Chapter 1
Introduction
1.1. Introduction and Motivation

Organic/inorganic hybrid materials are important because they can be designed at a molecular level to perform many processes including catalysis [1] adsorption [2-4], separation [5], drug delivery [6, 7] and sensing [7]. Due to their many different building blocks as well as the countless ways to combine the building blocks together, organic/inorganic hybrid materials will continue to have high importance in the future. This work focuses on the synthesis of mesoporous silica as inorganic robust material and surface functionalization of these inorganic materials with organic functionality like –NH₂ and –SH to obtain organic/inorganic hybrid materials, their characterization, and application in adsorption, catalysis and in drug delivery.

1.2. Silica

The silicon dioxide, also known as silica (from the Latin silex), an oxide of silicon with the chemical formula SiO₂ is most commonly found in nature as sand or quartz, as well as in the cell walls of diatoms. SiO₂ is more widely distributed in dusts, sands, planetoids and planets as various forms of silica or silicates. In Earth's crust, silicon is the second most abundant element after oxygen, making up 27.7 % of the crust by mass [8] exists in various forms. In Sosman’s text twenty two different forms of natural silica’s have been described [9]. Quartz, the main constituent of sand, is the most common crystalline form of silica. However, under different conditions in nature and in laboratory, other different phases of crystalline and amorphous silica are formed [10].

Silica is used for making glass and fused silica, its rock crystal is used in electronic equipment and the colored crystals of silica have gem value [11, 12]. Silica, however, can be manufactured in the form of sols or gels and precipitates. These silicas can be formed as colloidal silica, pyrogenic (or fumed) silica, silica xerogels, and as precipitated silica. Silica has been applied as fillers, lubricants, adsorbents and support for solid phase syntheses. Unger [13] has used four main features; crystal structure, dispersity, surface composition and porosity for classification of solid silica. Silica can be classified into the main two classes viz. crystalline and amorphous.
1.2.1. Crystalline Silica

Majority of crystalline silica are non porous and naturally occurring, such as different forms of quartz, tridymite and cristobalite are transformed spontaneously with temperature. Keotite, coesite and stishovite are formed under high pressure and temperature [10, 13, 14]. Silicalite is an example of synthetic, porous, hydrophobic, crystalline silica of uniform pore size (4 Å) [15, 16]. Quartz crystals possess a unique property like **piezoelectricity**. Piezoelectric quartz crystals are used to make electronic oscillators, which provide accurate frequency control for radio transmitters and radio-frequency telephone circuits. One of the major uses of crystalline silica is as a raw material for glass manufacture. It can also used as building materials, such as concrete and dimension stone (sandstone, granite, and limestone are examples) contain crystalline silica in the form of quartz. Quartz is also used as functional filler in plastics, rubber and paint [10].

1.2.2. Amorphous Silica

Unlike crystalline silica the amorphous silica are synthetic silica except diatomaceous earth a biogenic form of silica and opal. Amorphous silicas have been broadly classified into three types: (a) vitreous silica, made by fusing quatrz, (b) silica M, which is formed by irradiating either crystalline or amorphous silica with high speed neutrons, and (c) micro-amorphous silica includes sols, gels, powders and porous glasses, all of which are composed of ultimate particles or structural unit less than 1 µM in diameter. These silica have high surface area ranging from few m²/g to about 800 m²/g. Synthetic and natural amorphous silica are very important materials for their variety of technological applications due to its physico-chemical properties such as surface area, pore properties, bulk density etc. These properties synthetic silica can be tailored made for specific application [10, 17].

a) **Natural Silica**: Opal, the amorphous hydrous silica that may contain cryptocrystalline cristobalite. Vitreous silicas are volcanic glasses; lechatelierites are natural glasses produced by the fusion of siliceous material under the impact of meteorites. Biogenic silica is defined as any form of silica originating in living matter (known sources include bacteria, fungi, diatoms, sponges and plants); the two most relevant biogenic silicas are those associated with fossilized diatoms and crop plants. Diatomaceous earths (Fig. 1.1) are the geological products of decayed unicellular organisms (algae) called diatoms. Diatomaceous earths is mined, milled,
and processed in to myriad of types for large variety of uses. This material is mainly used as filter aid but Diatomaceous earths also used in paints, cosmetics, drugs and chemical insecticides, etc [10].

![Figure 1.1. Scanning electron microscope of diatomaceous earths](image)

**b) Synthetic Amorphous Silica:**

The synthetic amorphous silica’s (micro particulate) are aggregated silica particles of colloidal size and offer enormously large specific to geometric surface ratio. The amorphous silica is commercially important because the surface area, pore volume, pore size and particle size can be controlled to some extent independently. Synthetic amorphous silica can be classified in to two main classes on the basis of the process of synthesis; thermal process and wet process [10].

**Silica Prepared by Thermal Process**

- Pyrogenic or fumed silica

**Silica Prepared Wet Processes**

- Colloidal silica sol
- Precipitates
- Sol gel process based silica
- Surfactant templeted Ordered mesoporous silica

**1.2.3. Pyrogenic or Fumed Silica**

The products obtained by thermal process are called pyrogenic silica or fumed silica. Fumed silica consists of microscopic particles of amorphous silica fused into branched, chainlike, three-dimensional secondary particles which then agglomerate into tertiary particles. The resulting powder have an extremely low bulk
density and high surface area. Its three-dimensional structure results in, thixotropic behavior when used as a thickener or reinforcing filler [10, 18].

1.2.4. Colloidal Silica Sol

Colloidal silicas are suspensions of fine amorphous, nonporous, and typically spherical silica particles in a liquid phase. Usually they are suspended in an aqueous phase that is stabilized electrostatically. Colloidal silica is odorless, tasteless and nontoxic. Its chemical molecular formula is mSiO₂·nH₂O. The colloidal silica exhibit particle densities in the range of 2.1 to 2.3 g/cm³. Most colloidal silicas are prepared as monodisperse suspensions with particle sizes ranging from approximately 30 to 100 nm in diameter. Colloidal silica has variety of applications such as drainage aid in paper industry, high temperature binders, abrasives, carbonless papers, textiles fibers, railway trackes, finning agent and catalysis [10].

1.2.5. Precipitated Silica

Precipitated silica is the silica produced by precipitation, the synthesis of precipitated silica starts with the reaction of an alkaline silicate solution with a controlled addition of mineral acid. Sulfuric acid and sodium silicate solutions are added simultaneously with agitation into water or sodium silicate solution. Precipitation is carried out under alkaline conditions. The choice of agitation, duration of precipitation, the rate of addition of the reactants, reaction temperature and concentration, and pH can vary the properties of the silica. The formation of a gel is avoided by stirring at elevated temperature in presence of an electrolyte [10].

Major application of precipitated silica is in rubber and plastics as reinforcing and performance improvement agent; cleaning, thickening and polishing agent in toothpastes for oral health care food processing and pharmaceuticals additive as anticaking, thickening agent, absorbent to make liquids into powders. It is also used as antiblocking agent in manufacture of polymer films [10].

1.3. Sol-Gel Synthesis Route

Depending on the nature of the precursors, the sol-gel process can be classified into two different routes: a) inorganic route where the precursor is an aqueous solution of an inorganic salt (e.g. sodium silicate solution), or b) organic route where the precursor is a metal-organic compound (e.g. TEOS) [19].
Sol-gel chemistry originated in the mid-1800s with several studies on the creation of silicon dioxide (SiO$_2$) glass from the tetraethoxysilane (TEOS) precursor [20]. It has subsequently been defined as the preparation of a ceramic material (e.g. glass) by the preparation of a sol, gelation of the sol, and subsequent removal of the solvent [21-23]. Metal alkoxides or tetralkoxysilanes are most commonly preferred as precursors, because: they are soluble in organic solvents (providing high homogeneity), can easily be converted to the corresponding oxides, and are known for almost all elements [24-26].

Removal of the pore liquid under hypercritical conditions yields a network that does not collapse and results in the production of an aerogel [24]. When the pore liquid is removed by evaporation under normal conditions, shrinkage of the pores occurs and a xerogel is formed [10].

Over the years, the sol-gel chemistry approach has been developed into a powerful tool for making films and coatings, optics, fibres, powders, and membranes with desired characteristics. The potential benefits of sol-gel processing over the conventional powder route include the following: (i) good homogeneity, (ii) ease of chemical composition control, (iii) high purity, (iv) low-temperature processing, and (v) large area and versatile shaping over vacuum deposition techniques [21, 25].

1.4. Silica-Based Mesoporous Materials

Mesoporous silica can be mainly divided into two groups, mecelle templated ordered mesoporous silica belongs to different family depending of the synthetic routes like M41S family, SBA family and silica gel synthesized under hydrothermal condition in absence of structure directing agent.

1.4.1. Micelle Templated Mesoporous Silica

Ever since the disclosure of the M41S family of mesoporous materials in 1992, a veritable explosion of research effort has occurred in macromolecular and micelle templated syntheses of mesostructured materials. Mesoporous silica materials have large surface area (~1000 m$^2$/g), pore volumes (~1.0 cm$^3$/g) and narrowly distributed pore diameter around 20-100 Å. Depending on the surfactant to silica ratio, different mesoporous silica with ordered structure in the form of hexagonal (denoted as MCM-41) [28] cubic (denoted as MCM-48) [34, 36, 37, 41-49] and lamellar (denoted as MCM-50) [34, 50-52], have been reported (see Fig. 1.2). Consequently, many synthetic routes and strategies have been developed to
yield a wide diversity of various frameworks with different chemical compositions and pore structures. The actual differences are due to the nature of the electrostatic interactions between the organic and inorganic phases. Syntheses of very large numbers of mesoporous inorganic materials using different types of organic surface directing agents have been reported. Some of the examples of mesoporous materials under different conditions depending of types of organic template and inorganic material are summarized in table 1.1.

**Table 1.1.** Examples of mesostructured inorganic materials prepared by using different organic templates and inorganic materials interactions between the surfactant and inorganic framework

<table>
<thead>
<tr>
<th>Surfactant type</th>
<th>Synthesis condition</th>
<th>Interaction type</th>
<th>Example materials#</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cationic S⁺</td>
<td>Basic</td>
<td>S⁺T⁻</td>
<td>MCM-41 (hexagonal), MCM-48 (cubic), MCM-50 (lamellar), FSM-16 (hexagonal) KIT-1(hexagonal) HMM (hexagonal), HMA (hexagonal)</td>
<td>[26-30]</td>
</tr>
<tr>
<td>CH₃(CH₂)ₙ(CH₃)₃N⁺ (n=8 to 18)</td>
<td>Acidic</td>
<td>S⁺X⁻T⁺</td>
<td>SBA-1 (cubic), SBA-3 (hexagonal)</td>
<td>[31]</td>
</tr>
<tr>
<td>Gemini</td>
<td>Acidic</td>
<td>S⁺X⁻T⁺</td>
<td>SBA-2 (hexagonal)</td>
<td>[34]</td>
</tr>
<tr>
<td>Neutral S⁰</td>
<td>Acidic</td>
<td>S⁺T⁻</td>
<td>SBA-15 (hexagonal)</td>
<td>[39, 40]</td>
</tr>
<tr>
<td>P123, EO₂₀PO₇₀EO₂₀ P127, EO₁₀₈PO₇₀EO₁₀₆</td>
<td>Acidic</td>
<td>S⁺H⁺X⁻T⁺</td>
<td>SBA-16 (cubic)</td>
<td>[39, 40]</td>
</tr>
<tr>
<td>Brij56, C₁₆,EO₁₆ Brij76, C₁₈,EO₁₀</td>
<td>Acidic</td>
<td>S⁺H⁺X⁻T⁺</td>
<td>SBA-11 (cubic)</td>
<td>[39, 40]</td>
</tr>
<tr>
<td>Brij30, C₁₂,EO₄</td>
<td>Acidic</td>
<td>S⁺H⁺X⁻T⁺</td>
<td>SBA-12 (hexagonal)</td>
<td>[39, 40]</td>
</tr>
<tr>
<td>C₁₂H₂₅NH₂</td>
<td>Neutral</td>
<td>S⁰I₀</td>
<td>HMS (hexagonal)</td>
<td>[35, 36]</td>
</tr>
<tr>
<td>P64L, EO₁₃PO₇₀EO₁₃ Tween20</td>
<td>Neutral</td>
<td>S⁰I₀</td>
<td>MSU-3 (hexagonal)</td>
<td>[37]</td>
</tr>
<tr>
<td>Aninoic S⁻</td>
<td>Basic</td>
<td>S⁻T⁺</td>
<td>Aluminum oxide.</td>
<td>[33]</td>
</tr>
</tbody>
</table>

# Abbreviations, MCM: Mobil Composition of Matter; MSU: Michigan State University; PMO: Periodic Mesoporous Silica; SBA: Santa Barbara Amorphous; HMM: Hybrid Mesoporous Material; HMA: Hexagonal Mesoporous Aluminium Phosphate; HMS: Hexagonal Mesoporous Silica, FSM: Folded sheets mesoporous material; Gemini: CₙH₂ₙ₊₁N⁺(CH₃)₂(CH₂)ₙN⁺(CH₃)₂CₘH₂ₘ₊₁
The initial Mobil silicate-based materials were prepared in a process involving direct ionic bonding between the liquid-crystalline cationic surfactant assemblies and an anionic silicate species (S′T interaction) [28, 53], giving rise to the so-called liquid-crystal templating (LCT) mechanism. Post-M41S advances have led to the development of synthesis models based on the interfacial interactions between the surfactant and the inorganic species, and also on the fact that the silicate species promote the formation of a liquid crystal phase below the critical micelle concentration (CMC).

