Chapter 1

General introduction

This chapter of the thesis demonstrates a brief description on different nanoporous materials. Their classification based on pore dimensions viz. microporous, mesoporous and macroporous and diverse chemical compositions are discussed in detail. Synthesis, mechanism of formation, characterization as well as their applications in the field of catalysis, drug delivery, gas storage, optoelectronic property along with other promising non-traditional areas and objective and outlook of the present investigation are thoroughly described.
1.1 Introduction to porous materials

Porous materials have drawn immense attention because of their ability to interact with guests not only at their surfaces, but throughout the bulk of the material. The main features of these materials are: very high surface area, large pore volume, tunable pore sizes and rich surface chemistry. The distribution of sizes, shapes and volumes of the void spaces in porous materials is most important to determine their ability to perform the desired function in a particular application. In addition to the nature and size of the pores, the framework composition in the solid creating the void space is also very important. Hence the ability to manipulate the structures and composition of porous materials is of huge importance for their utility in the vast fields of scientific as well as industrial research. Till date, relentless efforts have been devoted to the development of porous materials with diverse pore structures and versatile compositions. The diameters of the pores generally vary from ca. 0.4 nm to more than 100 nm. Compositional diversity of porous solids ranges from pure inorganic materials to pure organic polymers through organic-inorganic hybrid materials. Introduction of porosity modifies the material’s properties to those having lower density and higher surface area when compared with non-porous materials. Not surprisingly, these porous solids have found applications in ion exchange, adsorption (for separation), catalysis, photovoltaic solar cells, batteries, biomedical imaging, sensor technology and in many other emerging applied fields.

Figure 1.1 Representative ball and stick model of a porous material (Nature, 2008, 453, 207)
1.2 IUPAC nomenclature of porous materials

According to International Union of Pure and Applied Chemistry (IUPAC), porous materials are classified into three categories based on their pore sizes. Pores with a diameter below 2 nm are called micropores, between 2-50 nm are called mesopores and those with diameter more than this are macropores.

1.2.1 Microporous materials

![Schematic representation of microporous material](Chem. Soc. Rev., 2007, 36, 770)

Although ancient Egyptians knew about porous materials, zeolites are undoubtedly the most prominently recognized class of microporous materials known to scientific society for long time. About 250 years ago, Axel F. Cronstedt (1722–1765), a famous Swedish mineralogist, was the first scientist to describe, the distinctive property of zeolites, i.e., the unique frothing characteristics when heated in a blow-pipe flame. Cronstedt also coined the term ‘zeolite’ in 1756. He combined the two Greek words ‘zein’ (to boil) and ‘lithos’ (rock) to form the word zeolite. Zeolites are basically hydrated alkaline or alkaline earth aluminosilicates with the general formula $\text{M}^{n+}\cdot\text{n}[\text{AlO}_2\cdot\text{SiO}_2\cdot]\cdot\text{nH}_2\text{O}$. Their framework, built from corner-sharing TO$_4$ tetrahedra (T= Al, Si), delimits interconnected tunnels or cages in which water molecules and M ions are inserted. Since silicon is tetravalent, pure silicate materials (SiO$_2$) do not contain framework charge. But aluminosilicates have negatively charged oxide...
frameworks (one charge per framework $\text{Al}^{3+}$) that require balancing and need extra-framework positive ions. Typically the cations in natural zeolites are alkali metal, e.g., $\text{Na}^+$, $\text{K}^+$, and alkaline earth, e.g., $\text{Ca}^{2+}$, $\text{Ba}^{2+}$, ions etc. In addition to natural zeolites, there are both synthetic analogues of natural zeolites and synthetic zeolites with no natural counterparts. Unlike natural zeolites, synthetic zeolites may contain both inorganic and organic cations, e.g., $\text{Na}^+$, quaternary ammonium ions, and protons. Overall, there are approximately 75 molecular sieve structures. The Structure Commission of the International Zeolite Association assigns a three-letter code to each framework topology of zeolites. The designations are based on the connectivity of the tetrahedral atoms using the maximum topological symmetry, regardless of the changes in unit cell size and symmetry that may result from differences in chemical composition. The first report of the synthesis of zeolites was that of Henry Etienne Sainte-Claire Deville, who, in 1862, claimed to have prepared levynite (levyne). In the early days the attempts of zeolite synthesis centered around mimicking geologic conditions that involve high temperatures ($T > 200 \, ^\circ\text{C}$) and pressures ($P > 100 \, \text{bar}$). Since the 1940s, systematic synthetic studies have been developed. In 1948, the first synthesis of a zeolite that did not have a natural counterpart was reported by Barrer. However, the large-scale production of zeolite was initiated in the late 1940s by synthetic methodologies of Milton and co-workers, who developed hydrothermal zeolite syntheses using reactive alkali-metal aluminosilicate gels at low temperatures (~$100 \, ^\circ\text{C}$) and pressures (autogenous). Hydrated alkali-metal cations may have structure directing effects and help to organize zeolite structural subunits and solution-mediated crystallization of the amorphous gel. The mechanisms of zeolite formation are very complicated due to the plethora of chemical reactions, equilibria, and solubility variations that occur throughout the heterogeneous synthesis mixture during the crystallization process. One can idealize the time evolution of the process by considering...
that the reaction proceeds via two steps from an initially random state to one with microscopic order (nucleation sites), then to the final state where long-range order is apparent (observation of crystals). For zeolites, there are two hypotheses for the crystallization process: the first supposed the reorganization of the initial gel and implied a diffusion of ionic species in the solid phases; in the second, the diffusion occurs in the liquid phase, the crystallization occurs after a progressive dissolution of the gel, and the dissolved species would aggregate around the organic molecule (template) to give the final solid. An example of solid phase transition process is the synthesis of ZSM-35 (FER) and ZSM-5 from nonaqueous reaction mixtures.16

Figure 1.3 Structures of four selected zeolites (from top to bottom: faujasite or zeolites X, Y; zeolite ZSM-12; zeolite ZSM-5 or silicalite-1; zeolite Theta-1 or ZSM-22) and their micropore systems and dimensions (Solid State Ionics, 2000, 175)

After dehydration of an initially formed aluminosilicate gel at 550 °C, the reaction mixture was obtained by adding this solid to liquid triethylamine and ethylenediamine and heated to 160 °C. There are several examples of solution-mediated transport in the crystallization of aluminum-rich zeolites. However, the best examples of this process are the syntheses of Zeolites Y, S (GME), and P (GIS) from clear solutions, i.e., no hydrogel (solid phase) was present. The role of the organic part (often an amine) is also mysterious.
If the above hypotheses were true, one amine would specifically lead to one structural type, which is not verified. According to the flexibility and the geometry of the pores, Davis and Lobo proposed two different roles of the template.\textsuperscript{17} If the structure is flexible, the template acts only as a space-filling agent. On the other hand, when the shape of the template and the framework are correlated, the template is said to be structure-directing.

Zeolites are, in their own right, most widely used catalysts in the industrial field. This popularity of zeolites is due to i) high surface area, ii) controllable adsorption properties and pore structure, iii) accessible active sites, iv) high stability. Despite these catalytically desirable properties, size limitation of pores is a major issue in dealing with molecules larger than the pore dimension. To overcome this problem the rational approach, in this case, would be to increase the pore size by maintaining the porous structure. In 1988, a crystalline microporous material VPI-5 with uniform pores larger than 1.0 nm was reported.\textsuperscript{18} This aluminophosphate VPI-5 with larger pores opened up a new area of extra-large pore crystalline materials. Extra-large pores are obtained when more than 12 oxygen atoms span the circumference of the pore. After the discovery of VPI-5, numerous extra-large pore materials were synthesized. Table 1.1 lists few representatives of such materials, all having structures containing rings made of more than 12 oxygen atoms and most of them are phosphate-based. But the number of phosphate-based extra-large pore materials is limited by their relatively poor thermal and hydrothermal stabilities as compared to those of silica-based molecular sieves. Although some of the phosphate materials are sufficiently stable for certain (low-temperature) application areas, the main concern was raised over whether all extra-large pore materials would lack stability, because of the presence of extra-large rings in their structures. However, the synthesis of extra-large pore crystalline silicas is a promising advance and few examples are shown in Table 1.2.
Table 1.1 Representative examples of crystalline materials with ring sizes above 12

<table>
<thead>
<tr>
<th>Material</th>
<th>Year reported</th>
<th>Main network composition</th>
<th>Ring size (oxygen atoms)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VPI-5</td>
<td>1988</td>
<td>AlPO₄</td>
<td>18</td>
<td>1.2</td>
</tr>
<tr>
<td>AlPO₄-8</td>
<td>1990</td>
<td>AlPO₄</td>
<td>14</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>Cloverite</td>
<td>1991</td>
<td>GaPO₄</td>
<td>20</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>ZDF-20</td>
<td>1992</td>
<td>AlPO₄</td>
<td>20</td>
<td>*</td>
</tr>
<tr>
<td>ULM-5</td>
<td>1994</td>
<td>GaPO₄</td>
<td>16</td>
<td>ND</td>
</tr>
<tr>
<td>UTD-1</td>
<td>1996</td>
<td>SiO₂</td>
<td>14</td>
<td>~ 1.0</td>
</tr>
<tr>
<td>ULM-16</td>
<td>1996</td>
<td>GaPO₄</td>
<td>16</td>
<td>ND</td>
</tr>
<tr>
<td>CIT-5</td>
<td>1997</td>
<td>SiO₂</td>
<td>14</td>
<td>0.8</td>
</tr>
<tr>
<td>ND-1</td>
<td>1999</td>
<td>ZnPO₄</td>
<td>24</td>
<td>ND</td>
</tr>
<tr>
<td>FDU-4</td>
<td>2001</td>
<td>Ge₂O₅</td>
<td>24</td>
<td>ND</td>
</tr>
<tr>
<td>NTHU-1</td>
<td>2001</td>
<td>GaPO₄</td>
<td>24</td>
<td>SD</td>
</tr>
</tbody>
</table>

ND: Not determined, * Structural collapse upon removal of template

Table 1.2 Synthetic framework materials with numerous three-membered rings

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
<th>FD (atoms per nm³)</th>
<th>Pore size (MR)</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lovdarite</td>
<td>Beryllosilicate</td>
<td>18.4</td>
<td>9</td>
<td>1986</td>
</tr>
<tr>
<td>VPI-7</td>
<td>Zincosilicate</td>
<td>17.1</td>
<td>9</td>
<td>1991</td>
</tr>
<tr>
<td>RUB-17</td>
<td>Zincosilicate</td>
<td>16.8</td>
<td>9</td>
<td>1995</td>
</tr>
<tr>
<td>VPI-9</td>
<td>Zincosilicate</td>
<td>16.7</td>
<td>8</td>
<td>1996</td>
</tr>
<tr>
<td>VPI-10</td>
<td>Zincosilicate</td>
<td>15.3</td>
<td>9</td>
<td>1996</td>
</tr>
<tr>
<td>RUB-23</td>
<td>Lithosilicate</td>
<td>17.7</td>
<td>8</td>
<td>2000</td>
</tr>
<tr>
<td>RUB-29</td>
<td>Lithosilicate</td>
<td>17.7</td>
<td>10</td>
<td>2001</td>
</tr>
<tr>
<td>ASU-15</td>
<td>Ge₂ZrO₅F</td>
<td>9.1</td>
<td>10</td>
<td>2000</td>
</tr>
<tr>
<td>OSB-1</td>
<td>Beryllosilicate</td>
<td>13.3</td>
<td>14</td>
<td>2001</td>
</tr>
<tr>
<td>OSB-2</td>
<td>Beryllosilicate</td>
<td>12.7</td>
<td>8</td>
<td>2001</td>
</tr>
</tbody>
</table>

FD: Framework density, MR: Membered rings
Metal organic frameworks (MOFs) are another type of microporous solids involving coordination of metal ions to organic ‘linker’ moieties, thus yielding open framework coordination polymers. Some representative ‘linkers’ are shown in Figure 1.4.

