-style-type: none"> • Removal of chlorophenols • preconcentration of Cr(VI) • CO₂ sorption 	48-50
Rhodium diphosphine complexes	Catalyst	51-53
Chiral Mn(III) salen complexes	Catalyst	54-56
Ni ²⁺ , Fe ³⁺ , Co ²⁺ and Cr ³⁺	Catalyst	57-61
Al; B	Catalyst	62-68
n-octadecyltrihydridosilane and n-octadecyltrimethoxysilane	-----	69
Octadecyl (C18)	-----	70
5-mercapto-1-methyltetrazole	Zn ²⁺ sorption	71
Sulfonic acid	Catalyst	72,73
Ru- and Fe-based N,N'-bis(2-pyridyl methyl)-N-methyl-(1S,2S)-1,2-cyclohexanediamine complexes	Catalyst	74
Molybdenum(VI) complexes molybdovanadophosphoric acids	Catalyst	75-77
3-phenyl-4-benzoyl-isoxazol-5-one (HPBI),	Extraction of Cu(II)	78
Nb and Sn	Oxidation properties	79
Thiophene-2-carbaldehyde	Extraction of palladium(II)	80
Au	Catalyst	81
Salicylaldehyde	Preconcentration of uranium	82
Al, Zr, W, B, or P	Catalyst	83,84
Phosphorus P ₂ O ₅	Catalyst	85
Copper-Schiff base complex	Catalyst	86
Titanium oxide	Sorption of CO ₂	87

N-methylglucamine	Preconcentration of boron	88
Ru/carboxyphosphine	Catalyst	89
Vanadium	Catalyst	90-92
polyethylenimine (PEI).	CO ₂ sorption	93
Uranyl groups (UO ₂ ²⁺)	Catalyst	94,95
Mn(II)	Catalyst	96,97
Tungstophosphoric acid	Catalyst	65,98

solvent extraction as the only possible method. Another advantage of co-condensation over post-synthesis grafting is to control the particle morphology of final mesoporous silicate very easily^{16,17}.

Different surface modification of MCM-41 and their application in the recent years (2000–2012) are summarized in Table 1. The methodologies to characterize the modified MCM-41 include structural analyses such as gas sorption studies, powder X-ray diffraction (XRD), and transmission electron microscopy (TEM). Compositional studies such as solid-state NMR, Fourier transform infrared (FTIR), and x-ray photoelectron (XPS) spectroscopic methods, as well as elemental and thermogravimetric analyses will also be used.

Applications of Mesoporous Silicas

Mesoporous silicas offer many favorable properties with potential for use in a vast array of applications. The major applications to be discussed include: catalysis, chemo- and biosensing and chemical separations.

Catalysis

Mesoporous silica provides a unique platform for catalytic processes with several advantages over traditional homogeneous catalysis. Highly tunable pore size distributions and arrangements (i.e. hexagonal, lamellar, cubic, spherical etc.) allow for size and shape selective catalysis. High surface areas and site isolation techniques allow for the covalent attachment of significant quantities of non-interacting catalytic

sites. Homogeneous materials such as organometallic compounds can be expensive to synthesize and require time-consuming and/or exotic recovery methodologies. Other catalytic reagents such as acids/bases in acid or base catalyzed reactions may limit the choice of solvent systems and require extensive work-up procedures. Unlike homogeneous catalysts, however, the silica mesostructure may be altered (i.e. hydrophilicity/hydrophobicity, size and shape) for stability in a wide range of reaction media, temperatures and pressures and may be easily separated from the reaction mixture by vacuum or gravity filtration and recycled for multiple uses with little or no loss of catalytic activity. To date there have been a plethora of organic, inorganic, and organometallic catalysts immobilized on highly ordered mesoporous silica. For example 3-aminopropyl functionalized mesoporous silicates have been shown as an efficient heterogeneous base catalyst for nitroaldol and Michael addition^{99,100}.

Mesoporous Chemosensors

One of the many significant potential applications of mesoporous silica is their use as platforms for chemosensing applications. Metal ion detection using fluorescence and UV-Vis spectroscopic measurements has been studied extensively to produce functionalized mesoporous silicates with high metal ion specificities¹⁰¹. Mesoporous silica has also proven an efficient scaffold for volatile organic compound (VOC) and explosive chemosensing applications¹⁰². In addition to the fabrication of sensors for metal ions and VOCs, many studies have utilized mesoporous silica as a scaffold in gas sensing applications¹⁰³.

Mesoporous Biosensors

There have been intensive studies using mesoporous silica as a scaffold for various biological sensing techniques. Large surface areas and pore diameters allow for the incorporation of biomolecules toward the fabrication of bioelectrochemical sensors^{104,105}. Surface functionalization with target specific compounds and the high biocompatibility of mesoporous silica allows for imaging biological processes. To date, there have been numerous studies dedicated toward the immobilization of biological species.

Chemical Separations

Mesoporous silicates have received considerable interest in chemical separations and as adsorbents due to their large surface areas, easily tunable pore size distributions, mechanical and thermal stabilities, and resistance to decomposition in a wide pH range. Furthermore, the ability to alter the hydrophilicity/-phobicity, via addition of non-polar organic groups (i.e. alkyl, vinyl, or phenyl substituents), or the addition of reactive functional groups (such as amines, thiols or specialized chelating agents) allows for size, shape or functionality specific reactivity. These properties have been taken advantage of in the separation/adsorption of heavy metals, organic compounds with high target material specificities and efficiencies. For instance, *N*-(2-aminoethyl)dithiocarbamate functionalized MCM-41 has been prepared by Stathi et al¹⁰⁶. These materials are promising heavy metal adsorbents

due to the presence of the effective dithiocarbamate groups and the low pH value (3.2) of the point of zero charge. As mentioned, functionalized mesoporous silicates have also proven very effective as chromatographic packings for the separation of organic compounds. In a study by Yasmin and Müller³⁵ various *n*-butyl and *n*-octyl functionalized MCM-41 spheres were tested for separation efficiency of NIST SRM 870, which consists of five organic components (uracil, toluene, ethylbenzene, quinizarin and amitriptyline). Chiral compound separations have also successfully been performed. Zhu et al¹⁰⁷ efficiently separated enantiomeric mixtures of *R/S*-1,10-bi-2-naphthol using mesoporous organic-inorganic spheres with covalently bridged *trans*-(1*R*,2*R*)-bis-(ureido)-cyclohexane synthesized by cocondensation of *N,N'*-bis-[(triethoxysilyl)propyl]-*trans*-(1*R*,2*R*)-bis-(ureido)-cyclohexane and 1,2-bis(trimethoxysilyl)ethane.

CONCLUSION

The synthesis, characterization, and application of novel porous materials have been strongly encouraged due to their wide range of applications. Functionalization of the surface of these mesoporous materials with organic or inorganic functional groups leads to new physical and chemical properties. These modified materials can be used in a variety of applications such as catalysis, adsorption, and separation as chromatographic column packing.

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