The mesopore size distribution of these mesoporous materials can be controlled by altering the reactant composition and the preparation variables. Their pore sizes can be tuned in the range 25-250 Å and the surface areas in the range between 400 and 1000 m²/g.

**Figure: 1.2.** Organic-inorganic phases of M41S materials

### 1.4.2. MCM-41 and SBA-15 Type Ordered Mesoporous Silica

MCM-41 and SBA-15 are extensively studied hexagonal type ordered mesoporous silica materials, wherein the pores are parallel to each other forming a hexagonal structure.

### 1.4.3. Synthesis Characterization MCM-41

Mobil researchers in 1992 disclosed the first family of highly ordered mesoporous molecular sieves M41S (pore size in the range 2-10 nm), where long chain cationic surfactants were used as the template, also known as pore forming or structure directing agents during the hydrothermal sol-gel [27-28]. It has been well documented in literature that the formation of meso-structures was influenced by surfactant concentration, pH, presence of cosurfactant, and its concentration and temperature [28].

Generally, the synthesis of MCM-41 silica involves hydrothermal treatment of precursor gel in the temperature range between 60–150 ºC for an extended time
(1–6 days) in presence of quaternary ammonium surfactants, \( \text{C}_n\text{H}_{2n+1} (\text{CH}_3)_3\text{N}^+ \), with different alkyl chain lengths \((n=8–18)\), using sodium silicate or tetraalkyloorthosilicate as silica sources [27, 28, 154]. Recently, MCM-41 silica was synthesized under refluxing [55] and microwave irradiation [56]. Generally siliceous MCM-41 materials are synthesized from gels with surfactant/silica molar ratio of more than 0.12 [54-57].

Attempts have been made to synthesize these materials under ambient conditions [58-60]. Voegtlin et al. [60] have prepared highly ordered MCM-41 at room temperature in 1 h, however, stability above 600 °C has not been reported. Different strategies have been employed to improve thermal and hydrothermal stability of these materials such as synthesis of materials with thicker pore wall under hydrothermal condition by using low surfactant to silica molar ratio in the range of 0.06 to 0.1 [61], by addition of salts in the synthesis gel before or during hydrothermal crystallization [62-64] and/or intermittent pH adjustment with the acid during hydrothermal treatment [64] and using highly condensed silica source such as fumed silica [65] and calcined MCM-41 silica [66]. Cheng et al. [67] synthesized MCM-41 using fumed silica at 165 °C for 48 h with pore wall thickness of 2.68 nm and showed improved thermal stability. Kumar et al. [68] have synthesized MCM-41 analogue at room temperature using hexadecylamine as templating agent showed improved stability [68].

Scientists have postulated that the formation of these molecular sieve materials highly depend upon the nature of the structure directing agent or template. Templating has been defined, in a general sense, as a process in which an organic species functions as a central structure about which oxide moieties organize into a crystalline lattice [69, 70]. Strictly speaking, a template is a structure (usually organic) around which a material (often inorganic) nucleates and grow in a “skin-tight” fashion, so that upon the removal of the templating agent, its geometric and electronic characteristics are replicated in the (inorganic) materials [71]. The above definition has also been elaborated to include the role of the organic molecules such as: 1) Space-filling species, 2) Structural directing agents and 3) Templates [69].

In the simplest case of space filling, the organic species merely serves to occupy a void about which the oxide crystallizes. Therefore, the same organic molecule can be used to synthesize a variety of structures or vice versa. Structural direction requires that a specific framework is formed from a unique organic
compound. This does not imply that resulting oxide structure mimics identically the form of the organic molecule. In true templating, however, in addition to the structural directing component, there is an intimate relationship between the oxide lattice and the organic form such that the synthesized lattice contains the organic “locked” into position. Thus, the lattice reflects the identical geometry of the organic molecule.

In M41S materials, a liquid crystal templating (LCT) mechanism has been proposed in which supramolecular assemblies of alkyltrimethylammonium surfactants serve as one component of the operative template for the formation of mesophase [27, 28]. Beck et al. [28] utilizing the surfactant templating mechanism. The surfactant aggregates (micelles) serve as a structure directing agent during the silica synthesis (Fig. 1.3). Initially the silica precursor was thought to condense and polymerize around already formed surfactant liquid crystals (LC) as shown in path 1. Since the concentration of surfactant used during synthesis is usually lower than the critical micelle concentration (CMC) for liquid crystal (LC) phase formation, therefore it is accepted that pathway 1 of Fig. 1.3 did not take place [47, 53] and investigations have suggested that the templating mechanism is influenced by numerous factors that drive electrostatic assembly through non-covalent bonding (ionic bonds, van der Waals forces, hydrogen bond and dipole-dipole bonds) [72-74]. The factors include the type of precursor used, type of surfactant (cationic, anionic, or non-ionic), relative concentrations of the surfactant to the inorganic species (e.g. Si), the pH of the synthesis medium (acidic or basic) and temperature [75, 76].

![Liquid-crystal templating (LCT) mechanism for self-assembly proposed by Beck et al. [31]](image)

**Figure: 1.3.** Liquid-crystal templating (LCT) mechanism for self-assembly proposed by Beck et al. [31]

Other models describing the micelle-templated synthesis of mesoporous silica have been proposed. Various instrumental techniques such as in situ X-ray diffraction (XRD) measurements, NMR spectroscopy, IR technique, EPR
measurements, Cryo-TEM and laser scattering measurements have been used to study the mechanism of formation of mesophase and are reviewed \[22, 27, 60, 77, 78\]. Some of these include silicate rod assembly \[79\], silicate layer puckering \[80\], true liquid crystal templating \[91\], and cooperative templating (generalized LCT model) \[72\]. A mechanism proposed for folded sheets mesoporous (FSM) material involves the transformation of lamellar phase first synthesized by incorporation of alkyl trimethyl ammonium cations between the layered silicate kanamite by ion exchange. This resulting layered structure transformed into hexagonal mesophase \[46\]. A charge density matching mechanism model was proposed by Monnier et al. and Stucky et al. \[45, 46\]. In this mechanism it was proposed that initial formation of lamellar structure due to electrostatic interaction between the anionic silicate and the cationic head group of the surfactant takes place. This lamellar structure transformed into the hexagonal mesophase due to decrease in charge density as a result of polymerization of silicate anions \[45, 46\]. Recently in 2009, mechanism of formation of pore structure of MCM-41 has been proposed by Nan et al. \[82\] which, involve the three steps. First, rodlike inorganic/surfactant complexes are formed which spontaneously pack into an ordered arrangement. Second, with the help of this new template, a new kind of pore structure is formed. Third, the interaction between the pore structures formed in steps 1 and 2 results in a new pore structure. This new pore structure is very similar to the structure formed in the first step \[82\].

Mechanism of formation of mesoporous silica particularly MCM-41 type has been extensively studied as summarized above. Interaction between the inorganic precursor and the surface directing agent plays a key role in the control of mesophase formation. However, the step where such interaction takes place remains yet to be understood completely \[78\].

1.5. SBA-15

SBA-15, was first synthesized by the research group lead by Stucky \[39, 40\] at University of California-Santa Barbara. SBA-15 earned much attention in the last decade owing to its excellent thermal stability, variable pore sizes, and tailored particle morphology. The pore topology consists of a two dimensional mesoporous network of uniform dimensions formed by microporous walls. Compared to zeolites having pores in the micro-range (4-14 Å), SBA-15 material is a new type of mesoporous material with micropores, hence it is expected to lower the diffusion
limitation that a microporous material typically experiences. Zeolites are crystalline while SBA-15’s pore walls are essentially amorphous; however, the mesopores of SBA-15 material are regularly spaced due to the templates liquid crystal micelle arrangement [83].

1.5.1. SBA-15 Synthesis

SBA-15 is synthesized by the use of amphiphilic triblock copolymers, poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) or PEO-PPO-PEO as the organic structure directing agent (template). PEO blocks are hydrophilic, while PPO blocks are hydrophobic. Hence, direct formation of cylindrical micelles with the PEO blocks on the outside can be achieved in the aqueous solution. The aqueous silica cations locate themselves within the hydrophilic regions of the self-assembled system and associate preferentially with the PEO blocks. Removal of the polymer results in a mesoporous solid due to the hexagonal arrangement of cylindrical polymer aggregates and also microporosity generated by PEO segments [83, 84]. The process to obtain solid powder of SBA-15 involves the dissolving of template polymer in acidic solution, adding a silica source, which is typically either tetraethyl orthosilicate (TEOS), tetramethyl orthosilicate (TMOS), or sodium silicate. The mixed solution is aged at a temperature slightly above room temperature for 20 to 24 hours and heated up to 80 to 100 °C either in a conventional oven or in a microwave oven for an appropriate time. Precipitated solids are centrifuged, washed and dried. Finally, the organic polymer is removed by calcination (e.g. 600 °C for 6 hours) [83, 84]. Fulvio and co-workers [85] synthesized SBA-15 with TEOS and sodium metasilicate and showed that an aging time of 2 hours is sufficient to prepare these material instead of aging time (20 ~ 24 hours) [40, 83, 84]. Both the samples exhibited similar surface areas. However, SBA-15 prepared with TEOS showed slightly larger pore volumes than that formed using sodium metasilicate. Sodium metasilicate precursor resulted in SBA-15 with higher microporosity and thicker pore walls [85, 86].

This motivated the studies on the formation mechanism of SBA-15. Results from in situ XRD [87] time-resolved NMR and TEM [87, 88], and SEM studies gave the insight that the hexagonally packed structure is obtained within 2 hours after the addition of the silica source. Flodstrom et al. [88] have, concluded that for Pluronic P123 amphiphiles as structure directing agents, the polymerization of the silica leads...
to the introduction of an attractive force between micelles due to a bridging mechanism. This attraction leads to the formation of flocs of micelles, and these flocs eventually reach a critical size where they precipitate. There is a continuing structural change within these clusters involving the coalescence of micelles that tend to form cylindrical aggregates, which order in a two-dimensional hexagonal pattern [88].

### 1.6. Factors Influence the Structure of Mesoporous Materials

#### 1.6.1. Effect of Surfactant

The surfactant: silica mole ratio and nature of surfactant govern the phase, symmetry of materials, pore size, structure of pores, and thickness of walls of materials [77, 89].

As shown earlier using CTAB three different mesophases viz., hexagonal cubic and lamellar were reported [28, 77] and is governed by the surfactant: silica mole ratio as shown in table 1.2.