In order to synthesize a coordination polymer it is, in principle, necessary for a potentially bridging ligand (or linker) to react with a metal ion which has more than one vacant or labile site. Examples of labile metal ions are Cu\(^+\), Cu\(^{2+}\), Ag\(^+\), Cd\(^{2+}\), Zn\(^{2+}\), Co\(^{2+}\) and Ni\(^{2+}\) and these feature prominently in the field of coordination polymers. A potential problem with labile metal ions is that they often do not impose strong preference for a given geometry compared to other ions. This can therefore lead to poor predictability over the structure of the network obtained. Flexibility in the bridging ligand is another potential problem. When a ligand has a number of possible conformations, again, framework geometry will be hard to predict. Orientational freedom of the ligand lone pairs may be restricted by using rigid backbones, such as in 4,4\(^{\prime}\)-bipyridine. Although this ligand can in
principle rotate about the central C–C bond, this rotation does not affect the mutual orientation of the two lone pairs. Although open frameworks comprising metal–organic units gained renewed interest in the 1990s, these materials have a long history, and examples include transition metal cyanide compounds (early examples are Hofmann-type clathrates, Prussian-Blue type structures and Werner complexes) and the diamond-like framework bis(adiponitrilo)copper (I) nitrate. In the years 1989 and 1990, the seminal work by Hoskins and Robson set the foundation stone for the future of MOFs. What they already envisioned, in their paper, has been subsequently shown by many scientists around the world: the formation of a large range of crystalline, microporous, stable solids, possibly using structure-directing agents, with ion-exchange, gas sorption, or catalytic properties that further allow introduction of functional groups by postsynthetic modification. The term MOF was made popular by Yaghi et al. around 1995. They reported a layered Co-trimesate that showed reversible sorption properties. In 1997, a 3D MOF exhibiting gas sorption properties at room temperature was reported by Kitagawa et al. The 3D MOFs \( \{[M_2(4,4'-bpy)_3(NO_3)_4](H_2O)_x\} \) \( (M = \text{Co, Ni, Zn}) \) are formed from \( M(NO_3)_2 \) and 4,4'-bipyridine in acetone/ethanol. Copper and zinc carboxylate based highly porous MOFs were reported in 1999 and up to now are among the most studied MOFs. Isoreticular synthesis of MOFs, introduced in 2002, is the popular way of tuning the pore size according to the requirement. In an isoreticular series it is possible to vary the pore size and functionality systematically keeping the framework topology same. Typically MOFs are synthesized by heating a mixture of ligand and metal salt in solvent for 12–48 h. Although this procedure can yield high quality crystals, it suffers from long reaction times and can be difficult to scale above ~1 g. Solvents, especially the frequently employed diethylformamide (DEF), can be costly and again cause difficulty in scale up.
So in recent time, other methods like microwave, sonochemical, mechanochemical syntheses have been developed.

1.2.2 Mesoporous materials

Synthesis of ordered mesoporous molecular sieves (M41S) from liquid-crystal templates, in 1992, by Mobil scientists\textsuperscript{26} made a breakthrough in the field of materials research because it solved the problem of size limitation of zeolite chemistry and gave total control over tuning the pore size. However, "mesopore" is not a new term according to IUPAC definition and in fact, in the early time (1969), Vincent \textit{et al.} had prepared MCM-41 analogues,\textsuperscript{27} but unfortunately they only claimed low-bulk density silica due to the lack of detailed characterizations. In April 1990, even before Mobil researchers, a group of Japanese scientists reported the synthesis of alkytrimethylammonium-kanemite complexes with a mixed phase. Although narrow pore size distribution at 2 ~ 4 nm was obtained from $N_2$ sorption isotherms for the products, the authors did not realize "mesopores" and "mesoporous molecular sieves". Since these discoveries, the soft-templating method has become a general pathway for the synthesis of ordered mesoporous materials involving a variety of framework compositions. There are two synthetic strategies \textit{viz.} cooperative self assembly and "true" liquid-crystal templating process for surfactant assisted syntheses. In the cooperative self-assembly process, inorganic species and organic template are added together and they interact with each other by Coulomb force or hydrogen bonding. The inorganic species polymerize and cross-link at the interface, and thus cooperatively assemble with surfactants. With the course of the reaction, the cooperative arrangements of surfactants and the charge density between inorganic and organic species influence each other. The charge density matching at the surfactant/inorganic interfaces governs the assembly process, thus resulting in phase separation and reorganization, finally leading to the formation of ordered 3-D
arrangement with the lowest energy. The “true” liquid-crystal templating process is based on the formation of true or semi-liquid-crystal mesophase micelles produced by high-concentration surfactants as templates. The condensation of inorganic precursors occurs around the pre-formed surfactant micelles, forming ceramic-like frameworks. After condensation, the organic templates can be removed by either solvent extraction or calcination at some suitable elevated temperature. By using this soft-templating method, large number of novel ordered mesoporous materials composed of inorganic, organic, and inorganic-organic composite frameworks have been prepared via various synthetic approaches such as aqueous processes, hydrothermal/solvothermal, nonaqueous method, which is also well known as evaporation induced self-assembly (EISA) process, hydrothermal method, etc. Various soft templates, including cationic, anionic and nonionic surfactants, and mixed surfactant systems, have been used to synthesize ordered mesoporous materials with controllable structures and tuneable pore apertures. Although the synthesis procedure of Mobil scientists involves use of cationic alkyltrimethylammonium halides as templates, it is possible to synthesize ordered mesoporous silica materials with thicker framework walls by using neutral primary amine templates. Use of triblock copolymers as templates for the synthesis of large-pore ordered mesoporous silica with a 2D hexagonal structure (SBA-15) by Zhao et al. have gained considerable importance in this context. In addition to these 2D hexagonal mesoporous silica materials, 3D hexagonal and cubic ordered materials have also been reported by tuning the proper synthesis conditions using this soft templating method. Not only silica materials, the supramolecular templating approach has been successful for the synthesis of several nonsiliceous mesoporous materials also. But despite the great success of the soft-templating method, specially for silica materials, it was soon realized that it was not sufficient enough to prepare many nonsiliceous mesostructured materials. The reason is
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Figure 1.5 Scheme of the main synthesis routes to mesoporous materials: (A) precipitation, (B) True Liquid Crystal Templating, TLCT, (C) Evaporation-Induced Self-Assembly, EISA and (D) Exotemplating.
that the non-siliceous precursors are more susceptible to hydrolysis, lack of condensation, redox reactions, weak interaction with surfactants or phase transitions accompanied by thermal breakdown of the structural integrity, which make it much more difficult to construct ordered mesostructures and remove the templates. So a hard template route\(^{29}\) by using a pre-synthesized mesoporous material as template was introduced and in general this process proceeds via three steps: i) precursor infiltration in the mesochannels of the porous hard template; ii) conversion of the precursor inside porous channels and iii) removal of the template. This strategy is well known as ‘nanocasting’ method because the entire process is the replication of traditional casting process but in the nanoscale. Synthesis of high quality ordered mesoporous materials is possible by this ‘hard template’ route and hence it has become a hot topic in the research field of ordered mesostructured materials. It is also important to mention here that small mesotunnels inside the template’s pore wall are necessary for nanocasting because these are replicated to nanorods which support the total mesostructure of the precursor. Moreover, another striking fact is that the resultant mesostructured replica can act as a new hard template, although with lower symmetry.

1.2.3 Macroporous materials

Macroporous materials with pore diameters greater than 50 nm have a wide range of applications in chemistry. Macroporous polymers, in particular, are used as catalytic surfaces and supports,\(^{30}\) separation and adsorbent media, biomaterials,\(^{31}\) chromatographic materials, and thermal, acoustic and electrical insulators. In nearly every case, the utility of the porous system largely depends on the internal pore diameters, their distribution, and their morphology. As a result, one of the most important targets during synthesizing these materials is to create internal voids with monodisperse and controllable diameters. The fabrication of polymeric materials with ordered submicron-sized void structures is
potentially valuable for many separation technologies as well as for emerging optical applications. Colvin et al. prepared macroporous polymer membranes with regular voids by using a colloidal silica microspheres as template and characterized their diffractive optical properties.\textsuperscript{32} There are reports for producing highly monodisperse macroporous silica,\textsuperscript{33} titania and zirconia\textsuperscript{34} materials with pore sizes ranging from 50 nm to several micrometers starting with an emulsion of equally sized droplets as templates around which material can be developed through the sol-gel process. Subsequent drying and heat treatment of which leaves behind the solid materials with spherical pores which can be used for heavy metal ion adsorbents and photonics. Ordered macroporous structures have been produced by templating echinoid (sea urchin) skeletal plates. The sea urchin comprised of CaCO\textsubscript{3} plates, are each a single crystal of magnesian calcite that exhibit a unique, sponge-like fenestrated structure comprising continuous macropores of diameter 15 mm and non-crystallographic curved surfaces.\textsuperscript{35} A novel mixed-surfactant based synthesis of a new honeycomb-like macroporous form of silica with dividing silica walls of mesolamellar structure was reported in 2004.\textsuperscript{36} Another interesting synthesis of ordered macroporous silica gel microhoneycomb was reported by Nishihara et al., using micrometer-sized ice crystals as template, having a continuous rod shape, polygonal cross section and ordered diameters.\textsuperscript{37}

![Figure 1.6 Representative TEM images of macroporous material](Phys. Chem. Chem. Phys., 2009, 11, 3628)
1.3 Classification of porous materials based on framework building blocks

Following the strategies of both soft and hard templating methods as well as using different linker molecules, a large number of porous materials having diverse compositions have been synthesized. Based on framework composition, nanoporous materials can be classified into three categories: purely inorganic, hybrid organic-inorganic and all-organic porous polymers and carbons.

1.3.1 Purely inorganic porous materials

Among the different inorganic porous materials, silica based materials including zeolites are the most studied system till date. The reasons are variety of possible structures, controlled hydrolysis, thermal stability etc. The main precursor for the synthesis of mesoporous silica is tetraethylorthosilicate (TEOS) or tetramethylorthosilicate (TMOS). Layered polysilicate precursors are also used for the synthesis of pure silica based materials.

![Structures of mesoporous M41S materials: a) MCM-41 (2D hexagonal), b) MCM-48 (cubic), and c) MCM-50 (lamellar)](Angew. Chem. Int. Ed., 2006, 45, 3216)

From the knowledge about excellent catalytic activities of zeolites, researchers extended the effort for the synthesis of transition metal doped silicon oxides, a class of materials useful in catalysis, electronic, and magnetic applications because of variable oxidation states, and populated \( d \)-bands feature. Incorporation of aluminium into silica framework
aroused immense interest because of the potential of aluminoslicate materials in the field of catalysis. Incorporated aluminium is the source of Lewis acidity while attached hydroxyl groups to 3-coordinate framework aluminium is the source of Brønsted acidity. As the incorporation of Al is vital for acid catalytic properties of doped silica materials, other metal ions can also be incorporated for the synthesis of silica materials with different catalytic properties. For example, metal elements such as Ti, V and Cr are also very important in order to prepare mesoporous catalysts with redox properties. Apart from these, incorporation of heteroatoms such as Cu, Zn, B, Ga, Fe, Sn, U into mesoporous silica framework has also been widely investigated.

Because of the diverse chemistry of transition metal oxides, a large variety of metal oxide/surfactant composite materials were synthesized by proper selection of a cationic or anionic surfactant. Stucky and co-workers first employed the surfactant templating strategy for the synthesis of non-silica-based mesostructures, mainly metal oxides. Both positively and negatively charged surfactants were used in the presence of water soluble inorganic species in their synthesis procedures. It has been found that for the formation of an organic-inorganic mesophase to be successful, three conditions should be fulfilled: (i) the inorganic precursor should have the ability to form polyanions or polycations allowing multidentate binding to the organic surfactant; (ii) the polyanions or polycations should be able to condense into rigid walls; (iii) a charge density matching between the surfactant and the inorganic species is necessary to control the formation of a particular phase of the mesostructured materials. Different mesoporous titania (TiO₂) materials have been synthesized by using cetyltrimethylammonium bromide (CTAB) and pluronic surfactants as structure directing agents. Titania is a fascinating semiconducting oxide having strong oxidizing and reducing ability under UV light irradiation. It has the potential of industrial applications like dye degradation, removal of hazardous organic
substances and also in dye sensitized solar cells. \( \text{\textsuperscript{45}} \) Mesostructured \( \gamma-\text{Al}_2\text{O}_3 \) has been synthesized from aluminium salts in the presence of both triblock and diblock surfactants as the structure directing agents. \( \text{\textsuperscript{46}} \) Several other oxides such as \( \text{ZrO}_2 \), \( \text{Nb}_2\text{O}_5 \), \( \text{Cr}_2\text{O}_3 \), \( \text{V}_2\text{O}_5 \), \( \text{WO}_3 \), and \( \text{Fe}_2\text{O}_3 \) with ordered structure were synthesized using this strategy by choosing appropriate metal precursor solutions. Mesostructured mixed metal oxides were also synthesized by different synthesis procedures.

A number of metal chloroaluminate such as \( \text{CdS} \), \( \text{CdSe} \), \( \text{ZnS} \) have been reported by following a soft templating method that closely resembles the true liquid crystal templating strategy. \( \text{\textsuperscript{47}} \) Hydrogen sulfide or hydrogen selenide was added to the composite of a lyotropic template and the metal ions to form the ordered metal sulfide or metal selenide nanocrystals. But by the same method, attempts to synthesize mesostructured \( \text{Ag}_2\text{S} \), \( \text{CuS} \), \( \text{HgS} \) and \( \text{PbS} \) were failed. Following this observation the authors concluded that a specific interaction between the metal ions or the precipitate and the liquid crystal is necessary.

Among different non-siliceous mesoporous materials, metal phosphates are one of the most important materials due to their applications in the fields of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and materials chemistry. Metal phosphates are well known active solid catalysts which can be used in various acid-base catalysis, redox catalysis and photocatalytic processes. Recently, much effort has been devoted to the synthesis of mesoporous metal phosphate materials since the characteristics of mesoporous materials are of high relevance for the catalytic application to the direct activation of large organic molecules. Extension of the synthesis strategies of mesostructured silica to aluminum phosphates was thought to be the most straightforward idea because of the similarities between zeolite chemistry and aluminum phosphate chemistry, with various isotypic structures. However, this has been proved to be much
more difficult than expected. Although mesophases was obtained for aluminum phosphates and silicon aluminum phosphates, removal of the template without structural breakdown was not possible for the products from the initial attempts.\textsuperscript{48, 49} Zhao \textit{et al.} described a series of aluminum phosphates and silicon aluminum phosphates stable upon calcination which were obtained by using cetyltrimethylammonium as the structure directing agent at pH 9.5.\textsuperscript{50} These materials show surface areas close to 1000 m\textsuperscript{2}/g, but the pore structure is much less ordered than that for the silica. The group of Kuroda reported very similar textural parameters, where the hexagonal mesostructure was obtained by the conversion of a layered aluminum phosphate/surfactant intercalate.\textsuperscript{51} Zhao and co-workers proposed a general ‘acid-base pair’ approach for the synthesis of ordered mesostructured metal phosphates.\textsuperscript{52} They showed that apart from the organic-inorganic interaction necessary for the formation of mesostructure, it is essential to match acid-base interactions of the various species present during nucleation of the mesostructured phases in the order $I_1I_2 \gg I_1I_1, I_2I_2$; and $O(I_1I_2) \gg OI_1, OI_2$ ($I$ and $O$ represent inorganic and organic species respectively). The generalized approach was verified by using elements such as Al, Ca, Ti, Zr, V, Nb, Sn, W etc. They used different phosphate sources like $\text{H}_3\text{PO}_4$, $\text{PCl}_3$, $\text{OP(OR)}_3$ etc.

Mesoporous metals, due to their metallic frameworks with high electroconductivity and high surface areas, are extensively promising for a wide range of potential applications, such as electronic devices, magnetic recording media, and metal catalysts. Attard \textit{et al.} prepared mesoporous platinum following liquid crystal templating method and by chemical reduction process.\textsuperscript{53} They also successfully synthesized mesoporous platinum films using an electrodeposition method. Mesoporous rhodium films with high surface area were synthesized by electrochemical deposition using liquid crystal templating method. Hexagonal and cubic mesostructured germanium was also synthesized by two
different groups. Various other metals such as Co, Ni, Sn have been fabricated by soft templating approach using chemical or electrochemical reduction of the corresponding metal salts.\textsuperscript{54,55} In addition to these, the same methodology has been successfully used for the preparation of mesoporous alloys such as Pt–Pd, Te–Cd, Ni–Co, Pt–Ru, and Pt–Ni through chemical or electrochemical coreduction of two-metal species.\textsuperscript{56,57}

1.3.2 Organic-inorganic hybrid porous materials

Hybrid mesoporous architectures merging the properties of inorganic materials and organic building blocks have found an incredible importance and attracted widespread interest as a fundamental and technological challenge to chemists, physicists and engineers during the past two decades.\textsuperscript{58} Part of the appeal of hybrid mesoporous materials originates from the unique and thorough molecular control of their intrinsic topological and chemical characteristics that self-assembly techniques and nanochemistry are able to provide. Proper choice of building blocks and self-assembly conditions can produce nanostructured materials \textit{via} sol–gel processes with precisely defined and tunable chemical functions incorporated into well-defined ordered mesostructured frameworks. This ‘biomimetic approach’ leads to the formation of organic-inorganic hybrid hierarchical nanosystems with unprecedented control over the positioning of functional groups, in a similar way to what nature does. For the synthesis of porous hybrid materials, the organic component can be added in three different pathways: (1) post synthesis grafting at the pore surface of the purely inorganic silica material, (2) co-condensation during synthesis of the silica material and (3) incorporation of bridged bis- or polysilylated organosilica.
1.3.2.1 Post synthesis grafting

In post synthesis grafting a pre-fabricated mesoporous material is modified by functional molecules usually after removal of the template. Post synthesis modification occurs through the condensation of the surface silanol groups with the organosilane precursors. For the retention of silanol groups at the pore surface, solvent extraction is preferred over calcination for template removal to generate the mesoporous material. One advantage of this route is that functionalization through this modification process does not disturb the mesostructure of the starting silica material. On the other hand, pore blocking is a serious drawback of this process due to uncontrolled functionalization. Another problem of this grafting process is that the external surface is more easily accessible and kinetically more favorable for functionalization over internal pore surfaces. The organic groups functionalized on external surface are also more readily available for subsequent catalytic reactions thus limiting the utility of pore confinement for different shape selective reactions. Two different methodologies have been adopted to overcome this problem. In one methodology, at first the external surface is functionalized with passive surface groups like Ph$_2$SiCl$_2$ and in the subsequent step desired functional group is attached to the surface of the porous channels. The other methodology for controlled functionalization demonstrates passivation of the external surface of as-synthesized material where the pores are still blocked with template molecules. After removing the template by solvent extraction, the pore surface is functionalized with suitable functional groups.

1.3.2.2 Co-condensation reactions

This method manifests co-condensation of tetraalkoxysilane with one or more organosilane precursors in one pot. By choosing suitable structure directing agent it is possible to synthesize porous hybrid material where the organic functionalities project towards the pores. Care should be taken during template removal so that the organic
functionality is not damaged. In co-condensation method pore blocking is not a problem since the organic functionality is already tethered to the silane precursor. Another advantage of this method is that the functional organic groups are more homogeneously distributed in the material compared to the grafting method. But deterioration of mesostructure ordering with increase in concentration of organic functionality is a drawback of this method. There is also problem of homocondensation of organic functionalities due to different hydrolysis and condensation rates of structurally different precursors leading to the formation of clusters with inhomogeneous and irregular distribution of organic functional groups in the material.

1.3.2.3 Co-condensation of bridged organosilanes

Periodic mesoporous organosilica (PMOs) materials are synthesized by co-condensation of bridged bi- or polysilylated organosilane precursors. Unlike the other methods, the organic functionalities are integrated in the pore wall of the material synthesized by this method. One advantage of this method is that the organic groups are homogeneously distributed in the pore wall and do not modify the size of the pores. Apart from enriching
the pore surface chemistry, by combining different bridged and terminal organosilane precursors, it is possible to modify the chemistry of the pore wall with diverse functionality bestowing improved hydrothermal and mechanical stabilities. There are several advantages and disadvantages of both post grafting and co-condensation strategies and these two routes are complementary. Choice and application of these methods depend upon the features required for the mesoporous material. Sometimes both methods can be applied to obtain multifunctional hybrids.

A number of silane-coupling agents with olefins, nitriles, alkylthiols, alkyl amines, alkyl halides, epoxides, and some other surface groups are reactive and permit further functionalization of the silica material. Olefins, such as vinyl group functionalized silica materials, can further be modified, e.g., by bromination or hydroboration. On the other side nitriles can be hydrolyzed to form carboxylic acids, and alkylthiols can be oxidized to sulfonic acids, which can be further employed as electrostatic anchoring points, e.g., for amino acids. Surface amines may be derivatized, for example, by alkylation, nucleophilic aromatic substitution, or formation of amides or imines. One of the most

Figure 1.9 Schematic overview of the synthesis of a PMO (Chem. Soc. Rev., 2013, DOI: 10.1039/C2CS35222B)
fascinating works in the area of post synthesis functionalization of silica phases was done by Mai et al., who successfully constructed a photochemically controlled system by anchoring coumarin to the pore openings of MCM-41 silica phases for compound uptake and release. When the sample was irradiated with UV light ($\lambda > 310$ nm), the grafted coumarins were dimerized, which resulted in sealing of the pore openings and enabled permanent incorporation. Final irradiation of the samples with UV light at around 250 nm led in turn to cleavage of the coumarin dimmers and allowed diffusion controlled release of the enclosed active compounds. Fu et al. developed a thermal stimuli responsive transport system based on chains of poly-N-isopropylacrylamide (a known thermosensitive polymer), which exist in a collapsed, hydrophobic state when exposed to heat, but an expanded, hydrophilic state in the cold. By this way, samples of mesoporous, spherical silica particles (particle diameter 10 $\mu$m) which were lined and coated with the thermosensitive polymer by atom transfer radical polymerization could take up greater or lesser amounts of the dye fluorescein.

Large number of organically modified silica phases have been synthesized by co-condensation through the use of the respective organosilane with organic functionalities such as alkyl, thiol, amino, cyano/isocyno, vinyl/allyl, organophosphine, alkoxy, or aromatic groups. However, care must always be taken that the organic group remains intact when the SDA is removed. It is possible to synthesize functionalized silica materials with far-more complex organic groups by means of co-condensation reactions, which opens up the path to further materials with interesting chelating or adsorbing properties. Corriu et al. anchored chelating cyclam molecules by substitution on previously synthesized 3-chloropropylfunctionalized silicas and showed that almost all cyclam units were localized on the pore surface and were thus freely accessible to complexation by Cu$^{II}$ and Co$^{II}$ ions. Jia et al. reported functionalization of silicas with
the chelate ligand 3-(2-pyridyl)-1-pyrazolylacetamide and after subsequent complexation of MoO(O$_2$)$_2$, the samples showed catalytic activity in the epoxidation of cyclooctene with tBuOOH. Huq and Mercier synthesized$^{70}$ cyclodextrin modified silicas in two steps: first they coupled the cyclodextrin units to 3-aminopropyltriethoxysilane (APTS) and then co-condensed with TEOS. Liu et al. synthesized calix[8]arene amide functionalized silicas and showed that they were suitable for the adsorption of humic acid from aqueous solutions. The synthesis of spherical mesostructured particles modified with the dipeptide carnosine (b-alanyl-l-histidine) has been reported by Walcarius et al. The peptide units of the ordered mesoporous materials were more accessible than those of analogously functionalized amorphous porous particles, as was demonstrated by complexation reactions with Cu$^{II}$ ions.