**Table 1.2. Mesophases of silicate molecular sieves and governing MCM synthesis parameters**

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Mesophase</th>
<th>Space group</th>
<th>Parameter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41</td>
<td>hexagonal</td>
<td>$P6m$</td>
<td>[surfactant]/[Si]&lt;1</td>
<td>[27, 28]</td>
</tr>
<tr>
<td>MCM-48</td>
<td>cubic</td>
<td>$Ia3d$</td>
<td>[surfactant]/[Si]=1-1.5</td>
<td>[27, 28, 53]</td>
</tr>
<tr>
<td>MCM-50</td>
<td>lamellar</td>
<td>$Pm3n$</td>
<td>[surfactant]/[Si]=1.2-2</td>
<td>[27, 28]</td>
</tr>
</tbody>
</table>

Surfactant molecules consist of hydrophilic polar head group and hydrophobic nonpolar hydrocarbon tail [90 - 92]. Structures of mesoporous materials are related to the shape and concentration of surfactant and can be expressed in terms of simple expression of surfactant packing parameter ‘g’, for lyotropic LC phase [93, 94]. The packing parameter g is expressed as shown in Eqn. 1

$$g = \frac{V}{al}$$

Where, $V$ is volume of surfactant tail, $a$ is effective head group area and $l$ is length of the extended surfactant tail. The relative sizes of surfactant tail and head group are the governing factors for optimum packing of the surfactants into different geometrical structures, The value of g and their respective mesophase are shown in table 1.3.
Table 1.3. Mesophases of silicate molecular sieves and governing SBA synthesis parameters

<table>
<thead>
<tr>
<th>Name</th>
<th>Mesophase</th>
<th>Space group</th>
<th>Parameter, $g = \frac{V}{\mathcal{A}l}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-1</td>
<td>cubic</td>
<td>$Pm\overline{3}n$</td>
<td>$g = \frac{1}{3}$</td>
<td>[34, 72]</td>
</tr>
<tr>
<td>SBA-2</td>
<td>hexagonal[a]</td>
<td>$P6\overline{3}Immc$</td>
<td>$g &lt; \frac{1}{3}$</td>
<td>[31]</td>
</tr>
<tr>
<td>SBA-3</td>
<td>hexagonal[b]</td>
<td>$P\overline{6}m$</td>
<td>$g = \frac{1}{2}$</td>
<td>[34]</td>
</tr>
<tr>
<td>SBA-15</td>
<td>hexagonal[b]</td>
<td>$P6mm$</td>
<td>$g = \frac{1}{2}$</td>
<td>[39, 40]</td>
</tr>
<tr>
<td>SBA-16</td>
<td>cubic</td>
<td>$lm\overline{3}m$</td>
<td>$g = \frac{1}{3}$</td>
<td>[40]</td>
</tr>
</tbody>
</table>


1.6.2. Effect of pH

pH is an important parameter which influences the synthetic chemistry of mesoporous materials as pH of medium influences the charge of inorganic precursor species and surfactant head groups; and consequently their mutual interaction. M41S family of molecular sieves was synthesized in basic pH using CTAB, whereas Stuky et al. synthesized SBA materials in acid medium [27, 28, 40].

Due to the high pH, negatively charged inorganic precursors preferentially interacted with the positively charged ammonium head groups of the surfactants resulting in condensation of inorganic silicate ions into solid organic-inorganic mesoporous structure. In case of SBA-15, at low pH polyethylene oxide chains gets protonated and interacts with positively charged silica species mediated by negatively charged halide ions to form $S^0H^+X^-I^-$ intermediate [39]. Using same surfactant different mesophases can be obtained by changing the pH of reaction medium from acidic to basic [95]. The change of pH leads to phase transformation of silica from lamellar to hexagonal phase [96]. Mechanism of formation of mesophases at acidic and basic extremes is completely different [72]. This is because of negatively charged silicate ions act as counter ions above isoelectric point (pH ~ 2.0) [10]. Generally, in strong acidic medium the rate of hydrolysis of TEOS is faster than the condensation rate, therefore, well ordered hexagonal arrangement of mesopores is obtained at acidic pH, whereas the rate of condensation is faster then hydrolysis in neutral or basic conditions [97]. Thus, pH plays a critical role in hydrolysis and condensation of inorganic silica species.

It has been observed that, slow growth rate is the fundamental requirement for formation of crystals having well shape morphology. Due to the slow condensation of silica, the surface charge is electronically neutral around isoelectric point at pH = 2. pH dependency of condensation rate was exhibited by SBA-1 when
its crystal shape showed transitions from sphere → decaoctahedron → truncated cube → cube, with change in pH from 1.0 to 2 [98]. The electrolyte concentration is also a factor which affects mesophase formation [99].

1.6.3. Effect of Silica Source

Mesoporous silica synthesis is very sensitive to source of silica used. Mesoporous structures have been synthesized by making use of several sources of silica, such as silicon alkoxides (e.g., TEOS, TMOS), sodium silicate, colloidal silica (Ludox) and fumed silica, etc [47, 54, 89]. Silicon alkoxides are not soluble in water but can be dissolved in a mixture of water and water miscible organic solvent (e.g., ethanol). They can be hydrolyzed by acid catalyzed or base catalyzed reaction resulting in cleavage of ester bond. They condense into aggregates containing Si-O-Si species and have negative charge due to silanol groups [21, 89]. It has been observed that the silica sources e.g. colloidal, fumed silica displaying Si(Q4) signals in the 29Si NMR are unsuitable as starting material in synthesis of mesoporous silica as those are highly polymerized one [100].

Setoguchi et al. [100] reported the interesting results for the synthesis of mesoporous silica from water glass. Type I (Na2O/SiO2/H2O = 19/37/44) water glass produced mesoporous silica but type III (10/30/60 wt %; Kishida Chemical) did not. However, using SiO2/Na2O mole ratio in the range of 3 to 3.3 highly ordered mesoporous silica of MCM-41 type was prepared at room temperature with improved thermal and hydrothermal stability [101]. Kim et al. have reported that in rapid hydrolysis conditions, TMOS acted as preferential precursor source than TEOS [97, 102].

The synthesis of ordered mesoporous materials is governed by a wide range of synthesis variables, the details of which depend largely on the specific wet chemistry of the system studied [76]. The formation of any mesostructured material proceeds via optimisation of relative kinetics and interactions between the inorganic and organic components of the synthesis. The important factors involved in the formation of organic-inorganic hybrid mesophases are the degree and rate of hydrolysis; condensation of inorganic precursor and assembly of the mesostructured template. Various ways of affecting these factors have been exemplified, by optimising the volume fraction of the surfactant and the hydrolysed inorganic precursor. It clearly appears that the interaction between the inorganic
precursor and the template is the key factor in the control of the material mesostructure. However, the step where such interactions occur is still not completely clear and seems to be strongly dependent on the synthesis conditions used [76, 78].

1.7. Mesoporous Silica gel

Silica gel is a chemically inert, non-toxic material composed of amorphous silicon dioxide. It has an internal network of interconnecting microscopic pores, yielding a typical surface area of 700-800 m²/g; or, stated another way; the internal surface area of a teaspoon full of silica gel is equivalent to a football field. Water molecules are adsorbed or desorbed by these micro-capillaries until vapour pressure equilibrium is achieved with the relative humidity of the surrounding air. Silica gel may be described as a coherent, rigid three-dimensional network of contiguous particle of colloidal silica. The formation silica gel takes place in two steps; i) the polymerization of silicic acid to form spherical particles and ii) aggregation of particles in 3D network. The synthetic route for producing silica gel was first patented by professor Walter A. Patrick at Johns Hopkins University, Baltimore, Maryland, USA in 1919 [10, 103, 104]. Silica gel was used in the adsorption of vapours and gases in gas mask canisters during World War I and World War II, it was commonly used as a dehydrating agent to protect military and pharmaceutical supplies, among a number of other applications. Its use as a buffering agent to control relative humidity within the mid-range rather than as a desiccant is a unique to museum applications.

The formation of silica gel, in general, involves two major steps: the formation of a wet gel, and drying of the wet gel to produce many forms of silica. Originally, wet gels were made by the aqueous condensation of sodium silicate, or a similar material. While this process worked well, the reaction formed salts within the gel that were to be removed by many repetitive washings [10]. Polysilicic acid is produced when silicon tetrachloride or silicon alkoxide is hydrolysed, which condenses further to produce a cross-linked gel. Over the last few decades, with the development of sol–gel chemistry, the alkoxy silanes such as Si (OR)₄ have been used with R = CH₃, C₂H₅ or C₃H₇ as precursors for silica synthesis [105]. Many other alkoxides, containing various organic functional groups, can be used to impart different properties to the gel. Alkoxide-base sol–gel chemistry avoids the formation
of undesirable salt by-products, and allows a much greater degree of control over the final products. By condensation, stable particles of colloidal size are formed. As condensation proceeds, small three-dimensional siloxane networks are gradually formed, which are accompanied by an increase in the viscosity of the medium, reaching the gel point. The formed gel is termed as hydrogel (or alcogel, if an alcohol has been used as the solvent). The resulting gel is constituted by a coherent continuous solid silica network impregnated by a liquid phase representing the solvent and the reaction by-product.

The hydrogel structure is controlled by temperature, pH of the medium, nature of the solvent, water content, concentration of silica, nature and concentration of the added electrolyte and the type of the silica source. All these parameters give additional degree of freedom to tailor specific properties such as pore volume, pores size, and specific surface area. According to the drying condition two types of gels are formed. When hydrogel is dried under normal condition a xerogel is formed, at supercritical temperature aerogel formed [10].

Aerogel was invented by Kistler in 1931 [106] and is defined as gel dried at temperature and pressure higher than the critical point of the pore fluid. By eliminating capillary stress, the hypercritical drying process largely replaces the original pore liquids with air resulting in little or no shrinkage associated with drying, which gives rise to the highly porous materials referred to as aerogels. Aerogels show promise in many applications such as, catalysts, thermal insulations, chemical adsorbers, sensors, fuel storage, energy absorbers and aero capacitors [106-108]. Some of the remarkable properties for the aerogels are high porosity, large pore volume, high surface area and very good morphological stability during heat treatment at high temperatures [109]. The sol-gel method offers several advantages for making aerogels, such as high purity, microstructure, homogeneity at molecular level, and low temperature at preparation [110].

Silica xerogel is normally synthesized by sol-gel process and is formed once the gel is dried under ambient condition [111]. Conventional gel drying in the air, however, resulted in considerable shrinkage of the gel. The phenomenon was explained by the formation of liquid-vapour interfaces within the gel network and [111, 112]. Thus, silica xerogel possesses lower surface area than silica aerogel. A xerogel is formed, with narrowing pores by capillary forces exerted by the liquid. Porosity and surface area depend on the pH, concentration of silica temperature and
time of aging of hydrogel. Xerogels may retain their original shape, but often crack. The shrinkage during drying is often extreme (~90%) for xerogels. Xerogel is a solid formed from a gel by drying with unhindered shrinkage. Xerogels usually retain high porosity (25%) and enormous surface area, along with very small pore size (1-10 nm).

Drying of gel is less than 50 °C does not change surface area significantly while drying at higher temperature (>100 °C) reduces the surface area [9]. Drying of gel at elevated temperature causes shrinkage owing to the surface tension of water in the pores. The normal commercial desiccant gel of high selectivity for water and other polar molecules is made at pH less than 4. The product is microporous having surface area of about 800 m²/g and pore volume ca. 0.4 cc/g known as regular density gels. Gel can be made from sols having wide range of concentration from 1 to 15% SiO₂ [9, 10]. Gel made at high concentration is designed as “S” type as the gel time is short and the particles have little opportunity to increase in size. This gel consists of about 1.5 nm of particles at low concentration grows further to 2.5x10⁶ molecular weight at the time of gel setting. The intermediate density gels having surface area of about 350 m²/g and pore volume of ca. 1.00 cc/g are obtained by hydrothermal treatment of hydrogel [9, 66]. According to Barby [9] the randomly packed separate ultimate particles of hydrogel are clustered together to about 10-20 nm diameter by the hydrothermal treatment of acid-set concentrated hydrogel.

Silica xerogel has immense number of applications. SiO₂-based xerogels are highly porous materials that may enhance the performance of microelectronic devices due to their extremely low dielectric constants. Xerogel also used as the biomedical sensers. Silica xerogel as a carrier material in controlled delivery indicate that silica xerogels are biocompatible and non-toxic materials. Since the incorporation of various biological molecules such as drug and proteins into silica xerogel can be carried out at room temperature, silica xerogel has been explored for various biomedical applications, including oral and implantable drug delivery systems [111, 113]. The application of silica xerogel for the controlled release of heparin showed that the released heparin from different xerogels studied retained about 90% of its biological activity [113]. In addition, the synthesis of silica xerogel is considerably easy, safe and inexpensive. By taking the chemical and physical parameters into account while preparing silica xerogels, different matrices with different properties can be produced.
1.8. Functionalization of Mesoporous Silica Supports

Surface of silica is relatively inert; immobilization of organic functional groups provides unique opportunity to engineer the interfacial properties of solid substrates while retaining their basic geometry and mechanical strength. Chemical bonding of functional groups offers a unique advantage since the detachment of grafted molecule is prevented due to strong covalent bonding of the molecule to the substrate, furthermore functionalized silica does not swell or shrink like polymeric resins [114]. Organo modified mesoporous silicas are of interest in the fields of analytical chemistry [115], materials chemistry [116], biochemistry [117], catalyst technology [118] and chromatography.

In recent years, there has been pronounced tendency to utilize mechanically stable synthetic or natural solid matrices in many applications, such as chemically bonded phase in chromatography, extraction of cations from aqueous and non-aqueous solvents, catalytic or ion-exchange reactions, electronics, ceramics and also in bioengineering. One of the important properties explored is related to the adsorption of trace elements onto solid surface taking preconcentration or separation into account, where from a complex mixture, a single element or a series of similar elements can be separated and quantitatively determined.