In the year 1999, three different research groups were successful in synthesizing PMOs through structuring with ionic surfactants by assembling bridged dipodal alkoxysilane [(RO)$_3$Si-R'-Si(OR)$_3$] precursors. Inagaki et al. were able to synthesize a new organic-inorganic hybrid material by the conversion of 1,2-bis(trimethoxysilyl)ethane (BTME) under basic conditions.$^{71}$ Materials with both 2D hexagonal and 3D hexagonal pore arrangements were obtained. In the same year, the group of Ozin reported$^{72}$ the synthesis of a PMO containing an unsaturated organic spacer using 1,2-bis(triethoxysilyl)ethene as a precursor, which was transformed under basic conditions. The first synthesis of PMO materials with aromatic bridges was reported by Yoshina-Ishii et al. in 1999.$^{73}$ They used 1,4-bis(triethoxysilyl)benzene (BTEB) and 2,5-bis(triethoxysilyl)thiophene (BTET) as precursors. The first syntheses of large-pore PMOs by structuring with triblock copolymers were reported by Muth et al. in 2001.$^{74}$ BTME was used as organosilane precursor in the presence of P123 as supramolecular template under acidic conditions to
synthesize the corresponding ethane-bridged silica, which exhibited a 2D hexagonal pore structure analogous to SBA-15.

Phosphonate based metal organic frameworks are a fascinating class of hybrid porous materials because of their application in ion exchange, gas adsorption, catalysis etc.\textsuperscript{75,76} The phosphonate containing MOFs of divalent metal ions are highly crystalline but those of higher valent metal ions are poorly crystalline. Hybrid aluminium and zirconium phosphonates were synthesized by using biphenylbis(phosphonic acid) as the multidentate ligand and the materials showed very high porosity. Alberti \textit{et al.} synthesized\textsuperscript{77} a Zr compound based on 3,3',5,5'-tetramethylbiphenylbis(phosphonic acid). The surface area of the material was 375 m\textsuperscript{2}g\textsuperscript{-1} and the pore size maximum was 6.0 Å in diameter, which is close to what would be expected based on the distance between the pillars. Clearfield and co-workers investigated\textsuperscript{78} the structure of zirconium phenylphosphonate Zr(O\textsubscript{3}PC\textsubscript{6}H\textsubscript{5})\textsubscript{2}. It has a layered structure with an interlayer distance of 14.82 Å. The inorganic portion of the layer has the same composition as that of α-zirconium phosphate, Zr\textsubscript{2}O\textsubscript{3}P\textsubscript{2} (formula Zr(O\textsubscript{3}PCH)\textsubscript{2}), except that the pendant -OH groups of the phosphate are replaced by a bilayer of phenyl groups in the interlayer space. In the case of the biphenyl analogue, the bipheryl groups cross-link the layers. The porosity varies from 250 to 400 m\textsuperscript{2}g\textsuperscript{-1} depending upon the solvent utilized, the temperature, and the time of heating during the synthesis. Zr(O\textsubscript{3}PC\textsubscript{12}H\textsubscript{8}PO\textsubscript{3}), zirconium biphenylbisphosphonate (Zr BPBP), prepared in DMSO exhibits an isotherm that is more like a type I with a small hysteresis loop. Large amount of the N\textsubscript{2} is adsorbed below a \textit{P/P\textsubscript{0}} value of 10-3 atm. Large N\textsubscript{2} sorption at this pressure indicates that a large percentage of the pores are <15 Å in diameter. Clearfield and co-workers also prepared porous products with monophenyl and terphenyl pillars.\textsuperscript{75} The interlayer spacings are 9.6 and 18.5 Å, respectively. Mal \textit{et al.} synthesized\textsuperscript{80} tin phenylphosphonate, Sn(O\textsubscript{3}PC\textsubscript{6}H\textsubscript{3})\textsubscript{2}, and
found that when prepared in the presence of sodium dodecylsulfate (SDS) it was microporous, but in the absence of SDS it was mesoporous with a broad distribution of pore sizes. Group of Clearfield synthesized biphenyl and terphenyl bisphosphonate of tin. Similarly to the corresponding Zr compounds, the monophenylbisphosphonates were characterized by type I isotherms, but those for the biphenyl derivatives were type IV. Here also the pore structure depended upon the choice of solvent. Synthesis in water-alcohol mixtures yielded products with surface areas ranging from 322 to 442 m²g⁻¹ with a broad distribution of pores from 9 to 22 Å in diameter, with a maximum at ca. 16 Å. However, carrying out the synthesis in a DMSO-H₂O mixture yielded a product with a type I isotherm and 385 m²g⁻¹ with internal porosity of 378 m²g⁻¹ and a peak in the pore size distribution at 9 Å diameter.

1.3.3 Purely organic porous polymers and carbons

Meso- and microporous polymers are of increasing interest in recent years because they might complement their inorganic counterparts, such as mesoporous silicas or zeolites, in a number of applications. This is particularly useful for applications where properties such as low weight and high flexibility are advantageous. Since the entire porous framework is composed of organic matter, any porous polymer or organic framework naturally exhibits some kind of organic functional group in the pore wall. Mesoporous polybenzimidazole (mp-PBI) was synthesized by polycondensation of an aromatic tricarboxylic acid ester with diaminobenzidine in the presence of silica nanoparticles as templates. After formation of the network when the silica template was removed, mp-PBI was formed with pores of 12 nm and a surface area of around 200 m²g⁻¹. In addition to the formation of a stiff aromatic benzimidazole network, basic functional groups are also introduced into the polymer. When these materials were treated with phosphoric acid, protonconducting membranes were obtained. The “hard-templating”
procedure in which silica nanoparticles or other inorganic nanostructures have been used as templates, has been demonstrated by the preparation of a variety of mesoporous polymers. But a better procedure for the synthesis of mesoporous polymers was reported by Zhao and co-workers, who used Pluronic surfactants as soft templates in the synthesis of highly ordered mesoporous phenolic resins called “FDUs”.83,84 Ikkala and coworkers showed that the self-assembly of functional block copolymers, that is, poly(styrene)-block-poly(4-vinylpyridine), could also be used for the synthesis of mesoporous phenolic resins.85 Phenolic resins with high specific surface areas ($S_{\text{BET}} \approx 550-650 \text{ m}^2\text{g}^{-1}$) could be produced by using this approach. When these resins were heated at high temperature, it led to their conversion into mesoporous carbons. Phenolic resins contain mainly hydroxy and benzene groups as the functional groups and hence little improvement is expected in their functional properties for applications (for example, as a catalyst support) compared to mesoporous silica. But when metals and metal oxides were incorporated into the phenolic resins and the supports showed good chemical and mechanical stability as well as reduced leaching of the metal species.86,87 Mesoporous phenolic resins functionalized with sulfonic acid were synthesized by sulfonation of phenolic resins with different pore structures (FDU-15 and FDU-14).88 Considerable amounts of sulfonic acid groups ($2 \text{ mmolg}^{-1}$) could be introduced into the materials without a significant change in the mesoporous structure. A series of amino-functionalized mesoporous phenolic polymers with different mesostructures has been synthesized by a two-step chloromethylation/amination sequence.89 Such materials showed, as expected, high activity in amine-catalyzed reactions, such as the Knoevenagel condensation. Soft templating method has recently also been applied to prepare mesoporous resins with novel chemical compositions. An ordered mesoporous melamine resin was prepared by using the precursor hexamethoxymethylmelamine (HMMM) and amphiphilic block
copolymers as templates. The resulting mesoporous melamine resins inherently contain a large number of basic functional groups.

A template-free approach towards the synthesis of porous polymers was developed which has certain similarities to the methods used for the formation of MOFs. In this method, structure-directing monomers (called knots or tectons), mostly rigid molecules having multiple functional groups extending into two or three dimensions, are covalently bound together directly or through linear linkers to generate two- or three-dimensional frameworks. These polymers are generally named as polymers of intrinsic microporosity (PIMs) or, in the case where fully aromatic compositions were used, these are called conjugated microporous polymers (CMPs). Since the entire network is covalently connected, such polymers are chemically stable. Tectons and linkers of versatile chemical structures can be connected by using different chemical reactions; thus by choosing suitable monomers, the functional properties can also be incorporated directly during the synthesis. Polymerization of porphyrin and phthalocyanine complexes with a spirobisindane results in porous polymer networks. Nitrogen adsorption/desorption isotherms for the porphyrin network showed a BET surface area of 980 m\(^2\)g\(^{-1}\). The phthalocyanine network showed different BET surface areas of 895 m\(^2\)g\(^{-1}\), 750 m\(^2\)g\(^{-1}\), 489 m\(^2\)g\(^{-1}\), and 535 m\(^2\)g\(^{-1}\) when loaded with different metal ions such as Zn\(^{2+}\), Cu\(^{2+}\), and Co\(^{2+}\) and an unloaded sample, respectively. The same concept for building porous organic networks was applied to incorporate hexaazatrinaphthylene (Hatn) groups. The nitrogen substituents in the Hatn motif are strong binding sites for metals. These early examples of PIMs demonstrate the possibility to create covalent organic networks with high porosities and surface areas, where functional groups—in these examples a ligand or even a complete metal–organic complex—are a supporting part of the pore wall. The high density of such functional groups in the pore wall makes these materials promising
heterogeneous catalysts. A cobalt-loaded porous phthalocyanine network was found to be an active catalyst for the degradation of hydrogen peroxide and for the oxidation of cyclohexene to 2-cyclohexene-1-one.\textsuperscript{94} When the Hatn network was loaded with Pd\textsuperscript{2+} ions, it catalyzed a model Suzuki aryl–aryl coupling reaction efficiently. Although leaching of the Pd was a problem in the first run, the amount of Pd was stabilized in the following runs.\textsuperscript{95} Thiophene-based conjugated microporous polymers prepared by oxidative polymerization of 1,3,5-tris- (thienyl)benzene are also known to be efficient catalyst supports.\textsuperscript{96} These microporous polymeric networks with specific surface areas as high as 1060 m\textsuperscript{2}g\textsuperscript{-1} contain large amounts of thio substituents (S content: 26.4 wt%). Since the thiophene units are part of the organic bridges it was assumed that they are accessible to molecules or ions entering the porous framework. Although most of these polymeric networks possess no decisive chemical functional groups, their conjugated structure could result in them exhibiting valuable physical functions, for example, for organic electronic devices. Porous networks synthesized from the coupling of spirobifluorenes have shown an intensive blue emission.\textsuperscript{97, 98} Different 2D and 3D architectures of p-conjugated polymers were synthesized in the form of large, fully conjugated, star-shaped molecules, which were subsequently applied to organic optoelectronic devices, from OLEDs to solar cells.\textsuperscript{99, 100} No such application has so far been described for CMP networks. There is possibility that the porosity of CMPs could further enable the introduction of a second phase (for example a dye, or a corresponding hole or electron conductor) by simple infiltration into the networks to yield defined interpenetrating networks. However, for the fabrication of the electrode, porous conjugated polymer networks first have to be produced as thin films, which is quite a synthetic challenge. A possible way to solve this problem would be to use soluble PIMs with conjugated backbones and coat these polymers on the electrode or by the direct
deposition of CMPs on electrodes by electropolymerization of suitable conjugated tectons.\textsuperscript{101, 102} The Yamamoto coupling reaction was used for the preparation of a microporous polymer by coupling of the tetrahedral monomer,\textsuperscript{98} tetrakis(4-bromophenyl)methane. The result was extremely interesting: Ben \textit{et al.} synthesized a microporous polyphenylene network (PAF-1) with very high BET surface area of 5640 m\textsuperscript{2}g\textsuperscript{-1}.\textsuperscript{103} This material also showed high uptakes of other gases, such as H\textsubscript{2} (10.7 wt\% at 77 K, 48 bar) and CO\textsubscript{2} (1.3 g g\textsuperscript{-1} at 298 K, 40 bar). The high surface area and porosities of PAF-1 was explained on the basis of a diamond-like ordering of the polymer network; however, the XRD analysis of the material confirmed the formation of a predominantly amorphous polymer network with little long range order. Shortly after this achievement, Trewin and Cooper showed\textsuperscript{104} that such high surface areas could also be explained using an amorphous “expanded silica analogue” model. Thus, the development of PAF-1 by Ben \textit{et al.} certainly opened up new direction towards the preparation of functional microporous polymers with exceptionally high surface areas.

Porous carbons are important class of materials with a wide range of technologically important applications, including separation science, heterogeneous catalyst supports, water purification filters, stationary phase materials, as well as the developing future areas of energy generation and storage applications.\textsuperscript{105} There are various methods for the synthesis of porous carbon materials. The representative traditional methods are: 1) Chemical activation, physical activation, and a combination of these two processes.\textsuperscript{106} 2) Catalytic activation of carbon precursors by using metal salts or organometallic compounds.\textsuperscript{107} 3) Carbonization of polymer blends\textsuperscript{108} 4) Carbonization of a polymer aerogel.\textsuperscript{109} Although the above-mentioned methods are employed for developing many porous carbon materials, the synthesis of uniform porous carbon materials has been very challenging. Molecular sieving carbons (MSCs) are a special class of activated carbons
that possess uniform micropores of several angstroms in diameter. The application of these MSCs has been found useful in various areas including the separation of gas molecules, shape-selective catalysts, and electrodes for electrochemical double-layer capacitors. The most general synthetic method for the synthesis of MSCs is the pyrolysis of appropriate carbon precursors. Miura et al. synthesized\textsuperscript{110} MSCs by pyrolyzing a mixture of coal and organic additives. They also used ion-exchange resins to produce MSCs.\textsuperscript{111} Spherical polystyrene based resin with a sulfonic acid group were ion exchanged with several different cations, and the resulting resin were carbonized at between 500 and 900 °C. To synthesize microporous carbon materials with ordered regular pore arrays, rigid inorganic templates are required. Kyotani group used USY zeolite as the template to prepare a microporous carbon.\textsuperscript{112} In the first step, a carbon precursor was incorporated into the pores and channels of the zeolites and in the second step it was followed by carbonization and subsequent removal of the zeolites template producing microporous carbon materials. Poly(acrylonitrile) or poly(furfuryl alcohol) was employed as the carbon precursor. Carbon precursors were also introduced into the channels of USY zeolite by chemical vapor deposition (CVD) method. The zeolite material was exposed to propylene gas at 700 or 800 °C. The resulting microporous carbons exhibited high surface areas of over 2000 m\textsuperscript{2}g\textsuperscript{-1}.

Over the last decade, significant advancement is observed in the synthesis of mesoporous carbon materials. Mesoporous carbon materials are very useful in applications involving large molecules, such as adsorbents for dyes, catalyst supports for biomolecules, and electrodes for biosensors. Catalytic activation using metal ions was employed to synthesize different types of mesoporous carbon materials. The group of Yasuda prepared mesoporous activated carbon materials by the steam invigoration of pitches mixed with 1–3 wt% of rare-earth metal complexes, such as Ln(C\textsubscript{3}H\textsubscript{5})\textsubscript{3} and Ln(acac)\textsubscript{3} (where Ln =
Sm, Y, Yb or Lu). All of the resulting mesoporous carbons showed high porosity with mesopore ratios of up to 80%, surface areas of ca. 200 m²g⁻¹, and pore sizes ranging from 20 to 50 nm.

Silica materials are excellent templates for synthesizing mesoporous carbons. The silica template can easily be removed by treating them with HF or NaOH. Knox et al. reported the synthesis of spherically shaped mesoporous carbon materials using silica gel and porous glass as templates. Both the Hyeon group and Ryoo group used MCM-48 (alumino) silica materials as the templates for the fabrication of mesoporous carbon. The carbon precursors were either sucrose or phenol resin. The phenol-resin/MCM-48 nanocomposite was prepared by the in situ polymerization of phenol and formaldehyde in the pores of the MCM-48 aluminosilicate template. First the phenol-resin/MCM-48 nanocomposite was carbonized and it was followed by the dissolution of the aluminosilicate template using aqueous hydrofluoric acid to produce an ordered mesoporous carbon (SNU-1). Ryoo and his co-workers synthesized mesoporous carbon (CMK-1) using sucrose as a carbon precursor using the same template (MCM-48). In another work, hexagonally ordered mesoporous silica SBA-15 was used as a template for the synthesis of a mesoporous carbon designated as CMK-3. By using SBA-15 silica as the template, Ryoo and his co-workers successfully synthesized an ordered mesoporous carbon fibers interconnected through thin carbon spacers. A nanopipe-type mesoporous carbon, designated as CMK-5, was also synthesized by Ryoo and co-workers from the partial wetting of poly(furfuryl alcohol) onto the SBA-15 silica channels and subsequent carbonization.

Recently, much effort has been made to find a way of directly synthesizing uniform pore-sized mesoporous carbon materials. Uyama and coworkers synthesized highly porous N-doped activated carbon monoliths (ACMs) by carbonization and physical activation of
Porous PAN monoliths with a bicontinuous structure have been developed from the commercially available polymer by a facile and unique non-templated procedure viz. thermally induced phase separation (TIPS). The carbon monoliths showed BET surface area as high as 2501 m$^2$g$^{-1}$. The monoliths exhibited exceptionally high CO$_2$ uptake; 5.14 mmolg$^{-1}$ at ambient pressure and temperature and 11.51 mmolg$^{-1}$ at ambient pressure and 273 K.

1.4 Applications of porous materials

1.4.1 Catalysis

Mesoporous materials have been extensively used for cracking and hydrocracking reactions. Mesoporous MCM-41 catalysts show substantial cracking activity for bulky substances such as palm oil and asphaltene.$^{119}$ The analogous FSM-16 mesoporous silicas are active in the thermal degradation of polyethylene to fuel oil.$^{120}$ The cracking activity of MCM-41 is much lower than that of USY or Beta zeolites for small molecules, such as 1-butene, n-hexane, n-heptane or small cyclic hydrocarbons such as tetralin and decaline.$^{121, 122}$ For both cumene and 1,3,5-triisopropylbenzene cracking, sulfated ZrO$_2$ supported on MCM-41 shows comparable activity with bulk sulfated ZrO$_2$ catalyst.$^{123}$ ZrO$_2$/SBA-15 also shows high activity for dehydration of 2-propanol. The Al-MCM-41 with a pore diameter of 3.0 nm is active in the Friedel–Crafts alkylation of 2,4-di-tert-butylphenol with cinnamyl alcohol followed acid catalyzed intramolecular ring closing reaction to give dihydrobenzopyran.$^{124}$ The activity of Al-MCM-41 (35%) was much higher than over HY zeolite (<1%) and it suggested that diffusion restrictions of the bulky 2,4-di-tert-butylphenol exist in the zeolite. Acetalization is an important reaction in organic chemistry for the protection of carbonyl functional groups. Acetalization of
heptanal, 2-phenylpropanal or diphenylacetaldehyde, for example, with trimethyl orthoformate was carried out over siliceous and Al-substituted MCM-41 and different zeolite catalysts.\textsuperscript{125} Acetalization is one of the reaction steps for the production of jasminaldehyde. Al-MCM-41 having uniform mesopores (around 3.5 nm) is found to be suitable for carrying out the three consecutive reactions in one-pot to produce a-namylcinnamaldehyde (jasminaldehyde) in good yield.\textsuperscript{126} Mesoporous aluminosilicate, ion-exchanged with ZnCl\textsubscript{2}, was found to be effective in the Diels–Alder reaction of cyclopentadiene and methylacrylate. The yield of products was as high as 90\%, and the amount of polymerized side products was lower when compared with a homogeneous BF\textsubscript{3}\textsuperscript{*OEt}\textsubscript{2} Lewis catalyst. Tin modified materials were found to be efficient catalysts for a number of important organic transformations. Sn-MCM-41 showed high activity in the Prins condensation reaction of b-pinene and paraformaldehyde to nopol.\textsuperscript{127} The Meerwein–Ponndorf–Verley (MPV) reaction is a useful reduction of a carbonyl substrate with a secondary alcohol. Zirconium 1-propoxide grafted SBA-15 showed high activity in this reaction and it was seen that the rate of reaction increased with increasing Zr loading level.\textsuperscript{128}

It was reported that microporous aluminosilicates can act as base catalysts when the negative charge on the aluminum was compensated by alkaline ions.\textsuperscript{129} Furthermore it is also known that the smaller the charge to radius ratio of the compensating cation is, the stronger the basicity of the associated framework oxygen is.\textsuperscript{129} Analogous to the zeolites, the negative charge of the tetrahedrally coordinated aluminum atom in MCM-41 was compensated by Na\textsuperscript{+} and Cs\textsuperscript{+} and the resultant samples were found to be active and selective for carrying out the base catalyzed Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate. As expected, although the H-MCM-41 was not able to catalyze the reaction, the Na\textsuperscript{+}-exchanged sample could perform the reaction. The Cs\textsuperscript{+}-exchanged
sample was comparatively more basic and therefore, it was more active than the Na⁺- 
exchanged sample. When the Na-MCM-41 sample was tested on a more demanding 
reaction such as the condensation of benzaldehyde with diethyl malonate, it was found 
that the reaction occurs at a much smaller rate. For instance, only 6% conversion was 
oberved after 3 h at 150 °C. When an excess of alkaline metal ions with respect to the 
exchange capacity is introduced, there was possibility of formation of Na₂O and Cs₂O 
particles and then the resultant catalysts show a stronger basicity than caesium- and 
sodium-exchanged MCM-41. Organic amine functionalization of mesoporous silica 
materials is an easy way for the synthesis of efficient base catalysts. When a silica gel 
functionalized with aminopropyl group has been used as a catalyst for Knoevenagel 
condensation reaction similar conversion is obtained compared to those conducted in 
presence of homogeneous and other heterogeneous catalysts. Trilla et al. have reported 
hybrid silica materials functionalized with imidazolium and dihydroimidazolium salts as 
efficient catalysts for Knoevenagel condensation under solvent free conditions and it 
provides a green and sustainable route for this reaction. Aldol condensation is a very 
facile reaction for the formation of C-C bonds. Conventionally different soluble bases like 
NaOH or KOH are used as homogeneous catalysts for this reaction. Later several 
heterogeneous catalysts such as anionic resins, KF, magnesium and aluminium oxides, 
hydrotalcites, clays, amine modified silica materials have been developed for base 
catalyzed reactions. Choudary et al. have reported for the first time an amine modified 
MCM material as a base catalyst for aldol condensation reaction. Shimizu et al. have 
reported an amine functionalized FSM-16 material that shows very good catalytic activity 
for self aldol condensation of unmodified aldehydes. Demicheli et al. have used 
primary, secondary and tertiary amine functionalized MCM-41 materials for catalyzing 
Henry reaction. The catalytic activity decreases in the order primary >> secondary >
tertiary and following this observation they have proposed the formation of imines by reaction between aldehydes and primary aminopropyl silica. Michael addition of nucleophiles to $\alpha,\beta$-unsaturated carbonyl compounds is a useful transformation because the resulting compounds are valuable synthons in different organic synthesis. Amine functionalized silica catalysts, in this context, are found to be effective for catalyzing this reaction. A guanidine base functionalized MCM-41 silica by Rao et al. shows excellent selectivities for typical Michael donors and enones.\textsuperscript{135}