Normally, metal ions exist in hydrated form or as complexes associated with anions with little or no tendency of transformation to polymeric matrix [119]. To convert the metal ion to an extractable species its charge must be neutralized and some or all water of hydration be replaced. Thus, the characteristics of metal ions and functional groups and/or donor atoms, which form complexes with the metal ions in solution, are the primary factors in extraction. The donor atoms involved in forming chelates usually include oxygen, nitrogen, phosphorous and sulfur atoms present in phenol, carbonyl, carboxylic, hydroxyl, ether, phosphoryl, amine, nitro, nitroso, azo, diazo, nitrile, amide, thiol, thioether, thiocarbamate, bisulphite, etc. However, the selectivity of the surface with the immobilized functional groups towards metal ion(s) depends on factors like size of the modifier [120], activity of the loaded group [121, 122] and the characteristics of hard–soft acid–base [123, 124]. The insertion of suitable specific functional groups into the polymeric matrix makes them capable of reacting with metal species under certain favorable conditions to form metal complexes.
Slow kinetics, irreversible adsorption of organic, swelling, sensitivity towards many chemical environments and loss of mechanical stability in modular operation are the main disadvantages exhibited by polymeric resin. These problems suggest the use of inorganic supports in place of polymeric resin. Some of the advantages of inorganic supports are: (a) good selectivity, (b) no swelling, (c) rapid sorption of metal ions, and (d) good mechanical stability [125].

Direct bonding of chelating groups to inorganic surfaces is difficult due to relative inertness of the surface in its ground state. However, this can be achieved after surface activation/ modification [126]. Surface modification via functional group immobilization provides unique opportunity to engineer the interfacial properties of solid substrates while retaining their basic geometry and mechanical strength. Surface engineering can be achieved either by physically adsorbing or chemically grafting functional groups onto a suitable matrix. Chemical bonding of functional groups offers a unique advantage since the grafted molecule detachment is prevented due to strong covalent bonding of the molecule to the substrate. Immobilization of molecules on organic/inorganic support has been extensively studied [127, 128] with much attention given to establishment of new covalent bond on the desired surface [129]. There are extensive reports [37, 38] on immobilization of modifiers like chelate forming organic reagents, polymers, metal salts, natural compounds and some microorganisms on solid matrices like ion-exchange resins, cellulose, fibers, activated carbon, sand, clay, zeolites, polymers, metal oxides and highly dispersed silica. Such investigations of immobilization of groups or compounds depend on substitution reaction between the modifiers and the surface of the supporting material. An active adsorbent should have good sorption capacity, chemical stability under experimental condition and especially high selectivity [130]. Among the different adsorbents, silica gel especially immobilized with various organic compounds with metal chelating ability has received great attention [131-137]. Immobilization of organic functional groups on a siliceous surface has been successfully employed to produce varieties of modified silica. In this process, organic reagent or synthesized organic molecule containing the desired organic functional group is directly attached to the support, or to the original chain bonded to the support via sequence of reactions to increase the main chain, where other basic centers can be added to ensure the enhancement of a specific adsorption [138]. The advancement in this field is associated with silylation process, which is employed to
generate products of coupling agents, to permit the fixation of a reagent that is able to fulfill predetermined specific applications. The silylated organo functional groups play an important role in co-ordination chemistry as a possibility of synthesis of new ligands with multi coordinating capabilities. Silica surface interacts with the silane reagent to form a covalent bond with the surface [10]. By the introduction of organic functional groups to silica surface there is a partial conversion of surface silanol to a new organofunctional surface that acquires organophilic properties. Thus, ligand-grafted silica gives a set of properties to the surface, which differs considerably from the original matrix [138].

Normally a chemical linker between the surface of silica and a functional group is introduced to facilitate the better adsorption (complexation) properties of functionalized materials (scheme 1.1).

![Diagram of Linking group with short hydrocarbon chain](image)

**Scheme: 1.1**

In this context, improvement in metal complexation properties of silica modified with trimethoxy (e.g. mercaptopropyl) silane is observed [139] because of (a) strong affinity of the immobilized group for metal ions, (b) increased probability to encounter with metal ions as the functional group is attached at the end of the short hydrocarbon chain that increases the mobility of the group, and (c) propyl chain produces steric effect at the silanol site allowing more functional groups to be available away from the silica surface for interaction with metal ions [114]. The systematic use of immobilization of organofunctional groups has increased in the past three decades, mainly on silica, because this support offers advantages over other organic/inorganic supports. Immobilization on silica results in great variety of silylating agents, allowing pendant functional groups in the inorganic framework [129]. Attachment is easier on silica surface than on organic polymeric supports, which have a high number of cross-linking bonds, requiring hours to reach
equilibrium for surface activation [140]. Silica gel being the most popular substrate for surface studies because it is the first commercially available high specific surface area substrate with constant composition, enabling easy analysis and interpretation of results and has high mass exchange characteristics and no swelling [140, 141]. Silica support has great resistance to organic solvents and very high thermal resistance [140, 142]. Mesoporous organic–inorganic hybrid silica materials with organic functionalities anchored to the silica structure may be good candidates to perform various organic transformations with increased selectivities [143].

1.8.1. Surface Chemistry of Silica

The active silica surface with large specific surface area is of great importance in adsorption and ion exchange. These properties are well studied, even though shape of silica surface is basically unknown. The only method involving direct measurement (imaging) of outer surface of silica or modified silica is atomic force microscopy (AFM) based on scanning of the surface with a special probe. At the surface, the structure terminates in either siloxane group (≡Si–O–Si≡) with the oxygen atom on the surface, or one of the several forms of silanol groups (≡Si–OH) [114]. The silanol groups could be isolated (free silanol groups), where the surface silicon atom has three bonds with the bulk structure and the fourth to OH group; and the vicinal or bridged silanols, where two isolated silanol groups attached to two different silicon atoms, which can be bridged by H-bond. A third type of silanols called geminal silanols consists of two hydroxyl groups attached to one silicon atom [142] (Scheme 1.2).

![Scheme 1.2](image)

The geminal silanols are close enough to have H-bond whereas free silanols are too far separated. Since the discovery of silanol groups on silica surface in 1936 by Kiselev [142], studies based on theoretical calculations, physical methods and chemical methods silanol concentration on the silica gel surface after activation at 423 K was found to be 4.5–8.0 groups/nm² depending on the type of silica [142,
Currently it is accepted that the estimated number of OH groups accessible on the porous silica surface is between 4 and 5 OH groups/nm [147]. However, the local density of silanol varies from place to place and silanol number varies as a function of temperature. Physiosorbed water molecules are removed by heating the silica sample up to 440 K. Above this temperature, surface silanol groups start getting condensed to liberate water molecule and at 673 K almost half of the silanols are removed. At temperature of 873 K to 1023 K, only isolated silanols remain on silica surface [10, 148]. Some silanols are very close to each other to have hydrogen bonds with their neighbors.

The grafting of the functional groups is achieved by reacting surface silanol groups with organofunctionalized silanes, as represented by the general formula $Y_3Si-R-X$. The applicability of these bifunctional silanes is determined by the reactivity of the X groups. Y is normally an alkoxide groups (RO) or Cl group, which reacts with surface silanol groups to form stable Si–O–Si–C linkage. Numerous organosilanes are commercially available; some of the examples are shown in scheme 1.3. The availability of the silanol groups can determine whether the grafted silicon atom is tethered via one, two, or three silicon-oxygen bonds. Silica based composites having high surface area and porosity are frequently used to remove metal ions from solutions, in catalysis, as carrier for drug due to their facile synthesis methodology chemical stability. Silica gel and ordered mesoporous silica is the best inorganic materials that can be used for these applications. There are many advantages to use this support, viz. its surface being both thermally and chemically stable during the reaction process. The presence of silanol groups on silica surface manifests the Brønsted acid behaviour [10, 149], and gives this surface properties of adsorbing an enormous variety of chemical species, such as cyclic amines [150], amides [151], proteins [152] and biologically active phosphates [153]. It is also used for sorption separation of platinum metals [154] and for grafting metal by using AlCl$_3$ or TiCl$_4$ [155], without previous modification with an organosilane. The type of functional group grafted on the surface of silica determines metal ion scavenging/catalytic/drug retaining properties of the materials [114, 156-163].
The aminosilicas is possibly the well-studied class of organic/inorganic hybrid materials. These are materials where primary, secondary, or tertiary amine functionalities are attached to the silica support via an alkyl or aryl linker. Due to the simplicity of their syntheses, aminosilicas have been studied for many different applications. For instance, aminosilica materials have been used in catalysis [164], adsorption [143, 165-167] separations [168] and as supports for more advanced organic synthesis [5, 7, 169-174].

Aminosilicas are synthesized by one of two routes: (1) co-condensation of an aminopropylalkoxysilane with the silica source to form the silica material [175] or (2) grafting [28] of the aminopropylalkoxysilane to the post-synthesized silica material. The difference between the two methods chiefly involves the location of the amine organic functionalities on the silica support with the co-condensed material having amine groups on the surface and within the walls of the silica framework and the grafted material only having amine groups on the surface. The co-condensation method usually begins by mixing dilute quantities of an aminopropylalkoxysilane and silica precursor with a structure directing agent to form the pore structure. After the silica precursor and aminopropylalkoxysilane co-polymerize, the structure directing agent can be removed via a solvent extraction to give functionalized porous channels. This method has allowed for the ability to easily alter the loading of the amino groups on the surface. However, in some cases, the aminopropylsilane can damage the structural integrity of the material [175].
Another drawback is that the location of the organic group may or may not be accessible, especially when high quantities of the aminopropylalkoxysilane are used [176].

The grafting of aminopropylalkoxysilanes to preformed silica structures is possibly the easiest approach to form aminopropylalkoxysilyl-groups tethered to a support. Knözinger and Rumpf first reported the synthesis of an amine-grafted silica material by refluxing (2-aminoethyl)-aminopropyltrimethoxysilane (AEAPTMS) with silica in 1978 [177]. Grafting of the aminopropylalkoxysilane directly to the silica surface occurs through a reaction between the surface silanols and the alkoxy silane. The alkoxy portion of the silane reacts directly with the surface silanol evolving corresponding alcohol (methanol in this case). The silane is therefore grafted to the surface via a covalent bond with an oxygen atom from the surface. This oxygen can either be from a reactive silanol or a siloxane bridge. Depending on the proximity of the surface silanols to one another and depending on how many alkoxy groups are on the silane, up to three tethering linkages can be formed. The resulting material is stable towards most organic solvents and moderate temperatures (~200 °C) [144].

Tripp and coworkers discovered that the addition of a base (triethylamine, ethylenediamine, or 3-aminopropyltrimethoxysilane (APTMS) activated the silanols for reaction with the alkoxy silane [178]. The advantage of this method to produce high amine loadings is that it can be performed in the non-aqueous. It was proposed that as the amines become relatively close to the surface, they form hydrogen bonds with the surface silanols. The hydrogen bonding activates the silanols to react with a nearby alkoxy silane. Since water was not present, the silanes were not able to oligomerize in solution or on the surface of silica, and a relatively high loading of surface amines could be achieved [178]. The disadvantage of forming high amine loaded materials with 3-aminopropyltrimethoxysilane is the formation of multiple types of amine sites on the silica surface. For instance, when APTMS and silica are mixed in toluene (the traditional method of preparing an aminosilica material), the amine groups can hydrogen bond in solution and produce amine sites on the surface that hydrogen bond with one another or with the surface silanols. The resulting aminosilica has different types of amine environments on the surface ranging from closely packed, interacting amines to isolated amines. The disadvantage with these materials is the differences in accessibility and reactivity of the amine groups.
McKittrick et al. [5, 7] determined that aminosilicas synthesized via a traditional method produced materials with some inaccessible amine sites.

In order to create grafted aminosilicas with uniform, accessible amine functionalities, protection/deprotection methods have been developed which prevent amine-amine interactions and cap excess surface silanols to prevent amine-silanol interactions. For instance, Wulff et al. created spaced amines on silica by immobilizing a template capable of being hydrolyzed [1]. The template was formed via the reaction between two equivalents of 4-(methoxydimethylsilyl) aniline and one equivalent of 4, 4'-methylenedibenzaldehyde. After reaction of the protected amine template with the surface, the protecting group was removed with an acid solution to form the resulting spaced, primary amine. However, very dilute concentrations of the template were required to ensure separation of most amine groups, because if high concentrations were used, two templates could react with the surface side by side, producing a distribution in amine separation. This method thus required amine loadings of less than 0.2 mmol NH₂/g to form spaced amines.

Katz and coworkers [2, 4] have synthesized aminosilicas using a molecular imprinting approach to produce isolated amines. Their approach utilized a co-condensation method for forming protected amines within the framework of bulk, amorphous, microporous silica. After synthesis of the material, the protecting group was cleaved by thermolysis (heating to 250 °C under N₂) or addition of trimethylsilyl iodide. Two disadvantages exist for these materials: (1) loadings of less than 0.25 mmol NH₂/g and (2) difficulties for large molecules to access amine sites in microporous materials [2, 4].

McKittrick and Jones developed a method to protect the primary amine of APTMS by reacting it with 3,3,3-triphenylpropanal to form a tritylimine with an alkoxysilane tail [5]. The trityliminealkoxysilane was tethered to silica in a simple one step reaction. Next, the unreacted silanols on the surface were capped with 1,1,1,3,3,3-hexamethyldisilazane to prevent amine-silanol interactions. Subsequently, the protecting group was cleaved to produce trityl-spaced amine groups on the surface. This method reduced or eliminated amine-silanol interactions and amine-amine interactions. Although the amine loading was roughly twice that of previously reported spacing methods (~0.4 mmol NH₂/g material), this method was deficient in amine loading compared to traditional methods (~1.2 mmol NH₂/g material) [5].
In summary, many techniques have been developed for the synthesis of aminosilicas. While all the methods address different properties of the materials and optimize certain parameters, none have yet been able to produce a material with a high amine loading and spaced amine sites.

1.8.2. Thiol Functionalized Silica

Thiol-functionalized mesoporous materials have attracted much attention since they are good heavy metal absorbers [179-181] and can act as solid acid catalysts [182] and ion exchangers [183] after oxidation of thiol to sulfonic acid. Functionalized mesoporous materials with sulfonic acid groups are promising solid acid catalysts, their successful application avoids the use of traditional homogeneous acid catalytic systems which have serious drawbacks such as hazards in handling, corrosiveness, toxic waste, and difficulties in separation.

Thiol-functionalized mesoporous materials can be synthesized either by introducing mercaptopropyl groups onto the pore wall surface via a secondary modification route [180, 182, 184-185] or by directly incorporating mercaptopropyl groups during the preparation of the materials via the co-condensation route [181, 186]. Secondary modification comprised the silylation of an absolutely dried pre-existing mesoporous support with 3-mercaptopropyltrimethoxysilane (MPTS) or the coating of a partially hydrated support with an MPTS layer in an organic solvent. In the secondary modification process, the surface concentration of organic groups is constrained by the number of reactive surface silanol groups present and by diffusion limitations. Consequently, it is often necessary to employ a large amount of the organic solvent and more superfluous organosiloxane precursors [187].

The first examples of heavy metal ion adsorbents based on functionalized micelle templated ordered mesoporous silica have been reported independently by two groups in 1997 [184, 188] and numerous subsequent investigations on a similar system (thiol–mercury) have led to important conclusions highlighting the interest of mesostructured adsorbents for heavy metal ions uptake. Highly effective Hg$^{2+}$ uptake by means of mercaptopropyl-functionalized monolayer on ordered mesoporous silica [184] or mercaptopropyl-grafted hexagonal mesoporous silica [188] was observed, demonstrating the ability of the adsorbents to bind mercury ions quantitatively to each thiol group because of its uniform and large framework structure. The advantage due to the ordered mesostructures was not observed with non-ordered
silica gel-based adsorbents functionalized with the same ligands because grafting such heterogenous porous frameworks led to pore clogging effects, resulting in inaccessible thiol groups to Hg\(^{2+}\) ions \[188\]. Mercaptopropyl-grafted silica gels gave rise to accessibility values ranging from 10 % to 95 % (based on a –SH to Hg\(^{2+}\) ratio of 1), depending on the porosity of the gels, but total access to all binding sites was never achieved in non-ordered silica gel-based adsorbents \[143, 188\]. With the exception of functionalized monolayer on ordered mesoporous silica, the amount of mercaptopropyl ligands that can be attached to the materials by post-synthesis grafting remained rather low (typically in the range 0.5–1.5 mmol/g), \[188\ - 190\] as restricted by the specific surface area and therefore the number of silanol groups available for grafting, so that many authors have proposed to resort to the one-step syntheses to increase the adsorbents capacity \[189, 192, 193\]. The highest loading capacity of thiol groups on silica is 7 - 8 mmol/g. When increase in the content of organosilane, in MCM-41 and MCM-48 series, only 30 – 40 % of mrcaptopropyltrimethoxysilane was accessible because of the significant loss in mesostructural order and dramatic decrease in pore sizes \[191, 194\].

Modification of the surface is mostly done by using an appropriate molecule designated as precursor silylating agent. Thus, a covalent bond can be formed to give new anchored surface, making it easy to immobilize a new molecule to increase the chain with a variety of organic functions able to act with increased activity as a chelating agent for many purposes. The anchored molecules usually contain nitrogen, oxygen or sulfur, or combination of these atoms acting as the basic centres, which can complex cations, in a given fashion in order to force a selective adsorption. These basic centres can itself are a catalyst for the organic transformations. These organic modified mesoporous silica materials are very good drug carrier for the biomedical application.

### 1.9. Metal Adsorption

Water pollution is a very serious problem in India, the second most populated nation in the world. It is estimated that over 70 % of all of India’s surface water is polluted in some way or other and many of the groundwater reserves have also been contaminated as a result of biological and industrial pollutants. Thus, water treatment poses both technical and economic challenges to industry. Heavy metals are very hazardous for living organisms, when exceeds the specific limits. Copper commonly
used in the electrical and electroplating industry, has agricultural applications and is used as an algicide in water purification; copper metal corrodes in water to yield soluble copper (II) salts ($\text{Cu}^{2+}$). The copper (II) salts exhibit high acute and chronic toxicity to aquatic organisms and may cause skin, brain, pancreas and heart diseases [196] as well liver and kidney damage when accumulated to the human body. Thus copper effluents are of strong concern to the Environmental Protection Agency (EPA) which has issued strong quality criteria for fresh water with regard to its copper content, i.e., 9.2 ppb acute and 6.5 ppb chronic level [198]. The EPA maximum contaminant level for As in drinking water is 10 µg/dm$^3$. Nine of sixteen districts of West Bengal have been reported to have groundwater arsenic concentrations above 0.05 mg/L. Mercury (Hg) is one of the extremely toxic metals in the environment that can cause irreversible neurological damage in human [199]. The harmful effect of mercury toxicity is manifested by hindering the transport processes in living cells, which is due to the high affinity of this element toward sulfur-containing biological molecules [200].

The World Health Organization (WHO) recommends a maximum human Hg uptake of 0.3 µg per week and a maximum acceptable concentration of 1 µg/L in drinking water. The USEPA permitted discharge limit of wastewater for total Hg is 10 µg/L while the limit for drinking water is 2 µg/L. Japan Ministry of the Environment establishes even more strict limits at 5 and 0.5 µg/L, respectively [199]. The mercury standard for drinking water adopted by EU countries, India and Canada is 1 ppb. Because mercury (as with other metals) cannot be destroyed, mercury released in our industrial past keeps recirculating between environmental matrices. Long range transport of the circulating mercury has caused global contamination, which poses ecological and potential human health risk far away from known point sources [192, 196, 201].

Several technologies exist today for the removal of metal ions from metals contaminated water [196]. Among the most common physical-chemical approaches used in metals treatment technologies are precipitation, coagulation/co-precipitation, and adsorption. Ion-exchange, chemical reduction, membrane separation, and microemulsion liquid membrane extraction are additional treatment schemes that are less commonly used [156, 196]. When deciding upon a treatment technology to remove metals from environmental systems, the performance of technology, secondary waste generation, and economics must be taken into account. Amongst these, adsorption based technologies are the most prominently used technologies for
the removal of metals because of their efficient removal capacity and overall low cost. Adsorbents also can potentially be regenerated further adding to cost savings. During the last twenty years new classes of solid adsorbents have been developed as microporous, mesoporous and nanoporous materials, such as modified silica gel [161], ordered mesoporous silica [156], activated carbon [202, 203], resins [204, 205], clays [206, 207], fullerenes and heterofullerenes [203]. These adsorbents are normally prepared by attaching organic and inorganic molecules to their surface. The synthesized functional materials can effectively be used to remove specific toxic metal ions from aqueous media, thus these properties revived great interest for chemical separation and environmental cleanup applications [156].

Mesoporous silicas such as MCM-41, HMS, SBA-15, PMO, silica gel and SBA-1 have been functionalized by functional groups such as –NH₂, –SH, and –S– etc. to make the materials capable to interact strongly with metal ions like Cu²⁺, Cd²⁺, Hg²⁺, Ni²⁺ etc [156, 160-163, 198, 207-240, 242-245]. Selective adsorption of anions [209] like PdCl₂⁻ from the binary solution of PdCl₂ and AuCl₃ at pH 1.0 and oxyanions [212] like Cr₂O₇²⁻ from the solution of Cu²⁺ and Cr₂O₇²⁻ at pH below 3.5 on amino functionalized MCM-41 has been reported. Lam et al. [208] have demonstrated the selective adsorption of metal ions from their binary mixture based on the Pearson’s hard-soft acid base (HSAB) concept by modifying the surface of MCM-41 silica with alkyl substituted amine group (-RNH) in order to decrease the hardness of the basic group and make it more selective for the Ag⁺ than that for Cu²⁺. MCM-41 grafted with –NH₂ group found to be more selective for Cu²⁺ at pH 5 than that for Ag⁺ and it was attributed to the interaction between hard base (–NH₂) and hard acid (Cu²⁺) [214] Lam et al. proposed for the interaction of amino functionalized MCM-41 with the CuSO₄ system and these complexes are stabilized by the SO₄²⁻ counter ions [156]. Blitz et al. [161] have grafted aminopropyl group using two different silanes, viz, 3-aminopropyldimethylmethoxysilane (APDMS) and 3-aminopropytriethoxysilane (APTMS) having one and three hydrolysable groups respectively and later was treated with water to hydrolyze the hydrolysable groups to form cross-linked polymeric type grafted modified silica gel. At higher concentration of Cu²⁺, adsorption of Cu²⁺ on later has been reported to be less than that on sample modified with APDMS. However, at lower concentration, uptake of Cu²⁺ on cross-linked aminopropyl grafted gel was found to be more than that of APDMS modified gel. This difference was attributed to the larger number of the
functional groups being at shorter distance between one another on the surface of cross-linked material and hence acts as bidantate ligand. Kudryavtsev et al. [216] reported that at small degree of adsorption of Cu\(^{2+}\) on the amino functionalized silica gel ML\(_2\) type of complex is formed, which, was converted to ML\(_1\) on increasing the degree of Cu\(^{2+}\) adsorption. Silica gel functionalized with 3-aminopropyltriethoxysilane was used for separation and preconcentration of Cu\(^{2+}\), Cd\(^{2+}\) and Cr\(^{3+}\) from seawater and thiol functionalized silica gel are selectively adsorbed the mercury ions [217, 218]. Modification of silica gel surfaces with covalently bonded diethylenetriamine and triethylenetetramine were found to be more superior for pre-concentration of Cu(II) and Ni(II) ions than silica gel bonded ethylenediamine [215].