There are numerous reports about redox reactions catalyzed by framework modified porous materials or materials with redox active species. Ti-zeolites, such as TS-1, TS-2, and Ti-$\beta$, are effective catalysts in the oxidation of a variety of organic compounds.\textsuperscript{136,137} Before the discovery of modified ordered mesoporous materials, only Ti-$\beta$, a large pore zeolite, allowed the use of relatively bulky peroxides as oxidants and to process sterically demanding substrates. Different (tert-butoxy)silox titanium compounds, such as Ti[OSi(OtBu)$_3$]$_4$ (denoted TiSi4), (iPrC)Ti[OSi(OtBu)$_3$]$_3$ (TiSi3) and (tBuO)$_3$TiOSi(OtBu)$_3$ (TiSi), were grafted on the surface of mesoporous materials such as MCM-41 and SBA-15. SBA-15 supported TiSi3 (0.25–1.77 wt% Ti loading) showed high activity in cyclohexene epoxidation; the yield of cyclohexene oxide, after 2 h, was 61% and 98% when TBHP or cumene hydroperoxide (CHP) were used as oxidant, respectively. When Fe[OSi(OtBu)$_3$]$_3$ was grafted on SBA-15, analogous to the titanium species mentioned above, gave isolated Fe centers.\textsuperscript{138} The calcined Fe/SBA-15 catalysts showed good selectivity in oxidation reactions of alkanes, alkenes and arenes with H$_2$O$_2$ as an oxidant. MCM-41 supported Mn catalysts showed high activity for the epoxidation of stilbene.\textsuperscript{139} Nb- or NbCo-substituted mesoporous MCM-41 are active in liquid phase oxidation of aromatic hydrocarbons such as styrene, benzene or toluene to benzaldehyde, phenol or benzalcohol, respectively, with H$_2$O$_2$.\textsuperscript{143} Co-MCM-41 and Ni-MCM-41 are
active for liquid phase oxidation of benzene or styrene to give phenol or benzaldehyde, respectively, with H$_2$O$_2$ as an oxidant.\textsuperscript{141, 142} Sn(IV) containing MCM-41 has a good activity in the catalytic Bayer–Villiger oxidation. In the oxidation of adamantane, the conversion and selectivity to the corresponding lactone was 71\% and 98\%, respectively by using H$_2$O$_2$ as an oxidant.\textsuperscript{141, 143}

Trypsin adsorbed on thiol-fuctionalized SBA-15 shows 84\% of the catalytic activity in hydrolysis of N-a-benzoyl-DL-arginine-4-nitroanilide as compared to free trypsin.\textsuperscript{144} Mesoporous MCM-41 material ion-exchanged with [Fe(phenanthroline)$_3$]Cl$_2$\textsuperscript{145} or [Fe(8-quinolinol)$_3$]Cl$_2$\textsuperscript{146} showed good catalytic activity in phenol hydroxylation with H$_2$O$_2$. There is also report of enantioselective epoxidation catalysts: Al-MCM-41, ion exchanged with Mn(OAc)$_2$ and subsequently modified with a chiral salen, (R,R)-(--)-N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexadiamine, is an effective enantioselective heterogeneous epoxidation catalyst for cis-stilbene.\textsuperscript{147} Epoxidation is also possible over molybdenum-based catalysts. The oxodiperoxo molybdenum complex, [(L-L)MoO(O$_2$)$_2$] (L-L = (3-triethoxysilylpropyl)(3-(2-pyridyl)-1-pyrazolylacetamide)) grafted on MCM-41 or Al-MCM-41 exhibited cyclooctene epoxidation activity at 60 °C.\textsuperscript{148} Ruthenium perfluorophthalocyanine complexes impregnated inside the mesopore channels of MCM-41 showed activity for cyclohexane oxidation with TBHP in the liquid phase under ambient conditions.\textsuperscript{149} For the hydrogenation of olefins, the hydrido chlorocarbonyl tris-(triphenylphosphine) ruthenium complex ([RuHCl(CO)(PPh$_3$)$_3$]) was immobilized on the surface of aminopropyl functionalized mesoporous silica \textit{via} ligand exchange.\textsuperscript{150} Immobilized Ru-BINAP (BINAP = (R)-(+)2,20-bis(diphenylphosphino)-1,10-binaphtyl) and Rh-BPPM (BPPM=(2S,4S)-N-(tert-butoxycarbonyl)-4- (diphenylphosphino)-2-[(diphenylphosphino) methyl] pyrrolidine), attached to the support
by direct impregnation, also showed activity as hydrogenation catalysts in aqueous media.\textsuperscript{151}

\textbf{1.4.2 Gas storage}

Hydrogen has long been considered as an ideal clean energy carrier due to its ubiquitous merits. It is carbon free, and oxidation of hydrogen releases only water as a byproduct thus generating "zero emission". In addition, it has an almost inexhaustible resource of water. Moreover, hydrogen has a high energy density which is nearly triple that of gasoline per mass unit; and in addition the performance of fuel cells is more than twice as efficient as that of internal combustion engines. Since the first report of hydrogen adsorption on a porous MOF in 2003,\textsuperscript{152} about several porous MOFs have been tested as physi-sorbents for hydrogen storage applications and they have shown superior performances when compared to other porous materials.\textsuperscript{153, 154} Great efforts have been devoted to the exploration of various strategies to enhance hydrogen uptake in porous MOFs at 77 K and 1 atm, and these studies are very useful and instructive at this early stage of exploration for hydrogen storage materials.\textsuperscript{155, 156} Existing studies have showed that the gravimetric excess hydrogen saturation uptakes of porous MOFs at 77 K generally scale up with their Langmuir surface areas, and it is also widely recognized that a high surface area is the first prerequisite for cryogenic hydrogen-storage application of porous MOFs. But it is also true that high surface area is not the sole factor determining high hydrogen uptake capacity of a porous MOF. For example, MOF-5 with a Langmuir surface area of 4400 m\textsuperscript{2}g\textsuperscript{-1} exhibits a record excess hydrogen uptake of 0.076 kgkg\textsuperscript{-1} at saturation,\textsuperscript{157} which is much higher than MIL-101 (0.061 kgkg\textsuperscript{-1})\textsuperscript{158} and UMCM-2 (0.069 kgkg\textsuperscript{-1})\textsuperscript{159} although they have much larger surface areas of close to 6000 m\textsuperscript{2}g\textsuperscript{-1}. Another example is a copper porous MOF, PCN-6, which can adsorb 0.072 kgkg\textsuperscript{-1} hydrogen at 77 K and 50 bar pressure despite its relatively lower Langmuir surface area of 3800 m\textsuperscript{2}g\textsuperscript{-1}.\textsuperscript{160}
A compromise between the surface area and crystal density should be met when porous MOFs with both high gravimetric and volumetric hydrogen uptakes are needed. This necessitates more extensive and insightful studies of hydrogen adsorption in porous MOFs to elucidate structure performance correlations. To be used as true hydrogen storage materials the adsorption capacity needs to be increased significantly at ambient temperature. Although MOFs and carbon materials show very good adsorption capacity at least at cryogenic conditions, unfortunately, low temperature cooling equipment will add to the complexity, weight, and cost of any gas storage system. The obvious question is therefore how one might improve the gas storage capacity of nanoporous solids at or near room temperature. Significantly increasing the surface area of the material is certainly one strategy for trying to increase the capacity. However, given the already high pore volumes of some of the largest MOFs it would seem unlikely that enough improvement could be made using this approach. Another strategy for high hydrogen adsorption is to increase the adsorption energy. Several other researchers have also shown that accessible metal sites in MOFs show good hydrogen adsorption. Utilizing the flexibility of MOFs may also be used to improve storage properties. Thomas and Rosseinsky et al. showed that the adsorption/desorption isotherms for hydrogen can show distinct hysteresis. The flexible linkers used in building the structure lead to the possibility of dynamical opening of the pores in the structure that means that hydrogen adsorbed at high pressure could not get released even at much lower pressures.

Methane is also considered as a clean energy gas because of its higher hydrogen-to-carbon ratio, and has much lower carbon emission. Although compressed natural gas (CNG) vehicles already exist commercially, current vehicles store the methane CNG in high-pressure (greater than 200 atm) tanks which are heavy and potentially explosive. The first report of methane uptake by a porous MOF could date back to as early as 1997.
reported by Kitagawa and coworkers but with very limited methane uptake.\textsuperscript{22} The field of methane storage on MOFs has not developed as quickly as the hydrogen-storage field, and studies on methane storage in porous MOFs are far less numerous than hydrogen. IRMOF-6 shows higher amount of methane uptake compared to the other members of the IRMOF series. It was ascribed to both the high accessible surface area and the functionality of the ligand. In IRMOF-6, the phenyl ring of the typical bdc ligand was modified to generate 1,2-cyclobutane-3,6-benzenedicarboxylate. The resulting porous MOF was found to adsorb 155 v(STP)/v (or 240 cm\textsuperscript{3}g\textsuperscript{-1}) methane at 298 K and 36 atm\textsuperscript{25} which is significantly higher than any zeolites material or any other porous MOF at the time, particularly in terms of gravimetric capacity. In an effort to solve the problems associated with extremely small pores, an extended ligand with additional phenyl rings to form 5,50-(9,10-anthracenediyl)-diisophthalate (adip) was used. The resulting porous MOF, PCN-14, was found to contain nanoscopic cages of a size suitable for methane adsorption, with an absolute uptake capacity of 230 v(STP)/v(excess: 220 v(STP)/v).\textsuperscript{164} Reports of methane storage in porous MOFs to date indicate that high surface area is necessary but not a decisive factor for high methane storage either in volumetric or gravimetric capacity.

In recent years global warming is a serious environmental problem worsening the climatic situation and leading to ecological imbalance. The main reason behind this is increasing emission of greenhouse gases, which originates from the combustion of fossil fuels. CO\textsubscript{2} is one of the major contributors of greenhouse gases. However, designing an economical CO\textsubscript{2} storage material for significant CO\textsubscript{2} adsorption is a daunting challenge today. Zeolites are the most widely examined materials for CO\textsubscript{2} capture among the different types of porous solids.\textsuperscript{165} But the main drawback of using zeolite as CO\textsubscript{2} adsorbent is the presence of moisture in the gas, which significantly reduces the adsorption capacity. In
these cases very high temperature is needed for the regeneration of the adsorbent. Recently, interest has grown to experimental and computational screening studies to assess CO₂ removal from low pressure flue gas using naturally occurring zeolites, such as X and Y Faujasite systems, as well as synthetic zeolites including 5A and 13X. It has been found that the adsorption can be enhanced by a low SiO₂/Al₂O₃ ratio and the presence of cations in the zeolites structure which involve in strong electrostatic interactions with CO₂. One major advantage of using porous materials for gas storage is the flexibility to modify the internal surface of the material by impregnating or tethering active functional groups. The most popular strategy to improve the CO₂ adsorption capacity of porous silica materials is incorporation of amine groups on the surface of the materials. Amine groups present at the surface help the chemisorption of Lewis acidic CO₂ molecules through the formation of carbamate species. Polyethylenimine impregnated into periodic MCM-41 mesoporous molecular sieves showed significant enhancement (24-fold) in the CO₂ absorption capacity of the solid support using a pressure swing adsorption approach. Amines immobilized mesoporous supports such as poly(methyl methacrylate) also show increased adsorption capacity. However, these materials impregnated with physisorbed amines often suffer from a lack of stability over repeated cycles. To solve these problems, alkylamines have been covalently tethered to the surface of mesoporous supports for improving their stability. For example, aziridine polymerization at the surface of mesoporous silica was used to generate a hyperbranched material and the material exhibited reversible CO₂ binding (with a capacity of 2 mmolg⁻¹) and multi-cycle stability under simulated flue gas conditions using a temperature swing adsorption (TSA) approach. SBA-15 grafted with monoamino, diamino, and triamino ethoxysilanes were used to investigate the influence of the amine type and the presence of moisture on CO₂ adsorption performance. Adsorption capacities of 0.52, 0.87, and 1.10
mmol g\(^{-1}\), respectively, were obtained. In the presence of a moist CO\(_2\) stream, the primary amine was found to exhibit slightly decreased capacity, but increased by ca. 3 and 10\% for the secondary and tertiary amine grafted materials, respectively. In addition to amine modified silica materials, chloropropyl as well as vinyl functionalized mesoporous materials were also found to be highly efficient as CO\(_2\) adsorption materials.\(^{174}\)