The adsorption of toxic metal cations has been explored for functional groups fixed on mesoporous silica. The divalent cations (Cu, Zn, Cr and Ni) present in waste-water are adsorbed to a greater extent on amino-functionalized SBA-15 than on thiol functionalized SBA-15, whereas Hg\(^{2+}\) is preferably adsorbed on thiol-functionalized SBA-15 [210]. Unlike cation capture by amino- or thiol-functionalized groups, the studies of anion adsorption by functional groups fixed in the pores of mesoporous silicas are rare. Fryxell et al. [176, 219] have shown that diamino-functionalized MCM-41 exhibits a marked capacity for adsorption of Cu\(^{2+}\), giving rise to a positively charged mesoporous host, which achieves nearly complete removal of arsenate and chromate by selective binding of the anions. The leaching of Cu\(^{2+}\) during the adsorption was not significant because of the affinity of the ethylenediamine ligand. In a related study on the adsorption of chromate and arsenate by amino-functionalized MCM-41 and SBA-1, Yoshitake et al. [220] found that triaminosilane-grafted mesoporous silica adsorbed more oxyanions than mono- and di-functionalized mesoporous silicas. Some of the examples of organo functionalized mesoporous silica and their applications for adsorption of metal ions are summerised in table 1.4.
**Table 1.4. Removal of heavy metal species using organically-modified mesoporous silica adsorbents**

<table>
<thead>
<tr>
<th>Organic functional groups</th>
<th>Mesoporous supports</th>
<th>Loading of functional group (mmol/g)</th>
<th>Maximum ads. capacity (mmol/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aminopropyl</td>
<td>Silica gel</td>
<td>2.61</td>
<td>0.57(Cu$^{2+}$), 0.29(Ni$^{2+}$), 0.167(Co$^{2+}$), 0.35(Zn$^{2+}$) 0.17(Cd$^{2+}$), 0.19(Pb$^{2+}$)</td>
<td>[215]</td>
</tr>
<tr>
<td>Aminopropyl</td>
<td>MCM-41</td>
<td>2.26</td>
<td>0.84(Cu$^{2+}$), 0.62(Ag$^{+}$)</td>
<td>[214]</td>
</tr>
<tr>
<td>Aminopropyl</td>
<td>MCM-41</td>
<td>2.3</td>
<td>0.56(Cd$^{2+}$), 0.50Ni$^{2+}$</td>
<td>[223]</td>
</tr>
<tr>
<td>Aminopropyl</td>
<td>MCM-41</td>
<td>2.53</td>
<td>0.82(Cu$^{2+}$), 0.91(Cr$^{2+}$)</td>
<td>[212]</td>
</tr>
<tr>
<td>Aminopropyl</td>
<td>MCM-41</td>
<td>2.01</td>
<td>0.71(Co$^{2+}$)</td>
<td>[163]</td>
</tr>
<tr>
<td>Aminopropyl</td>
<td>MCM-41</td>
<td>2.26</td>
<td>1.40(Au$^{3+}$)</td>
<td>[224]</td>
</tr>
<tr>
<td>Aminopropyl, SBA-15</td>
<td>1.9</td>
<td></td>
<td>0.25(Cu$^{2+}$)</td>
<td>[201]</td>
</tr>
<tr>
<td>Aminopropyl, SBA-15</td>
<td>1.41</td>
<td></td>
<td>1.9(Hg$^{2+}$)</td>
<td>[213]</td>
</tr>
<tr>
<td>Aminopropyl</td>
<td>HMS</td>
<td>-</td>
<td>0.10(Cu$^{2+}$), 0.001(Ni$^{2+}$), -Co$^{2+}$</td>
<td>[237]</td>
</tr>
<tr>
<td>Aminopropyl</td>
<td>HMS</td>
<td>-</td>
<td>0.39(Cu$^{2+}$), 0.41(Pb$^{2+}$), 0.37(Zn$^{2+}$), 0.27(Mn$^{2+}$), 0.43(Ag$^{+}$)</td>
<td>[238]</td>
</tr>
<tr>
<td>Aminopropyl</td>
<td>MCM-41</td>
<td>2.53</td>
<td>1.40(AuCl$_4^{-}$), 0.55(PdCl$_4^{2-}$)</td>
<td>[209]</td>
</tr>
<tr>
<td>Aminopropyl</td>
<td>MCM-41</td>
<td>2.1</td>
<td>0.78(Pb$^{2+}$), 0.92(Hg$^{2+}$)</td>
<td>[226]</td>
</tr>
<tr>
<td>Dipropylamine</td>
<td>MCM-41</td>
<td>1.01</td>
<td>0.33(Au$^{3+}$)</td>
<td>[224]</td>
</tr>
<tr>
<td>tripropylamine</td>
<td>MCM-41</td>
<td>0.94</td>
<td>0.20(Au$^{3+}$)</td>
<td>[224]</td>
</tr>
<tr>
<td>Propyl ethylenediamine</td>
<td>Silica gel</td>
<td>1.30</td>
<td>0.58(Cu$^{2+}$), 0.28(Ni$^{2+}$), 0.20(Co$^{2+}$), 0.35(Zn$^{2+}$) 0.17(Cd$^{2+}$), 0.19(Pb$^{2+}$)</td>
<td>[215]</td>
</tr>
<tr>
<td>Propyl ethylenediamine</td>
<td>MCM-41</td>
<td>2.53</td>
<td>0.27(Co$^{2+}$)</td>
<td>[163]</td>
</tr>
<tr>
<td>Propyl ethylenediamine</td>
<td>SBA-15</td>
<td>2.59</td>
<td>2.5(Hg$^{2+}$)</td>
<td>[213]</td>
</tr>
<tr>
<td>Propyl ethylenediamine</td>
<td>SBA-15</td>
<td>4.0</td>
<td>0.82(Cu$^{2+}$)</td>
<td>[201]</td>
</tr>
<tr>
<td>Propyl ethylenediamine</td>
<td>HMS</td>
<td>-</td>
<td>0.50(Cu$^{2+}$), 0.15(Ni$^{2+}$), 0.06 Co$^{2+}$</td>
<td>[237]</td>
</tr>
</tbody>
</table>
Amine-bearing organo-functional groups have been attached to mesoporous silica adsorbents. A wide range of metal species are likely to be immobilized onto amine-modified mesoporous silica [228-230]. Anion effects have also been reported to influence sorption capacities due to speciation changes like, e.g., improvement of Cu$^{2+}$ binding to amine-grafted MCM-41 in the presence of SO$_4^{2-}$ ions (instead of NO$_3^-$), which was ascribed to the formation of –NH$_2$–Cu$^{2+}$–SO$_4^{2-}$ moieties on the adsorbent surface [156, 214]. Amino-functionalized adsorbents prepared by one-step co-

<table>
<thead>
<tr>
<th>Material</th>
<th>Adsorbent Type</th>
<th>α (Metal)</th>
<th>β (Metal)</th>
<th>γ (Metal)</th>
<th>δ (Metal)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propyl diethylene triamine</td>
<td>Silica gel</td>
<td>0.63</td>
<td>0.41</td>
<td>0.32</td>
<td>0.35</td>
<td>[215]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.16</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Propyl diethylene triamine</td>
<td>MCM-41</td>
<td>3.80</td>
<td>0.07</td>
<td></td>
<td></td>
<td>[163]</td>
</tr>
<tr>
<td>Propyl diethylene triamine</td>
<td>SBA-15</td>
<td>4.00</td>
<td>3.62</td>
<td></td>
<td></td>
<td>[213]</td>
</tr>
<tr>
<td>Propyl diethylene triamine</td>
<td>HMS</td>
<td>-</td>
<td>0.50</td>
<td>0.15</td>
<td></td>
<td>[237]</td>
</tr>
<tr>
<td>2-aminomethylpyridine</td>
<td>Silica gel</td>
<td>0.76</td>
<td>0.75</td>
<td>0.40</td>
<td></td>
<td>[221]</td>
</tr>
<tr>
<td>2-mercaptophenylthiourea</td>
<td>MCM-41</td>
<td>1.19</td>
<td>1.1</td>
<td></td>
<td></td>
<td>[228]</td>
</tr>
<tr>
<td>Mercaptopropyl</td>
<td>MCM-41</td>
<td>1.0</td>
<td>0.97</td>
<td></td>
<td></td>
<td>[214]</td>
</tr>
<tr>
<td>Allylpropylthiourea</td>
<td>MCM-41</td>
<td>1.7</td>
<td>1.5</td>
<td></td>
<td></td>
<td>[207]</td>
</tr>
<tr>
<td>2-Mercaptothiazoline</td>
<td>MCM-41</td>
<td>1.28</td>
<td>0.70</td>
<td></td>
<td></td>
<td>[230]</td>
</tr>
<tr>
<td>2-Mercaptobenzothiazole</td>
<td>MCM-41</td>
<td>1.14</td>
<td>0.21</td>
<td></td>
<td></td>
<td>[231]</td>
</tr>
<tr>
<td>Mercaptopropyl</td>
<td>SBA-15</td>
<td>1.01</td>
<td>1.1</td>
<td></td>
<td></td>
<td>[233]</td>
</tr>
<tr>
<td>N-propylsalicylaldimine</td>
<td>SBA-15</td>
<td>0.73</td>
<td>0.38</td>
<td></td>
<td></td>
<td>[234]</td>
</tr>
<tr>
<td>2-Mercaptothiazoline</td>
<td>SBA-15</td>
<td>0.95</td>
<td>0.99</td>
<td></td>
<td></td>
<td>[235]</td>
</tr>
<tr>
<td>2-Mercaptothiazoline</td>
<td>SBA-15</td>
<td>1.22</td>
<td>1.10</td>
<td></td>
<td></td>
<td>[230]</td>
</tr>
<tr>
<td>Mercaptopropyl</td>
<td>HMS</td>
<td>2.3</td>
<td>1.26</td>
<td>0.89</td>
<td></td>
<td>[239]</td>
</tr>
<tr>
<td>Mercaptopropyl</td>
<td>HMS</td>
<td>1.47</td>
<td>1.5</td>
<td>0.17</td>
<td></td>
<td>[240]</td>
</tr>
<tr>
<td>2-Mercaptothiazoline</td>
<td>HMS</td>
<td>0.89</td>
<td>2.345</td>
<td></td>
<td></td>
<td>[210]</td>
</tr>
<tr>
<td>Bis[propyl]ethane + mercaptopropyl</td>
<td>PMO</td>
<td>1.49-1.69</td>
<td>1.7</td>
<td>0.4</td>
<td>1.3</td>
<td>[181]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.2</td>
<td>1.7</td>
<td></td>
</tr>
</tbody>
</table>

*Abbreviations: HSM: Hexagonal Mesoporous Silica, MCM: Mobil Composition of Matter. Silica; SBA: Santa Barbara Amorphous; PMO: Periodic Mesoporous Silica.*
condensation in the presence of anionic surfactant template showed higher capacity than amino-functionalized MCM-41 prepared by the classical cocondensation method using a conventional cationic templating route [163].

Adsorption is the preferred technique for the removal of Hg$^{2+}$ from the water systems. Various adsorbents such as biological materials [241], activated carbons [192], and modified inorganic materials like clay minerals and oxides [184] have been reported. Amongst these materials surface functionalized mesoporous silica with thiol groups is one of the most suitable class of the materials. Various mesoporous silica such as silica gel, and micelles templated ordered mesoporous have been functionalized with $-\text{SH}$ group for their application in the adsorption of Hg$^{2+}$ from aqueous media as summerized in table 1.5. From the environmental point of view, it is interesting to notice that the great affinity of thiol groups for Hg(II) species offers very high distribution coefficients ($K_d \sim 108 \text{ mL/g}$) [137-139], and thereby extremely low residual mercury concentrations in solution after adsorption. The performance of this novel family of materials was even better than existing commercial adsorbents [192, 221, 222].

**Table 1.5.** Comparison data for Hg(II) binding to thiol- functionalized mesoporous silica

<table>
<thead>
<tr>
<th>Mesoporous materials type</th>
<th>Thiol group content (mmol/g)</th>
<th>Hg (II) ads. capacity (mmol/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica gel</td>
<td>1.37</td>
<td>0.42-0.49</td>
<td>[191]</td>
</tr>
<tr>
<td>MCM-41</td>
<td>0.57 – 2.8</td>
<td>0.55-2.1</td>
<td>[179,186,191,224]</td>
</tr>
<tr>
<td>SBA-15</td>
<td>0.27-2.9</td>
<td>0.26-2.88</td>
<td>[190,192,242]</td>
</tr>
<tr>
<td>SBA-16</td>
<td>0.40</td>
<td>0.38</td>
<td>[242]</td>
</tr>
<tr>
<td>MCM-48</td>
<td>2.7</td>
<td>1.4</td>
<td>[190]</td>
</tr>
<tr>
<td>HMS</td>
<td>0.57-1.5</td>
<td>0.55-1.5</td>
<td>[179, 239]</td>
</tr>
<tr>
<td>MSU</td>
<td>0.5 – 1.49</td>
<td>0.52 – 1.49</td>
<td>[243]</td>
</tr>
<tr>
<td>PMO</td>
<td>6.5 – 7.7</td>
<td>2.2 – 2.5</td>
<td>[193]</td>
</tr>
<tr>
<td>PCH</td>
<td>1.1</td>
<td>0.74</td>
<td>[195]</td>
</tr>
</tbody>
</table>

*Abbreviations, HMS: Hexagonal Mesoporous Silica, MCM: Mobil Composition of Matter. MSU: Michigan State University; PMO: Periodic Mesoporous Silica; SBA: Santa Barbara Amorphous; PCH: Porous Clay Heterostructure.*

Organically-modified mesoporous silica materials are basically good adsorbents, being promising for the removal and immobilization of inorganic and organic pollutant species. This is mainly due to the attractive properties of such highly ordered structures exhibiting exceptionally large specific surface area and regular porous framework ensuring easy and fast access to a high number of organo-functional groups per mass unit of the material. This is also due to the rich surface
chemistry of silica enabling the design of adsorbents bearing a wide range of
tailormade functionalities. This has led to numerous investigations utilizing such
nanoengineered materials for the removal of inorganic and organic pollutants.
Pioneering works dealt with accumulation of heavy metals but this was rapidly
extended to other contaminants like toxic anions, radionuclides, dyes, aromatic
hydrocarbons and related compounds, pesticides and, to a lesser extent,
pharmaceuticals. Depending on the target species, special attention was given to the
elaboration of an organic-inorganic hybrid likely to ensure strong binding and, if
possible, selective recognition of the pollutant.