Since MOFs possess very high surface area, these are expected to show high CO\(_2\) adsorption capacity. Because of their high surface area-to-weight ratio MOFs are found to exhibit enhanced capacities for CO\(_2\) capture at moderate pressures compared with zeolites. Although zeolites possess higher storage capacities at pressures less than 10 bar, it has been seen that their maximum capacities are limited to one third those of MOFs at pressures greater than 10 bar. The framework \([\text{Zn}_4\text{O(btbb)}_2] \) (MOF-177, \(\text{btbb}^{3-} = 1,3,5\)-benzenetribenzoate) having surface area (SA) of 4500 m\(^2\)g\(^{-1}\) exhibits very high capacity for CO\(_2\), taking up 33.5 mmol g\(^{-1}\) at 32 bar pressure.\(^{175}\) By comparison, zeolite 13X adsorbs 7.4 mmol g\(^{-1}\) CO\(_2\) at 32 bar. MOFs with very high surface area such as \([\text{Cu}_2\text{(BpnDC)}_2\text{(bpy)}] \) (SNU-6, \(\text{bpy}=4,4'\)-bipyridine, \(\text{BpnDC}^{2-} = \text{benzophenone-4,4'-dicarboxylate}, \text{SA}_{\text{BET}} = 2590 \text{ m}^2\text{g}^{-1}\)) also possess a high CO\(_2\) uptake capacity and additionally it shows preferential CO\(_2\) adsorption over CH\(_4\).\(^{176}\) CO\(_2\) adsorption capacities of other terephthalate-based materials have been extensively investigated. For example, room temperature CO\(_2\) adsorption has been reported in a series of isoreticular frameworks including \([\text{Zn}_4\text{O(bdc)}_3] \) (MOF-5, \(\text{bdc}^{2-} = 1,4\)-benzenedicarboxylate) and \([\text{Zn}_4\text{(NH}_2\text{bdc)}_3] \) (\(\text{NH}_2\text{bdc}^{2-} = 2\)-amino-1,4-benzenedicarboxylate).\(^{175}\)

1.4.3 Drug delivery

Designing controlled drug-delivery systems (DDSs) for human health care is an ever-evolving field for biomedical materials science.\(^{177,178}\) With the development of
nanotechnology in recent years, researchers are engaged in designing new nanostructured materials for biomedical applications. In 2001, the mesoporous material MCM-41 was proposed as a DDS. The silica mesoporous matrices are believed to be potential drug carriers due to the following features: a) An ordered pore network with homogeneous size allowing fine control of the drug load and release kinetics; b) A high pore volume to host the required amount of drug; c) A high surface area, necessary for drug adsorption; d) A silanol-containing surface that is available for functionalization to allow better control over drug loading and release. These unique features make mesoporous materials excellent candidates for controlled drug-delivery systems, and intensive research has been carried out on this topic during recent years. The drug is commonly incorporated by soaking of the matrix in a highly concentrated drug solution and subsequent drying. Therefore, the process is mainly based on the adsorption properties of mesoporous materials. The size of the molecule that can be adsorbed into the mesopores depends on the pore size of mesoporous materials. Thus, size selectivity is an important factor for the adsorption of molecules in the mesoporous matrix. Commonly, pore diameters slightly larger than the drug molecule dimensions (pore/drug size ratio>1) are considered for the adsorption of drug inside the pores. Hata et al. reported in 1999 that an anticancer substance taxol was adsorbed into FSM-type mesoporous silica when the pore size was larger than 1.8 nm. Although the proposed system was not designed as a DDS, their studies set an important example for this field. When MCM-41 was first tested as DDS, C_{12}TAB and C_{16}TAB were used as structure directing agents (C_{12}TAB=dodecyltrimethylammonium bromide, C_{16}TAB=hexadecyltrimethylammonium bromide). When C_{16}TAB was used, the resulting larger pore MCM-41 released 68% of the loaded ibuprofen (IBU) after 24 h in simulated body fluid (SBF). In contrast, small pore MCM-41 obtained with C_{12}TAB released only 55% of the drug after the same period.
of time. When IBU is incorporated into MCM-41 mesoporous materials with pore diameters between 2.5 and 3.6 nm, it has been found that release rate increases with pore size. Qu et al.\textsuperscript{181} reported the release of captopril from several 2D hexagonal structures (MCM-41\textsubscript{12}, MCM-41\textsubscript{16}, and SBA-15). The authors described the influence of pore size on the kinetic processes: not only on the kinetic release of drug, but also on the kinetic loading (the final amount of drug adsorbed essentially depends on the surface area). They also pointed out the role of morphology at the microstructure level. Since the drug-loading process is mainly based on the adsorption properties of mesoporous materials, the surface becomes the most determining factor for the amount of adsorbed drug. When MCM-41 and SBA-15 (both 2D hexagonal structures) with SA\textsubscript{BET} values of 1157 and 719 m\textsuperscript{2}g\textsuperscript{-1}, respectively were loaded with alendronate under the same conditions, the maximum loads of alendronate obtained were 139 and 83 mgg\textsuperscript{-1} for MCM-41 and SBA-15, respectively.\textsuperscript{182} Thus, the value of SA\textsubscript{BET} is closely correlated with the maximum load of the matrix surface. The well known MOFs MIL-100 and MIL-101 have surface areas of 3340 and 5510 m\textsuperscript{2}g\textsuperscript{-1}, respectively, which are 3 and 5 times larger than the SA\textsubscript{BET} values measured for the MCM-41 inorganic mesoporous materials alone. It has been observed that MIL-100 is able to adsorb 350 mgg\textsuperscript{-1} IBU, and MIL-101 loads 1400 mgg\textsuperscript{-1} under the same conditions. These differences were due to the pore sizes and structural effects, particularly the accessible dimensions of the windows of the cages in the solids, which are larger in MIL-101. The behavior of these MOF materials has been also compared with that of silica-based MCM-41. MCM-41 and MIL-100 materials showed very similar IBU dosage and kinetics, whereas the drug content of MIL-101 is 4 times larger than in MCM-41. The advantage of silica mesoporous materials as DDSs relies on the scope of modification or functionalization of the surface through organic groups.\textsuperscript{183,184} This process provides innumerable possibilities to control drug adsorption and release.
The drug release can be effectively controlled by different methods, the most developed of which is increasing the drug–surface interaction. For this purpose the surface is functionalized with chemical groups that are able to link to the drug molecules through ionic bonds or through ester groups.\textsuperscript{185} One of the most studied cases is the adsorption of IBU on functionalized porous matrices. IBU was incorporated in these systems on the assumption that its carboxy group could link with the silanol groups at the surface. The IBU linkage is quite different when the surface is functionalized with different organic groups. It has been seen that functionalization of MCM-41 and SBA-15 with amino groups is an effective method to control IBU release. The release rate of IBU from amino-functionalized SMMs (SMM=silica mesoporous material) can be controlled by the ionic interaction between the carboxy groups in IBU and the amino groups on the matrix.

Another strategy for effective control of drug release is functionalization of the surface with hydrophobic species and it does not deal with the drug–surface interactions but regulates drug transport out of the matrix. In recent years, development of stimuli-responsive DDSs is of significant importance. For example, Xiao and co-workers designed pH-responsive carriers in which polycations are grafted to anionic, carboxylic acid modified SBA-15 by ionic interactions.\textsuperscript{186} The polycations act as closed gates to store the drug within the mesopores (Figure 1.10). When the ionized carboxylic acid groups are protonated in response to a change in pH value, the polycations are detached from the surface and the drug is released from the mesopores. Thermo-responsive mesoporous materials have been developed as hybrid systems by combining the silica inorganic phase with thermally active polymers, such as poly(Nisopropylacryl amide) (PNIPAm), to produce spongelike phases.\textsuperscript{187} Direct encapsulation of magnetic nanoparticles into the mesoporous silica can lead to delivery systems that respond to external magnetic fields. Mesoporous materials with magnetic response were synthesized
by functionalization with mercaptopropyl silanes and subsequent linkage through the SH groups with 2-carboxyethyl-2-pyridyl disulfide to yield acid-functionalized mesoporous silica.

![Schematic representation of pH-responsive storage-release drug delivery system](image)

**Figure 1.10** Schematic representation of pH-responsive storage-release drug delivery system *(Chem. Mater., 2005, 17, 5999)*

The mesopore entrances of the MCM-41 materials were then closed with magnetic Fe₃O₄ nanoparticles by placing the acid-functionalized silica in a suspension with magnetite nanoparticles and the drug whose incorporation should be tested. Light sensitive modified mesoporous silica materials can be employed for triggering the drug release or even molecular recognition. Fujiwara and co-workers have developed a photocontrolled release system for direct-drug release by modifying the pore entrance with coumarin groups. These coumarin groups undergo reversible dimerization upon irradiation with UV light at wavelengths longer than 310 nm and return to the monomer form by subsequent irradiation at shorter wavelengths *(ca. 250 nm)*.
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Figure 1.11 Left: Postsynthetic functionalization of silica phases with coumarin. Right: A system for the controlled release of active compounds (Angew. Chem. Int. Ed., 2006, 45, 3216)

1.4.4 Dye sensitized solar cell

Dependence of modern society upon energy resources based on non-renewable fossil fuels has direct relation with global economic and political consequences. Finite nature of these resources is the matter of major concern because of increasing energy demand day by day. On the other hand, combustion of fossil fuels is leading to serious environmental pollution which is responsible for global warming. For these reasons, environmentally benign and renewable energy resources are desperately needed for the sake of the coming generation. Presently it is a major challenge for the scientific society to develop alternative energy sources that can meet with the increasing demand of modern world.