1.10. Catalysis

Catalysis is widely used in nature for affecting various kinds of chemical
transformations since the evolution of life, though human being knows it since 400
years [244]. Today catalysis is used to satisfy human needs right from food and
clothing to drugs, plastics, detergents, fuels, agrochemicals and pesticides accounting
for more than one sixth of the value of all goods manufactured worldwide.
Furthermore, catalysis is playing an important role in environmental protection by
providing cleaner alternative routes for stoichiometric organic synthesis and
converting hazardous emissions to harmless streams. Thus, the importance of
catalysis to society is not only in economic aspects but also from the environmental
considerations [244].

1.10.1. Catalysis and Catalyst

Catalysis, from the Greek kata (cata), meaning down, and lyein (lysis)
meaning to loosen, to free, may come from the “philosopher’s stone” or “quinta
essential” of the medieval alchemists [244]. The chemical concept of catalysis was
first developed by the great Swedish chemist Berzelius (1779–1848) in 1835 to
correlate observations made by other chemists in Europe [245, 246], such as the
enhanced conversion of starch to sugar by acids; the hastening of gas combustion by
platinum; the stability of hydrogen peroxide in acid solution but its decomposition in
the presence of alkali and transition metals, such as manganese, silver, platinum, and
gold; and the observation that the oxidation of alcohol to acetic acid was
accomplished in the presence of finely divided platinum [247]. According to the
definition of catalysis introduced by Berzelius and scientifically defined firstly by
the German chemist Ostwald (1853–1932) in 1894, catalyst is a substance which
alters the rate of approaching of chemical equilibrium without itself being changed or substantially consumed in the process [248]. In a catalyzed reaction the catalyst generally enters into chemical combination with the reactants but is ultimately regenerated so that the amount of catalyst remains unchanged. Very small quantities of catalyst can catalyze the reactions containing thousands or even millions of times their own weight of chemicals. Equally astonishing is just how selective they can be. A catalyst may increase the rate of only one reaction out of many competing reactions [249, 250]. It is also interesting to note that over 80 % of industrial processes involve catalysts and the number is rising; more than half of the elements in the periodic table are involved in catalytic systems.

1.10.2. Heterogeneous (Solid) Catalysts

Catalysts are classified roughly according to their phase behavior into homogeneous and heterogeneous catalysts. For heterogeneous catalysis, catalyst and reactants are in different phases. The reactants may be either gases or liquids (or solutions) and usually the catalyst is a solid. Therefore, heterogeneous catalysts are also called as solid catalysts [251].

Catalysis by solid materials has been observed quantitatively at temperatures as low as 78 K and as high as 1500 K; at pressures between $10^{-9}$ and 103 bar; with reactants in the gas phase or in liquid phase; with or without assistance of photons, radiation, or electron transfer at electrodes; with pure metals as unreactive as gold and as reactive as sodium; with multi-component and multi-phase inorganic compounds and acidic organic polymers; and at site time yields as low as $10^{-5}$s$^{-1}$ (one turnover per day) and as high as $10^{9}$s$^{-1}$ (gas kinetic collision rate at 10 bar) [252].

Nowadays the increasing social and environmental pressure on industry to substitute traditional homogeneous-catalyzed reactions by environmentally friendly technologies represents the most important driving force for the development of heterogeneous catalysis. Indeed, the solid catalysts have many advantages over liquid catalysts [252]. They are noncorrosive and environmentally benign, presenting fewer disposal problems. Their reuse is possible and their separation from liquid products is much easier. Furthermore, they can be designed to give higher activity, selectivity and longer catalyst life….
The ultimate example of selectivity in catalysis has been provided by nature over millions of years of evolution in the form of cellular enzymes. Enzymes have evolved extremely high specificities to reactants consumed and products formed within a cell even in the presence of all other cellular chemistries. Although synthetic, non-biologic catalysts rarely replicate the selectivity and specificity of enzymatic biocatalysts, enzymes serve as inspiration for which novel homogeneous catalysts are designed [241].

The study of catalysis is a fundamental aspect of chemical engineering, as its implications affect all chemical transformations. Before any industrial process can be designed, the catalytic implications of any process must be thoroughly examined. Fundamental properties such as kinetics, diffusion, activation energies, activity, selectivity, deactivation, etc. must be understood, as they have profound influences on the overall design.

An everyday example may be found in the catalytic converters of gasoline powered automobiles. Platinum alloys convert pollutants in the exhaust to more benign compounds, drastically reducing emissions of harmful pollutants into the environment. Because homogeneous and heterogeneous catalysts each have their own advantages and disadvantages, it is important to understand basic concepts of both and where they are best applied.

Heterogeneous catalytic processes may be divided into two large groups: redox reactions and acid-base reactions. The first group includes all those reactions in which the catalyst affects the homolytic bond rupture in the reactant molecules with the appearance of unpaired electrons, and formation of homolytic bonds with the catalyst with the participation of catalyst electrons. The second group includes reactions in which, the reactants form heterolytic bonds with the catalyst by using the free electron pair of the catalyst or reactants, or the free electron pair formed in the course of reaction by heterolytic rupture of bonds in the reactant molecules [253].

A heterogeneous catalytic reaction begins with the adsorption of the reacting molecules onto the surface of the catalyst, where intramolecular bonds are broken or weakened. Next, the adsorbed species react on the surface, often in several consecutive steps. Finally, the products desorb from the surface into the fluid, thereby regenerating the active sites on the surface for the following catalytic cycle. Variety of solid supports such as, e.g. polymers [253], mesoporous materials [254-258], activated carbon [259], pillared clays [260], zeolites [261] have been reported.
for their application in organic transformations as heterogeneous catalysts. Silica supported heterogenized catalysts have been applied efficiently in many organic transformation e.g. epoxidation [262], alkane oxidation [263], hydrogenation [264], carbonylation [265], polymerization [266], C-C coupling reaction [267] and many others [268] Immobilization of enzymes on mesoporous silica for the enzymatic esterification of mono- and disaccharides with fatty acids as well as acylglyceride production using lipases as catalysts condensation of glycerol or sugars with fatty acids [241]. Immobilized enzymes were found to be more stable and could be recycled.

A number of methods may be used to immobilize catalysts to form hybrid materials [269]. Adsorption, encapsulation, direct incorporation, and covalent grafting are the main method for the immobilization of catalyst in solid supports. The specific reaction conditions may dictate which method is best suited for the particular circumstance [269].

The insoluble solid supports are generally inorganic oxides. The most common supports include porous aluminas and silicas. For any support to be useful in a post-synthesis covalent grafting application, the surface must bear reactive surface species capable of subsequent chemical modification. For inorganic oxides, these modifications are achieved by reaction with surface hydroxyl groups. The most common method of chemically modifying the inorganic oxide surface involves co-condensation of alkoxysilanes with the surface hydroxyl groups. This reaction uses alkoxy silane (generally methoxy or ethoxy silanes). This reaction forms a covalent Si-O-Si bond between the solid support and functional group. The functional group on the alkoxysilane can be any number of chemically reactive species. Common commercially available examples include amines, alcohols, carbonyls, halogens, thiols, olefins, etc. Additionally, alkoxysilanes can be custom synthesized from reaction of terminal olefins with trialkoxy silane (SiH(OR₃) where R = Me or Et) [143, 269].

1.10.3. Acid Catalyzed Heterogeneous Reaction

Notable in the context of catalysts based on mesoporous silica phases are efforts to create solid-state acids that could be used a heterogeneous acid catalysts, in analogy to Bronsted acidic zeolites, but as they possess larger pores they should be able to incorporate larger substrates. Hitherto, mainly sulfonic acid derivatives were
anchored by using both one- and two-step functionalization strategies. Functionalized MCM-41 and MCM-48 materials post synthetically with propylthiol groups initially, so as to be able to convert them into propylsulfonic acid groups under mild oxidative conditions with H₂O₂. This pathway was also pursued for the corresponding functionalization of FSM-16 and SBA-15 materials [270]. An interesting approach to the introduction of sulfonic acid groups into SBA-15 phases was also pursued by Dufaud et al.[271], who obtained materials by functionalization with a bis-silylated disulfide reagent followed by cleavage of the disulfide bridges and oxidation of the resulting thiols into sulfonic acid groups. This results in a material in which each two of the sulfonic acid groups possess a specific spatial separation from one another. Mbaraka and Shanks [272] anchored hydrophobic alkyl residues to the remaining free silanol groups so as to keep the disruptive water produced during esterification of fatty acids away from the immediate neighbourhood of the catalytic center. Also of note is the production of a Nafion analogue by Alvaro et al. [273], who lined MCM-41 and SBA-15 phases with perfluorosulfonic acid groups in a single-stage functionalization reaction.

1.10.4. Base Catalyzed Heterogeneous Reaction

Base-catalyzed condensation, addition, and isomerization reactions are some of the important steps for building large and complex molecules for the synthesis of many fine chemicals and pharmaceutical products. Recently, the heterogenization of organic bases has become an interesting subject owing to a variety of basic compounds showing unusual performance for different catalytic reactions. For example, amino-functionalized mesoporous materials have attracted much attention for their wide applications in Knoevenagel condensation, aldol reaction, nitroaldol reaction, Michael additions, and epoxide ring-opening reactions [274-276]. Notably, it was reported that some amino-functionalized materials were efficient catalysts for the transesterification reactions of esters (i.e., ethylene carbonate, diethylmalonate and β-ketoester) with alcohols [277].

Mesoporous silica materials have also been employed in the development of heterogeneous base catalysts. A comprehensive survey of work up to 2000 may be found in a review by Weitkamp et al. [278]. Two more studies have dealt with the role of the solid support materials of the actual active catalytic species and the effectiveness of these species in relation to the quality of their dispersion in the
support material. Corma et al. [279] have studied MCM-41 samples functionalized with 1,8-bis(dimethylaminonaphthalene) which have proven to be highly efficient catalysts in the Knoevenagel condensation of benzaldehyde with activated methylene compounds and in the Claison–Schmidt condensation of benzaldehyde with 2-hydroxyacetophenone. Macquarrie et al. [280] investigated the role of the distribution of aminopropyl groups in correspondingly functionalized MCM-41 phases in the catalysis of classical C - C coupling reactions such as the nitroaldol condensation of nitromethane with benzaldehyde and the Michael addition of nitromethane with 2-cyclohexene-1-one [280].

1.10.5. Knoevenagel Condensation

Knoevenagel reaction is one of the important base catalysed reactions. Knoevenagel condensations are the reactions between a ketone and active methylene compounds and proceed over a variety of basic solid catalysts, including alkali-ion-exchanged zeolites, alkali-ion-exchanged sepiolite, oxynitrides, and hydrotalcite-related catalysts. The Knoevenagel condensations of benzaldehyde and substituted benzaldehydes with ethylcyanoacetate, ethylmalonate, and ethylacetoacetate [scheme 1.4] were catalyzed by basic faujasite zeolites [281, 282] to obtain intermediates for the production of dihydropyridine derivatives. The catalytic activity increased with the basicity of the zeolite.

\[
\text{Scheme: 1.4}
\]

Rehydrated hydrotalcite was reported by Kantam et al. [283] to give quantitative yields for a variety of Knoevenagel condensations at room temperature using toluene or DMF as solvent in liquid phase [283]. Mesoporous silicas modified with amino groups [284] and mesoporous silicon oxynitride [285] were also effective in similar reactions.

Knoevenagel condensations of malononitrile with cyclohexanone, benzophenone and \( p \)-amino acetoacetone yield alkenes containing electron withdrawing nitrile groups, which facilitate additions to the double band. These
alkenes are useful in anionic polymerization reactions leading to plastics, synthetic fibers or the production of liquid crystals. They can be synthesized using ion-exchanged zeolite X, sepiolite and hydrotalcite as catalysts [286].

Dicyanomethylene derivative dyes could be prepared by two-step synthesis using different solid bases via Knoevenagel condensations. The first step is the condensation of acetophenone and malononitrile to give the corresponding α-methylbenzylidene-malononitrile, which was catalyzed by a variety of solid bases such as MgO, calcined hydrotalcites, and aluminophosphate oxynitride (AlPON). Subsequent condensation with benzaldehyde gives the 1,1-dicyano-1,3-butadiene dye, which was catalyzed efficiently by AlPON. Interestingly, the reaction can also be performed in a one-pot system using an optimized AlPON as catalyst [287].

Knoevenagel condensation is also chosen for the synthesis of unsaturated arylsulfones. For instance, phenylsulfonylacetonitrile and phenylsulfonylaceto phenone reacted with benzaldehyde and 4-substituted benzaldehydes using high-surface-area MgO, calcined Mg-Al hydrotalcites or ALPON type materials leading to α-phenylsulfonyl-cinnamoni nonitrile and derivatives as well as α-phenylsulfonylchalcone. [288]. The first results of the use of silica-supported amines as base catalysts in the Knoevenagel condensation were published by Angeletti et al. in 1988 and 1989 [289]. By grafting aminopropyl and N, N-dimethylaminopropyl moieties onto silica gel, catalysts containing 0.79 and 0.68 mmol/g, respectively, of organic groups were synthesized. These were used in a variety of Knoevenagel condensation reactions. The yields obtained with primary amines are high, in some cases close to 100 %, and only slightly lower for the tertiary amine, but the reaction was performed in a continuous system similar to a liquid chromatographic process [289].

HMS materials functionalized with aminopropyl groups by co-condensation in discontinuous batch mode gave good results (with yields up to 98 %) for most of the Knoevenagel reactions tested, with exception of the most bulky ketones methyl-t-butylketone and benzophenone [290-292]. It was found that choice of solvent and removal of water played important roles in the reaction, the most favored being apolar solvents such as cyclohexane. Higher reaction rates and turn-over numbers were observed for materials containing phenyl groups as well as the aminopropyl functionalities, even though they contained only 1.15 mmol of active centers per gram. These materials were prepared in the usual way by co-condensation [293]. The
difference in surface polarity was thus shown to be a major determining factor in the
activity of the catalysts.

There are several studies which report characteristic phenomena attributed to
the regular mesopore system, which seem to influence the catalytic activity. Detailed
studies of these phenomena are in progress in many laboratories. If in the future the
effects of the pore system are understood and rationalized, the way to better control
the catalytic activity of complex catalyst systems will be more clearly visible and
catalysts improved by design on different length scales will become accessible.

1.11. Controlled Drug Delivery

Over the past three decades, there has been rapid growth in the area of drug
delivery, in searching of new drug delivery systems (NDDS). Both natural and
synthetic materials have been tested and proposed as components of NDDS and
many efforts have been made to synthesise materials with the biological,
technological, and mechanical properties “ad hoc” for each application in drug
delivery [294]. Increasing attention has been focused on methods that deliver
pharmacologically active compounds (e.g. drugs, peptides and proteins) in a
controlled fashion, as numerous drugs are required to be released at a controlled rate
so that constant, sustained, site-specific or pulsatile action is obtained. The system
that delivers a pharmacologically active substance at a relevant \textit{in vivo} location with
minimal side effects is called \textit{controlled delivery systems}. The main aim of this type
of system is to facilitate the dosage and duration of the drug effect, the minimal harm
to the patient and improving human health, since they allow for the reduction of the
dosage frequency [295]. It is a valuable management tool of drug lifecycle.
Controlled drug delivery technology represents one of the most rapidly advancing
areas of science in which chemists and chemical engineers are contributing to human
health care [296]. Moreover, this technology is based on interdisciplinary approaches
that combine polymer science, pharmaceutics, bioconjugate chemistry, and
molecular biology [297]. Pharmaceutical dosage forms for drug delivery includes
tablets, pills, capsules, aerosols, suppositories, ointments, creams, liquids, and
injections [298]. On this basis, there are four key routes of drug delivery involves
oral, inhalation, transdermal, and injection. Reproducible sustained delivery of a
drug at a target site is one of the main themes in controlled drug-delivery systems.
The most commonly used drug-delivery systems, which can release drugs longer
than one week, are parenteral injections and implants. Oral drug delivery has been known for decades as the most widely utilized route of administered among all the routes that have been employed for the systemic delivery of drug via various pharmaceutical products of different dosage forms. The reasons that the oral route achieved such popularity may be in part attributed to its ease of administration [299].

As the orally administered pharmaceutical dosage form passes through the human gastrointestinal tract, drug should be released from the dosage form and be available in solution at or near the optimal site for drug absorption to occur [300]. The rate at which the drug is released from a dosage form and goes into solution is important for the kinetics of drug absorption. The dosage form and hence the active pharmaceutical ingredient (API) is subjected to varying pH levels during gastrointestinal transit [301]. Specifically, pH varies from a minimum of about 1.2 to a maximum of around 7.4. Volume of GI fluid and its agitation can vary significantly, which has substantial impact on drug dissolution and absorption. Moreover, transit time may vary significantly in individual parts of the gastrointestinal tract, depending on individual size and prevailing local conditions [302]. Depending on the delivery system and the pharmaceutical in use, different release mechanisms are applied. However, there are three primary ways by which active agents can be released from such system: diffusion, degradation, and swelling followed by diffusion. Any or all of these mechanisms may occur in a given release system. Diffusion occurs when a drug or other active agent passes through the system (a ceramic or polymer based matrix) that forms the controlled-release device. The diffusion can occur on a macroscopic scale as through pores in the matrix or on a molecular level, by passing between, for instance, polymer chains. The diffusion controlled release could be activated by several means, including ionic strength, pH, thermal, magnetic or chemical changes. The ability to control over the drug delivery can be an important factor especially at times when traditional oral or injectable drug formulations are difficult to distribute. In some cases there might be a need of a slow release of a water soluble drug or a fast release of low-solubility drugs. Normally solubility of crystalline materials is less than that of amorphous powder of the same drug. It has been reported that drugs loaded in the mesopores are comparatively less crystalline than that of bulk and these enhances the solubility of the drug and hence availability of the drug in the GI fluid [302]. It might also be convenient for drug delivery to specific sites, drug delivery using nanoparticulate
systems, delivery of two or more agents with the same formulation, and also systems based on carriers that can dissolve or degrade and be readily eliminated. The ideal drug delivery system should be inert or biodegradable, biocompatible, mechanically strong, comfortable for the patient, capable of achieving high drug loading, safe from accidental release, simple to administer and remove, and easy to fabricate and sterilize [303].

In recent years, many types of materials including inorganic silica, carbon materials and layered double hydroxides [304] as well as polymeric [305] matrix have been employed as substrates for drug delivery. In silica-based systems, drugs are known to be adsorbed on commercially available silica. However, direct mixture of both silica sol and the drug results often in heterogeneous dispersion of drug through the gel, which can affect the release rate of the drug between different samples [306]. Controlled drug delivery systems can achieve precisely spatial and temporal delivery of therapeutic agents to the target site. Generally, the controlled drug delivery systems can maintain the concentration of drugs in the precise sites of the body within the optimum range and under the toxicity threshold, which improve the therapeutic efficacy and reduce toxicity. In the past years, controlled drug delivery has been developed in polymer-based system and also novel inorganic materials-based systems [307]. Lot of investigations have been done in this area, developing different types of mesoporous materials with varying porous structure and functionality for sustained drug released and stimuli-responsive release. The progress of this novel application of mesoporous materials as carriers for various drugs, comparing the different behaviour of drug/mesoporous-solid systems has been reviewed [304].

MCM-41 as one of the importantly synthesised mesoporous materials, M41S [19], has been firstly employed as drug delivery matrix. MCM-41 shows hexagonal arrays of cylindrical mesopores. The structure of the wall of the pores consists of a disordered network of siloxane bridges and free silanol groups that could act as reacting nuclei against appropriate guest chemical species, behaving as a matrix for controlled adsorption and liberation of organic molecules. Other groups of mesoporous materials with larger pore size such as SBA including SBA-15 [309], SBA-16 [309], SBA-1 [298], SBA-3 [298], HMS [310] and MSU [311] were also used for drug delivery. In those new drug/mesoporous-solid systems, ibuprofen, an anti-inflammatory agent, is the widely tested drug, other drugs are also employed.
The first investigation using Si-MCM-41 for drug delivery system was reported by Vallet-Regi and her colleagues [304]. In the preliminary work, two kinds of MCM-41 with different pore sizes were tested. The drug employed is ibuprofen. The drug release plots showed a different behaviour depending on the method for charging the drug in the material but not the pore size. In this study, the in vitro tests were performed under static conditions (without stirring the solution while the release was taking place) and hence diffusion limitations at the external surface of the particles might have overshadowed the influence of the pore size.

**Table 1.6. Different mesoporous materials as drug carrier**

<table>
<thead>
<tr>
<th>Mesoporous materials</th>
<th>Drug</th>
<th>Modification</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoporous organo silica SBA-15</td>
<td>Tetracycline</td>
<td>-</td>
<td>Sustained release</td>
<td>[314]</td>
</tr>
<tr>
<td>Hollow mesoporous silica MCM-41</td>
<td>Atenolol</td>
<td>Modified synthesis temperature Prepared with polyvinlypyrolidine</td>
<td>Sustained delivery drug</td>
<td>[315]</td>
</tr>
<tr>
<td></td>
<td>Ibuprofen</td>
<td>With different morphology &amp; variable pore geometry</td>
<td>Controlled release</td>
<td>[317]</td>
</tr>
<tr>
<td>AlSi-MCM-41</td>
<td>Diflunisal</td>
<td>-</td>
<td>Controlled release</td>
<td>[294]</td>
</tr>
<tr>
<td>AlSi-MCM-41</td>
<td>Ibuprofen</td>
<td>-</td>
<td>Controlled release</td>
<td>[294]</td>
</tr>
<tr>
<td>AlSi-MCM-41</td>
<td>Naproxen</td>
<td>-</td>
<td>Controlled release</td>
<td>[294]</td>
</tr>
<tr>
<td>MCM-41</td>
<td>Ibuprofen</td>
<td>Surface modification with amine groups</td>
<td>Controlled release</td>
<td>[318]</td>
</tr>
<tr>
<td>MCM-48</td>
<td>Erythromycin</td>
<td>-</td>
<td>Delayed release</td>
<td>[319]</td>
</tr>
<tr>
<td>MCM-41</td>
<td>Ibuprofen</td>
<td>-</td>
<td>Faster release of drug and increase dissolution of drug</td>
<td>[320]</td>
</tr>
<tr>
<td>SBA-15</td>
<td>Ibuprofen</td>
<td>-</td>
<td>Faster release of drug and increase dissolution of drug</td>
<td>[308]</td>
</tr>
<tr>
<td>MCM-41</td>
<td>Sodium alendronate</td>
<td>Surface modification with amine groups</td>
<td>Enhanced release rate of drug.</td>
<td>[321]</td>
</tr>
<tr>
<td>SBA-15</td>
<td>Itraconazole</td>
<td>-</td>
<td>Faster release of drug and increase dissolution of drug</td>
<td>[322]</td>
</tr>
</tbody>
</table>
Both reactive and passive organic groups can be incorporated in the porous solids by grafting methods or by co-condensation under surfactant control [44]. For drug delivery based on mesoporous materials, several investigations using organic modified mesoporous silica have also been reported. It is generally found that functionalisation usually will affect the adsorption and delivery.

Organic modification with aminopropyl group of two MCM-41 materials having different pore sizes was carried out in order to control the delivery rate of ibuprofen from the siliceous matrix. It has been found that functionalisation procedure is determinant in both the adsorption of the drug and its release profile. A slower delivery rate has been observed for a two-step method, calcinations and functionalisation [312]. Zeng et al. [313] carried out a similar study using MCM-41 materials modified by organic aminopropyl groups as drug-controlled delivery system of aspirin. The results showed that the releasing properties of this delivery system were affected by the amount of aminopropyl groups on the pore wall and the ordered structure of mesoporous materials. Plenty of drugs were evaluated for their loading and release characteristics with respect to mesoporous material and all have showed a very potential effect for its controlled and immediate release pattern [303]. List of such drugs materials provided in table 1.6.

Ordered mesoporous silica with stable mesoporous structure, large surface area, good biocompatibility and tailored size of mesopores and functionalisation has exhibited promising application as controlled drug delivery system. The mesoporous silica demonstrates higher drug loading and controlled sustained release as well as responsive release under certain external stimuli such as light, magnetite, chemical, pH and temperature [303]. Among various mesoporous silicas, HMS silica exhibits the highest drug loading. The drug release rate is dependent on pore size and functional groups on the wall. Silylation introduces extra functional groups to occupy the walls of silica resulting in pore size decrease and lower drug loading; however, it brings in controlled drug release. In most cases, drug release is a diffusion-controlled process and exhibits a two-stage profile. However, few investigations has been attempted to explore the drug release kinetics and more work should be focussed because the understanding of kinetics will help in the achievement of controlled drug release. Surface functionalisation with various
groups can change electrostatic, hydrophobic/hydrophilic forces, and the adhesive interactions of drug and matrix, inducing varying drug loading and delivery rate.

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