There are several carbon-free energy sources like solar, wind, tidal, geothermal etc. from which it is possible to harness energy. Among these, solar energy seems to be the most efficient energy source because huge amount of energy \((3 \times 10^4 \text{ J/yr})^{189}\) is supplied from sun and this supplied energy is about 104 times more than the total energy consumed in the entire planet. But converting this solar energy into electricity is a daunting task. After the pioneering discovery of photoelectric effect by French scientist Edmond Becquerel, researchers and engineers are always fascinated by the idea of
converting light into electricity. Although significant development has been carried out for this purpose, they are not economically proper substitute of fossil fuels and hence searching for economically viable technologies for cost effective conversion of solar energy is one of the most important scientific goals to modern day scientists. A remarkable achievement was obtained by O’Regan and Grätzel\textsuperscript{190} in 1991 when they got 7\% conversion efficiency from a dye sensitized solar cell (DSSC) based on nanocrystalline TiO\textsubscript{2}. After their pioneering work in 1991, Grätzel \textit{et al.} quickly improved the efficiency to 10\%.\textsuperscript{191} In the last two decades several efforts have been paid to improve the efficiency of DSSCs. These include new techniques for synthesizing nanostructured TiO\textsubscript{2},\textsuperscript{192-196} use of gel-polymer and molten-salt-electrolytes,\textsuperscript{197-200} application of analytical or electrochemical techniques\textsuperscript{201-204} to characterize DSSCs \etc. In TiO\textsubscript{2} the titanium ions are in Ti\textsuperscript{4+} state and it has 3d\textsuperscript{0} electronic configuration with a distorted octahedral geometry. Valence band of TiO\textsubscript{2} is primarily the hybrid of oxygen 2p and titanium 3d orbitals. On the other hand the conduction band is of pure 3d character of titanium. Since the valence band and the conduction band are of different symmetry, probability of electron transition is low and it prevents the electron-hole pair recombination. There are three different naturally occurring crystalline polymorphs of TiO\textsubscript{2}: rutile, anatase and brookite. Among these, rutile is the most stable form of TiO\textsubscript{2}. Rutile and anatase have tetragonal structure while brookite is orthorhombic. Park \textit{et al.} have showed\textsuperscript{205} that electron transport in rutile is slower than that in anatase. To enhance the electron flow, significant amount of efforts were paid for the development of one dimensional TiO\textsubscript{2} nanomaterials like nanorods,\textsuperscript{206-208} nanotubes,\textsuperscript{209-215} nanowires\textsuperscript{216-218} \etc. Although in the initial stages ZnO was more popular for energy conversion, performance of TiO\textsubscript{2} is better than that of ZnO.\textsuperscript{219} The lifetime of the transferred electron in ZnO is more but lower electron injection efficiency and lower dye regeneration efficiency of.
ZnO leads to its worse performance for energy conversion compared to TiO₂. TiO₂ gained more attention after the work by O'Regan and Grätzel. They not only used porous TiO₂ electrode, but also introduced organic solvent that came out to be very effective because previous report of using ruthenium complex with aqueous solvent was not successful. The ruthenium complex they used was cis-X₂-bis(4,4'-dicarboxy-2,2'-bipyridine) ruthenium with X = Cl⁻, Br⁻, I⁻, CN⁻, or NCS. Best result was obtained when X was NCS. They constructed the cell with a 10 μm thick layer of TiO₂ nanoparticles coated with ruthenium complex as the sensitizer. They obtained overall light-to-electric energy conversion yield of 7.1-7.9 % under simulated solar light and 12 % under diffuse daylight. After their huge success in converting light to energy they tried to mimic natural photosynthesis process with an artificial TiO₂ solar cell. Modification of the TiO₂ photo anode by doping the titanium by other metal ions can lead to change in optoelectronic properties of the solar cell. Due to enhanced electron injection rate and reduced recombination, an Nb doped TiO₂ electrode showed 33.3% increase in overall energy conversion efficiency. In another study Nb content was varied between 0.5 to 3.0 mol% in a TiO₂ solar cell sensitized by cis-[Ru(dcbpyH)₂(NCS)₂](NBu₄)₂, N719 dye. Under low Nb content (≤ 1.5 mol%), the Fermi level of TiO₂ shifted away from the conduction band minimum (CBM) and when the Nb content was high (≥ 2.5 mol%) Fermi level shifted towards CBM. Passivation of oxygen vacancies at the TiO₂ surface with low Nb doping was responsible for the shifts in Fermi level. 2.5 mol% Nb doping produced the best result of 8.0% energy conversion efficiency. In ZnO, Zn²⁺ has completely filled 3d orbitals. The valence band is of pure d character and conduction band is the hybrid of s and p orbitals. In this case also dissimilar parity leads to reduced recombination probability. ZnO electrode sensitized by rhodamine B showed 8.5% incident photon to current conversion efficiency (IPCE) at peak wavelength of 555 nm.
But mercurochrome sensitized ZnO thin film electrode showed overall 2.5% energy conversion efficiency and IPCE of 69%.\textsuperscript{225} It indicates efficient electron injection from mercurochrome to ZnO and also from the redox electrolyte to the oxidized dye. Using a ruthenium bipyridyl complex as the sensitizer, overall conversion efficiency of 5% was achieved.\textsuperscript{226} Diffusion coefficient of one dimensional ZnO nanostructures was found to be higher than that of TiO2 and ZnO nanoparticles.\textsuperscript{227} There are reports of ZnO nanorods,\textsuperscript{228, 229} nanotubes,\textsuperscript{230} nanowires\textsuperscript{231, 232} for efficient energy conversion process. Ravirajan \textit{et al.} showed\textsuperscript{233} that charge recombination is very slow in vertically aligned ZnO nanorods having half life of several milliseconds and it is over two orders of magnitude slower than that of randomly oriented ZnO nanoparticles. The band gap of Nb2O5 is ~ 3.5 eV and it behaves like an insulator at room temperature. But under oxygen deficiency, it becomes n-type semiconductor and Nb2O4.978 shows conductivity of 3 X 103 Scm\textsuperscript{-1}.\textsuperscript{234} Sayama \textit{et al.} showed\textsuperscript{235} that ruthenium(II) cis-bis(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) complex sensitized Nb2O5 electrode showed higher VOC compared to TiO2 electrode. Moreover, the IPCE of Nb2O5 (18\%) was next to that of TiO2 electrode. By treating the Nb2O5 electrodes with niobium alkoxide, it was possible to improve the IPCE to 32\%.

\subsection*{1.4.5 Other emerging applications}

When a fluorophore moiety is anchored inside the pore wall of a mesoporous material it can show interesting optical properties. A multifunctional luminescent hybrid mesoporous silicas (LHMS) containing a tunable chemosensor diimine moiety inside the pore wall was synthesized.\textsuperscript{236} The fluorophore precursor was synthesized by reaction of APTES with 4-methyl-2,6-diformyl phenol. The material showed very strong affinity for metal cations (Fe\textsuperscript{3+}, Zn\textsuperscript{2+}, \textit{etc.}) and one can tune the emission spectra in the presence of exogenous ions, which could be utilized for possible application to metal ion...
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chemosensors. On other hand this property can be very efficiently utilized for the removal of these heavy metal ions from wastewater. Post modification grafting of 4-methyl-2,6-diformyl phenol on 3-aminopropyl functionalized silica produces another chemosensor that shows excellent selectivity for Zn$^{2+}$ ions. This material could monitor trace amount of Zn$^{2+}$ ion and it was examined in cultured living cells (A375 human melanoma and human cervical cancer cell, HeLa) by fluorescence microscopy.\textsuperscript{237}

Mesoporous materials have been widely used as selective adsorbents of gases, liquids, and metals. The functionalized mesoporous silica materials are known as efficient adsorbents to remove trace amounts of mercury and cadmium in various gas streams. Porous materials functionalized with different organic groups have been widely used in the removal of heavy metal ions from waste water. In many cases, these adsorbents can be regenerated by washing with alkaline or acid solution to recover both the adsorbents and the adsorbent dyes, like in the case of adsorbents prepared by grafting amino- and carboxylic-functional groups onto MCM-41 for the removal of blue dyes from wastewater. Mesoporous silica materials can also be used in the selective adsorption/desorption of biomolecules, such as proteins.\textsuperscript{238}

1.5 Objective and outlook of the thesis

Metal phosphates are of great importance for their applications in catalysis, ion exchange, proton conduction, bone engineering, Li-ion batteries \textit{etc.} Low effective surface area and small pore size are the main drawbacks of metal phosphates, in general, for their successful utilization in different applications. The main objective of this present work is to delve into the unexplored area of research of the phosphate based molecular sieves.
Synthesis of advanced mesoporous materials is done by the reaction of different structure directing agents (SDA) and various metal ions as well as bridging ligands in basic or acidic medium. The structure directing agents are P123, F127, CTAB, CPC, SDS, lauric acid, myristic acid, palmitic acid, stearic acid, dodecyamine and hexamethyleneimine. These structure-directing agents are used as template. They have a polar hydrophilic head and hydrophobic tail. In solution, depending upon the solvent nature, they form micelle or reverse micelle after reaching the critical micelle condition (CMC). If the template molecules are removed successfully from the as-synthesized products, porosity could be generated. So using different templates, we have synthesized different phosphate based mesoporous materials. It is also well known that presence of hierarchical porosity as well as interparticle porosity in a catalyst enhances mass diffusion during catalytic reactions. So we have tried to introduce both of these features to our porous catalysts.

Although template based syntheses generate porous structure with well ordered pore arrangements, removal of these templates, to generate porosity, often leads to collapse of pore structure. Hence, besides template assisted synthesis, it is desirable to synthesize porous materials without using any SDA. For this reason different organic-inorganic hybrid phosphonate sources with different numbers of bridging phosphonate groups are also used. Again fabrication of organic functionality into the inorganic framework opens up possibilities to extend the use of these materials in medicine, sensing applications, organo catalysis etc. We have chosen different organic-inorganic hybrid phosphonate sources for synthesizing porous metal phosphonates without using any template. Morphology of a particular material is also important for some specific applications. We have synthesized phosphate based hybrid nanomaterials with well defined and tunable morphologies and compared their efficiencies in a catalytic process.
Porous materials are known to be efficient catalysts for large variety of organic transformations and also excellent adsorbents for different types of guests. In addition to utility in different emerging fields, sustainability of a nanomaterial is also an important issue in present scenario. So our primary target was to find applications of our nanomaterials in environment friendly and sustainable processes. We have used the nanoporous catalysts for biofuel synthesis. Different organic reactions were also carried out in aqueous medium by using hybrid porous metal phosphonates as catalysts. We have also used our porous materials for carbon dioxide adsorption.

Chapter 1 of this thesis gives general introduction to porous materials and their applications.

Chapter 2 provides introduction to different characterization techniques used during experiments.

Chapter 3 presents hydrothermal synthesis of a mesoporous organic-inorganic hybrid tin phosphonate material HMSnP-1 by using pentaethylenhexamine-octakis-(methylphosphonic acid) hexadecasodium salt (PEHMP) as the organophosphorus precursor and N-cetyl-N,N,N-trimethylammonium bromide (CTAB) as the structure directing agent. This novel material showed excellent catalytic activity in the liquid phase oxidative cleavage of the acyclic ring of cyclohexanone to adipic acid in one pot using molecular oxygen and showed excellent CO₂ adsorption capacity at 273 K. Thus, industrially important synthesis of adipic acid by avoiding the emission of nitrous oxide (N₂O) and environmentally demanding carbon dioxide capture could make HMSnP-1 an ideal material to explore green and sustainable applications in future.

In Chapter 4 synthesis of a new porous organic-inorganic hybrid nickel phosphonate material HPNP-1 is discussed. The material has been synthesized hydrothermally using hexamethylenediamine-N,N,N',N'-tetrakis-(methylphosphonic acid) as phosphorus...
precursor. Powder XRD results suggested the tetragonal crystal structure, whereas N$_2$ sorption analysis revealed the presence of micropore/mesopores of dimensions of ca. 1.27 and 2.64 nm in HPNP-1 material. Due to the presence of surface phosphonate groups and donor N sites in the framework this organic-inorganic hybrid material shows very strong affinity for metal cations like Cr$^{3+}$, Pb$^{2+}$, Hg$^{2+}$ and Cd$^{2+}$, and thus can be very efficiently utilized for the removal of these heavy metal ions from polluted water. Further, this material showed strong catalytic activity in liquid phase selective reduction of $\text{-NO}_2$ to $\text{-NH}_2$ group in the presence of NaBH$_4$ as reducing agent. Thus this new hybrid phosphonate material has the potential to be utilized as an efficient catalyst for the reduction of organic functional groups.

Chapter 5 presents synthesis of hierarchical macro/mesoporous titanium phosphate with aggregated nanoparticles at low temperature followed by slow evaporation by using orthophosphoric acid and titanium isopropoxide as the inorganic precursors. This material shows excellent catalytic activity for the dehydration of biomass derived carbohydrates, fructose, glucose, mannose and sucrose, into HMF and also catalyzes the direct conversion of cellulose substrates and lignocellulosic biomass, sugarcane bagasse into HMF under microwave-assisted heating in various solvents. Because of estimated future scarcity of hydrocarbons, 5-hydroxymethylfurural (HMF) is a promising carbon-based alternative and a very important intermediate in the biofuel and fine chemical productions. So MTiP-1 may be a potential material and an active catalyst for maintaining adequate supply of energy resources.

Chapter 6 gives description about one pot hydrothermal synthesis of a new organic-inorganic hybrid porous iron phosphonate material. Nanoparticle, nanorod and flake like morphology of the material can be obtained just by tuning the synthesis temperature. The
material shows very good catalytic activity for the synthesis of benzimidazole derivatives from various substituted aromatic aldehydes and o-phenylenediamine.

The summary and conclusions that can be drawn out of this research work have been pointed out in Chapter 7.
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Introduction

Chapter 1


